



## Two-phase coexisting state of *n*-hexatriacontane in the first-order phase transition

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### Abstract

The small crystal of *n*-hexatriacontane was observed by a polarizing microscope in the rotator phase transition temperature region. In the temperature region, the rotator phase coexists with the solid phase (low-temperature ordered phase). The boundaries of two phases move reversibly with the temperature change. The area fractional change of the rotator phase can be described by the Debye relaxation. The relaxation time decreases and the relaxation strength increases as the sample temperature is raised. The relaxation time agrees well with that of the dynamic specific heat, which was measured in the frequency range of  $0.0003 \leq f/\text{Hz} \leq 0.05$ .

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### 1. Introduction

The study of first-order phase transitions has been of great interest in the recent years [1,2]. To investigate the first-order phase transition of the molecular crystal, we measured the dynamic specific heat in the first-order phase transitions of *n*-hexatriacontane (*n*-C<sub>36</sub>H<sub>74</sub>) by temperature modulated calorimetry in previous studies [3,4]. Temperature modulated calorimetry is one of the methods to measure specific heat. Specific heat is obtained from the relation between periodic heat flow and periodic temperature change. When the time lag between the temperature change and the influx of heat is measured, the specific heat is expanded to the dynamic specific heat. The lag lengthens in the glass-forming liquids near their glass

transition temperatures and the polymeric materials in the first-order phase transition temperatures [5–7]. Thus, low-frequency dynamic specific heat has been measured widely for investigation of condensed matter systems. In the previous study [3], we showed that the specific heat becomes the dynamic specific heat in the first-order phase transition temperature regions in the measured frequency range,  $0.0003 \leq f/\text{Hz} \leq 0.05$ . One of the regions is the rotator phase transition [8–10]. The dynamic specific heat can be described by the Debye relaxation. In the rotator phase transition, the relaxation parameters show different trends in the lower half temperature region (we called the region  $I_R$ ) and the higher half temperature region ( $II_R$ ) in the phase transition. The relaxation time is about 600 s in  $I_R$ , and reduces to reach 15 s in  $II_R$ . The values of the relaxation strength in  $I_R$  are smaller than those in  $II_R$ .

As mentioned above, we showed data that clearly support the temperature dependence of the dynamic

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specific heat. However, it is difficult to imagine the phenomena related to the measured dynamic specific heat. Therefore, we need to investigate the first-order phase transition by methods other than the temperature modulated calorimetry. Among the many studies related to the rotator phase transition, the studies with a polarizing microscope provide us the attractive results. Nozaki and Hikosaka investigated the rotator phase transition process of *n*-pentacosane (*n*-C<sub>25</sub>H<sub>52</sub>) [9,10].<sup>1</sup> They found the following results.

1. The “wrinkles” appear at 1 °C below the phase transition point, when the temperature is raised (see footnote 1).
2. The solid phase<sup>2</sup> coexists with the wrinkles and the rotator phase. Furthermore, the density of the wrinkle and the area fraction of the rotator phase change reversibly with the temperature change. This result is very interesting because these changes do not show the hysteresis though these phenomena occur in the first-order phase transition.
3. If all the parts of the single crystal change into the rotator phase completely, condition of supercooling is required to return the rotator phase to the solid phase. This means that the sample shows the hysteresis phenomenon only when the complete transition is established and that the rotator phase transition is surely the first-order phase transition.

In the previous studies, we used *n*-C<sub>36</sub>H<sub>74</sub>, which is different sample from *n*-C<sub>25</sub>H<sub>52</sub>. Therefore, in this study, we continued to use *n*-C<sub>36</sub>H<sub>74</sub> as the sample and observed the sample by polarizing microscope in the rotator phase temperature region, in which the dynamic specific heat measured.

In this paper, we show two results. One is that *n*-C<sub>36</sub>H<sub>74</sub> shows two-phase coexisting state the same as *n*-C<sub>25</sub>H<sub>52</sub>. The other is that the area fractional change of the rotator phase is described by the Debye relaxation. We report the temperature dependence of the relaxation parameters in detail, and we compare it with that of the dynamic specific heat. The comparison shows that area fractional change of the rotator

phase is considered to be the origin of the dynamic specific heat.

In Section 2, we introduce the apparatus. In Section 3, the results are presented. We discuss the relation between our results and the phenomena associated with *n*-C<sub>25</sub>H<sub>52</sub> in Section 4. In this section, we compare the results with the data of the dynamic specific heat. We present our conclusions in Section 5.

## 2. Experimental

We developed the apparatus shown in Fig. 1. The sample was prepared by cutting what was used in the previous studies to be a convenient size. The powder sample (Tokyo Kasei Kogyo Co. Ltd.) was melted and crystallized at the cooling rate 0.1 °C h<sup>-1</sup>. The purity of the sample is 98.0% (GC).<sup>3</sup> The sample shows two-phase transitions in 68.3–74.0 °C. One is the solid–solid phase transition and the other is the rotator phase transition. The low-temperature monoclinic form (M<sub>L</sub>) is transformed into the high-temperature monoclinic form (M<sub>H</sub>) in the solid–solid phase transition [8]. M<sub>H</sub> phase is transformed to the rotator phase in the rotator phase transition [4,8]. The temperatures, about 71.0 and 73.9 °C, correspond to the end of the solid–solid phase transition and the rotator phase transition, respectively. The sample is inserted between two cover glasses in order to improve contact with the hot stage. The hot stage consists of a slide glass and heaters. The heaters are set under the slide. The temperature of the heaters is controlled by a temperature controller (REX-F400, RKC instrument Co. Ltd.). The temperature of the hot stage is also raised by the light of an incandescent lamp. The slide glass is painted black for getting better absorption of the light. A thermistor (No. 96 426 482, Technol Sesven Co. Ltd.) is put on the cover glass at a position of about 1 mm from the sample. The thermistor is in contact with the cover glass through grease and is connected to the digital multi-meter (3478A, Yokogawa Hewlett-Packard Co. Ltd.). The precision of the thermistor temperature,  $T_t(t)$ , are estimated within 10<sup>-2</sup> °C. The relation between  $T_t(t)$  and the sample temperature is discussed in Section 4. We observed the sample on the hot stage by polarizing microscope

<sup>1</sup> Nozaki and Hikosaka explained that the “wrinkle” is considered to be a kind of precursor of the rotator phase.

<sup>2</sup> We use the “solid phase” in the meaning of the low-temperature ordered phase [9]. In the case of *n*-C<sub>36</sub>H<sub>74</sub>, M<sub>L</sub> and M<sub>H</sub> phases are the solid phase.

<sup>3</sup> Specification paper (Tokyo Kasei Kogyo Co. Ltd.).

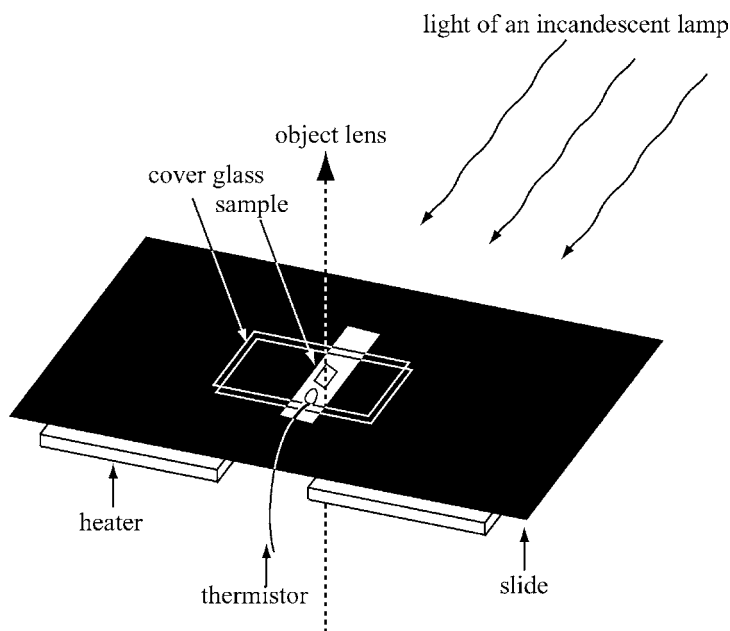


Fig. 1. Schematic diagram of the temperature control attachment. The sample is inserted between two cover glasses. The temperature is measured by the thermistor put on the cover glass. The heaters raise the sample temperature to the rotator phase transition temperature and the light of an incandescent lamp modulates it.

(BX50, Olympus Co. Ltd.). The micrograph was captured to the computer at about 1 s intervals.

We raised the temperature,  $T_t(t)$ , to the phase transition temperature by the heaters set under the slide. The heating rate is  $3.5\text{ }^\circ\text{C h}^{-1}$  in about  $68.3\text{--}73.4\text{ }^\circ\text{C}$ , and  $0.8\text{ }^\circ\text{C h}^{-1}$  in  $73.4\text{--}73.5\text{ }^\circ\text{C}$ . The temperature was held constant at  $73.55\text{ }^\circ\text{C}$ . When  $T_t(t)$  reached  $73.55\text{ }^\circ\text{C}$ , the temperature was modulated by the light of an incandescent lamp.

### 3. Results

The observed states of the sample are shown in Fig. 2. We summarize the results in the three points.

1. The “wrinkles” appears at  $T_t(t) = 70.65\text{ }^\circ\text{C}$  (Fig. 2b). Temperature  $70.65\text{ }^\circ\text{C}$  is about  $0.4\text{ }^\circ\text{C}$  below the end of solid–solid phase transition temperature and  $3.24\text{ }^\circ\text{C}$  below that of the rotator phase transition.
2. The rotator phase coexists with the solid phase in  $T_t(t) = 73.68\text{--}73.89\text{ }^\circ\text{C}$  (Fig. 2d). The optical

length observed in the parts of the sample in the rotator phase does not change, even if time passes and temperature is raised. This result shows that the rotator phase grows so fast in the vertical direction to the slide that we can not observe the phase growth in the direction [9]. The area of the rotator phase changes reversibly with the temperature change. The example of the area change is shown in Fig. 3. As shown in the figure, we found that the equation:

$$\Delta A(\omega) = C_t^* \Delta T_t(\omega). \quad (1)$$

It is fitted to the area change of the rotator phase  $\Delta A(\omega)$ , where  $\Delta T_t(\omega)$  is the Fourier transform of the temperature change  $\Delta T_t(t)$  and  $\omega$  is the angular frequency,  $C_t^*$  is

$$C_t^* = \frac{\Delta C_t}{1 + i\omega\tau_t}, \quad (2)$$

$\Delta C_t$  and  $\tau_t$  are the relaxation strength and the relaxation time respectively. Eqs. (1) and (2) mean that the area change of the rotator phase  $\Delta A(t)$  is

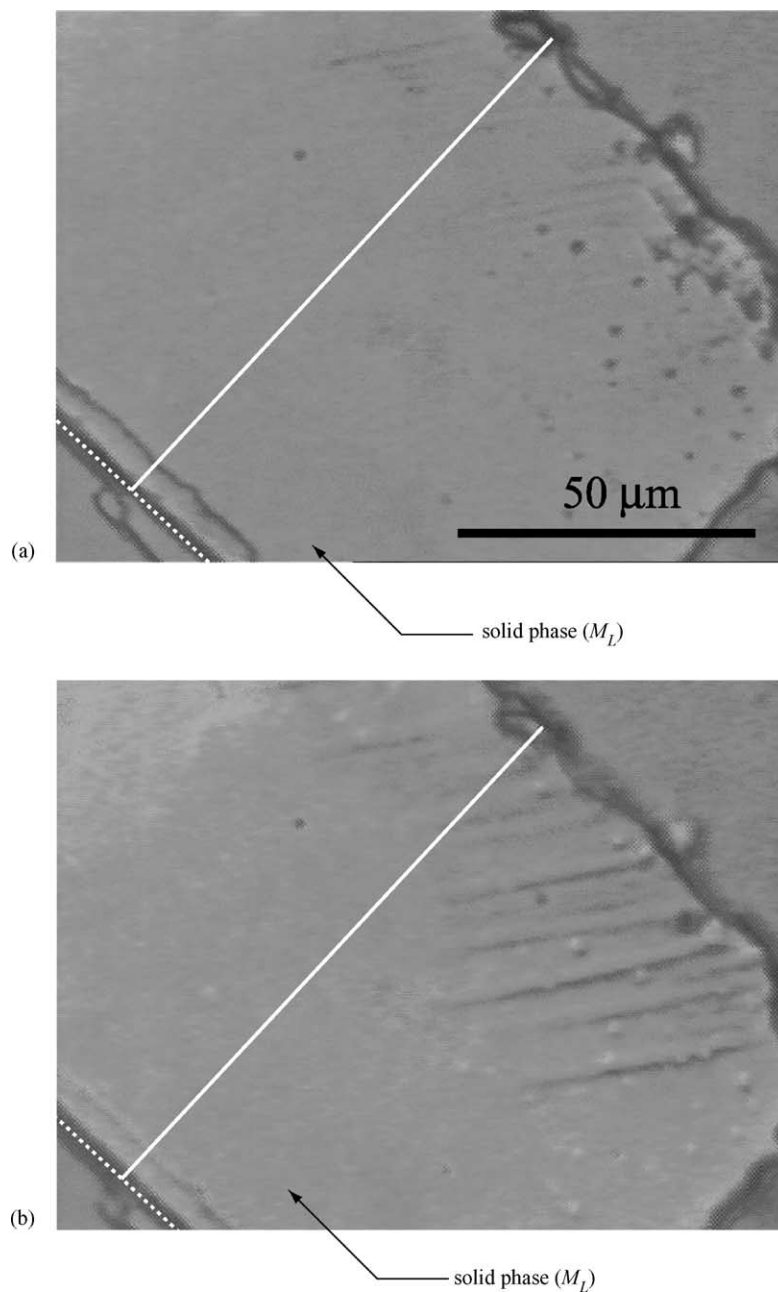


Fig. 2. A series of the optical photographs of the small crystal on heating. The sample temperatures ( $T_i$ ) are: (a) 69.24 (solid phase ( $M_L$ )), (b) 70.65 (solid phase ( $M_L$ )), (c) 73.67 (solid phase ( $M_H$ )), and (d) 73.80 ( $M_H$  and rotator phase). The “wrinkles” appeared at 70.65 °C. Temperature 73.67 °C is just below the rotator phase transition point and the two-phase coexisting state was observed in 73.68–73.89 °C. The white solid lines are drawn in order to compare the widths of the small crystal. These lines are perpendicularly drawn to the boundary of the small crystal, which is emphasized by the dotted lines. All the lengths of the white lines are the same. In the direction of the parallel to the solid lines, the small crystal does not expand.

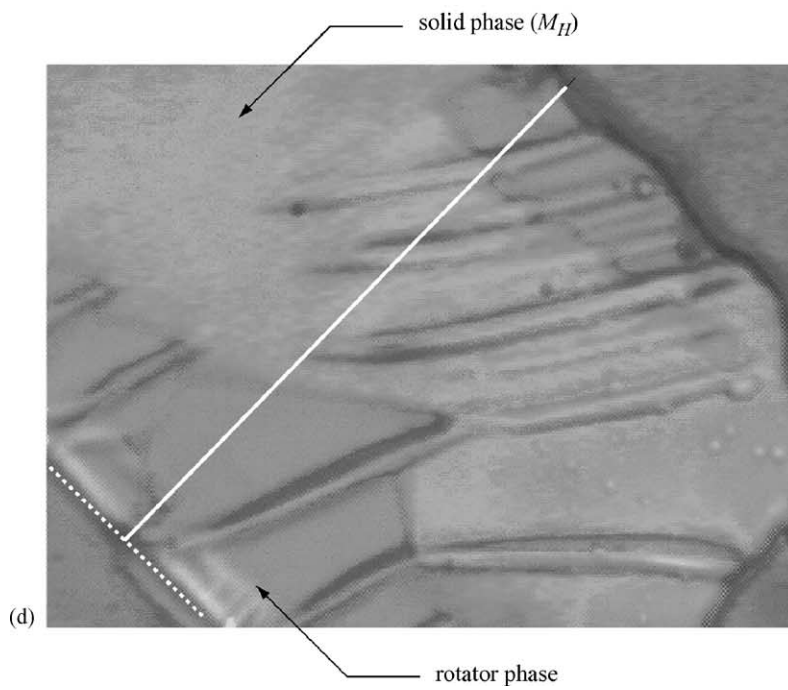
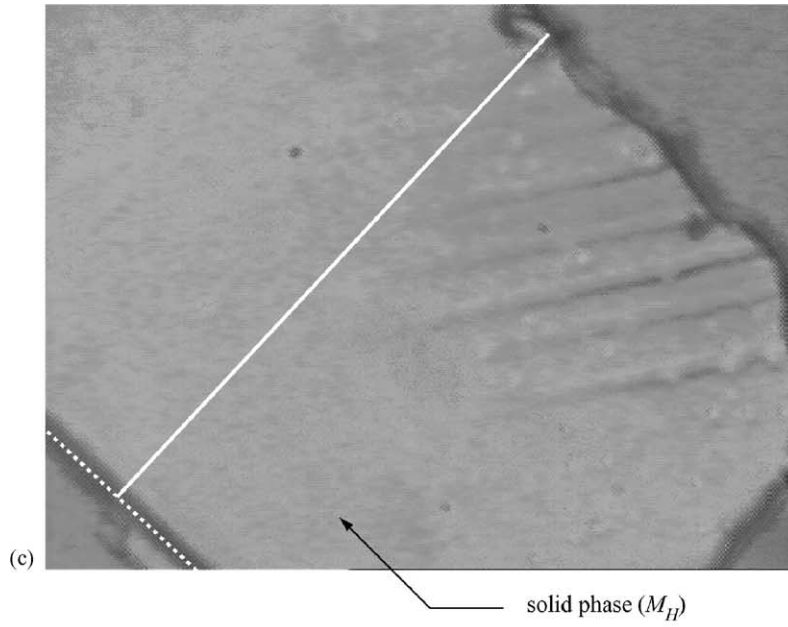


Fig. 2. (Continued).

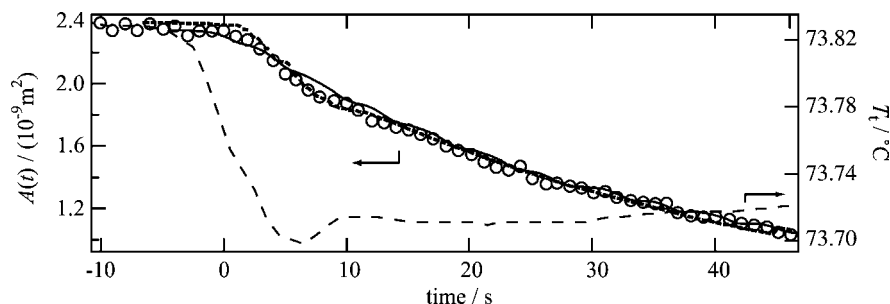


Fig. 3. Example of the area change of the rotator phase. The open circles are the measured data of the area of the rotator phase  $A(t)$ . The broken line is measured temperature  $T_t(t)$ . The solid line shows the fitted curve calculated using Eqs. (1) and (2) (the relaxation time  $\tau_t$  is 35 s). The dotted line is calculated using Eqs. (7) and (8) and the relaxation time  $\tau_s$  is 91 s.

the function of the temperature and the coefficient,  $C_t^*$ , can be described by the Debye relaxation function.  $\tau_t$  changes from 42 to 10 s. The temperature dependences of  $\tau_t$  and  $\Delta C_t$  are shown in Figs. 4a and b.  $\tau_t$  becomes smaller and  $\Delta C_t$  becomes larger as  $T$  is raised. In Fig. 4a and b, the solid lines and the dotted lines are drawn. The data shown as the solid lines were obtained when the modulated temperature,  $\Delta T_t(t)$ , was gone down. One of those was obtained by the fitting shown in Fig. 3. The data shown as the dotted lines were obtained when  $\Delta T_t(t)$  was raised. The trends of the temperature dependence of  $\tau_t$  and  $\Delta C_t$  are almost the same, whether  $\Delta T_t(t)$  is raised or gone down.

- All the parts of the small crystal change to the rotator phase at  $T_t(t) = 73.89^\circ\text{C}$ . The rotator phase returns to the solid phase through the state of supercooling, when  $T_t(t)$  is gone down from  $73.89^\circ\text{C}$  and higher. The degree of the supercooling is about  $0.4^\circ\text{C}$ .

## 4. Discussion

### 4.1. Temperatures of the sample

In Section 3, we showed the relation between the area change  $\Delta A(t)$  and the temperature of the thermistor  $T_t(t)$ , which is not the temperature of the sample. The sample is too small to measure the sample temperature directly. Furthermore, the temperature of the thermistor  $T_t(t)$  does not strictly equal to the sample temperature  $T_s(t)$  because the thermistor and

the sample are not at the same position. However, the end of the rotator phase transition measured in this study ( $T_t(t) = 73.89^\circ\text{C}$ ) and that measured by temperature modulated calorimetry in the previous study [3] ( $73.89 \pm 0.08^\circ\text{C}$ ) are almost the same (the time dependence of the relation between  $T_t(t)$  and  $T_s(t)$  is discussed in Section 4.3). Therefore, we consider that the equilibrium value of the sample temperature,  $T_s(t)|_{t \rightarrow \infty}$ , and that of the thermistor,  $T_t(t)|_{t \rightarrow \infty}$ , are sufficiently near values. We write  $T_s(t)|_{t \rightarrow \infty}$  and  $T_t(t)|_{t \rightarrow \infty}$  as  $T$ , hereafter.

Because it is not able to measure  $T_s(t)$  directly, we can not know the temperature gradient within the sample. However, we consider that the temperature gradient has no effect on the results. Even if there is the temperature gradient in the vertical direction to the slide, the results do not change because the phase transition in the direction occurs so fast, compared with that at the horizontal direction [9]. Furthermore, we consider that the temperature gradient at the horizontal direction is negligible. The two-phase coexisting state keeps for at least 1 h when the temperature is held constant, and the positions of the rotator phase do not change for this time.<sup>4</sup> If the two-phase coexisting state is due to the temperature gradient, the positions of the rotator phase should change as time passes and the temperature gradient decreases.

<sup>4</sup> This means that the phase change was not observed in the resolution of our microscope. We expect that the chain molecule conformational fluctuation causes the relaxation phenomena of the area change of the rotator phase, and thus, the temperature gradient is expected to occur spontaneously on a smaller scale than the measurable scale in the resolution.

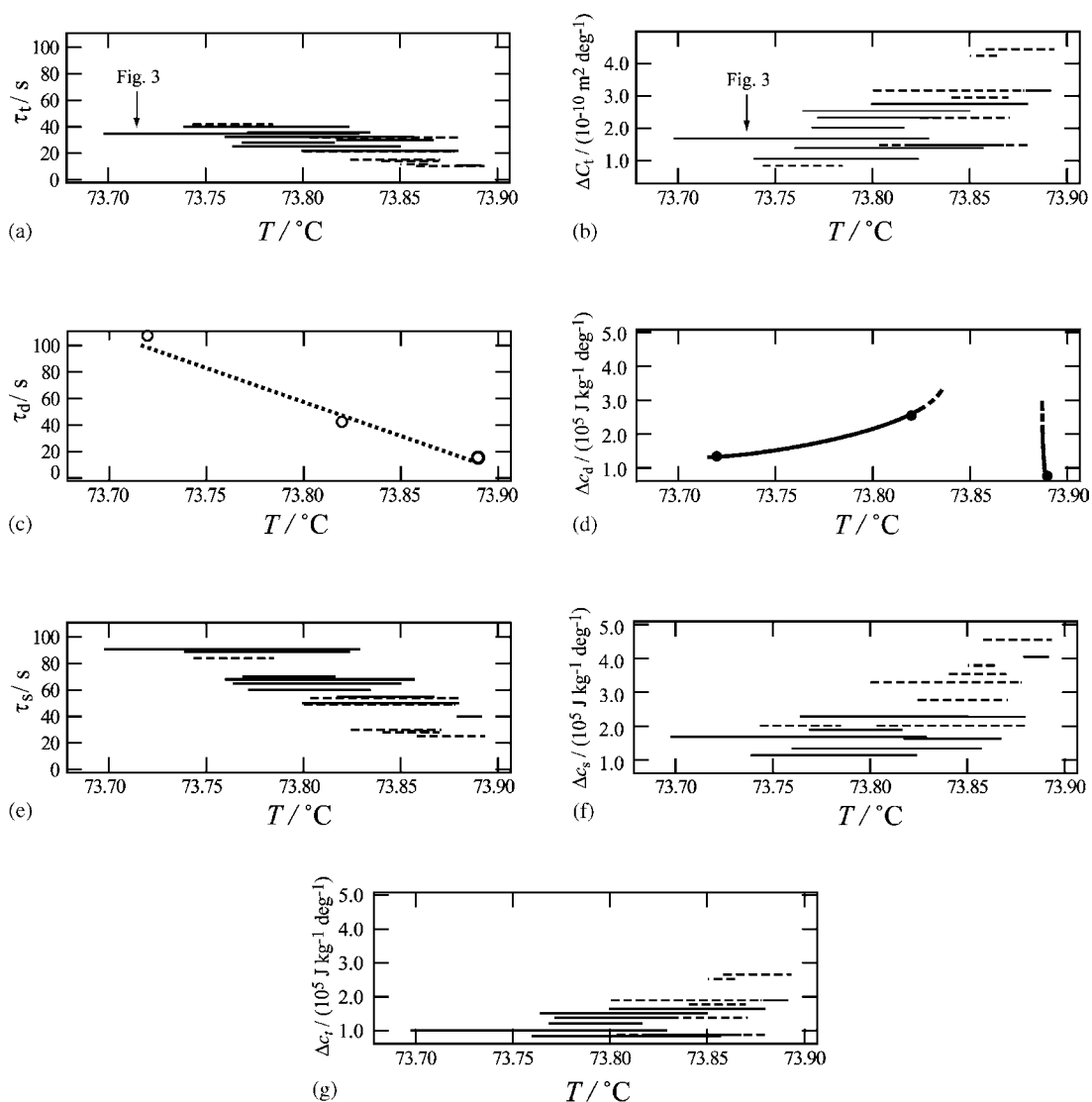


Fig. 4. (a) The temperature dependence of  $\tau_t$ . In order to obtain the relaxation time, the temperature is changed as shown in Fig. 3. The width of the lines are the width of the temperature changes  $\Delta T_t$ . The dotted and the solid lines are the data measured when the temperature is raised and gone down, respectively. The relaxation time becomes smaller in the higher temperature region. (b) The temperature dependence of  $\Delta C_t$ . The relaxation strength becomes larger in the higher temperature region. (c) The temperature dependence of  $\tau_d$ , which is the relaxation time of the dynamic specific heat [3]. The dotted line is guide for eyes. (d) The temperature dependence of  $\Delta c_d$ , which is the relaxation strength of the dynamic specific heat [3]. The solid line is the guide for eyes. (e) The temperature dependence of  $\tau_s$ . (f) The temperature dependence of the relaxation strength  $\Delta c_s$ , which is calculated using Eq. (19). We use the value,  $6.6 \times 10^4 \text{ J kg}^{-1}$ , as the latent heat  $L$ , which is measured by DSC (heating rate is  $1^\circ \text{C h}^{-1}$ , Thermo Plus 2, DSC8230, Rigaku Co. Ltd.). (g) The temperature dependence of the relaxation strength  $\Delta c_t$ , which is calculated using Eq. (20).

#### 4.2. Comparison of the results measured by using $n\text{-C}_{25}\text{H}_{52}$ and $n\text{-C}_{36}\text{H}_{74}$

The observed phenomena occurred in  $n\text{-C}_{36}\text{H}_{74}$  are similar to those in  $n\text{-C}_{25}\text{H}_{52}$  shown in [9,10].<sup>5</sup> The wrinkles appear and the two-phase coexisting state is observed in  $n\text{-C}_{36}\text{H}_{74}$  and  $n\text{-C}_{25}\text{H}_{52}$ . Nozaki and Hikosaka consider that the wrinkles appear in order to reduce the strain, which is due to the thermal expansion, and the two-phase coexisting state is caused by the increase in the internal pressure. Ubbelohde also made the same suggestion [11]. We agree with the suggestion. The density changes about 7% from  $T = 70.0\text{--}74.0^\circ\text{C}$  according to [12]. Furthermore, [8,13–15] showed that the lattice constants of all the axis change in the phase transition. However, in this study, the sample does not expand in the direction which is parallel to the white lines shown in Fig. 2 in this temperature region. Therefore, to reduce the elastic energy, the wrinkles are considered to appear. The reason why the growth of the rotator (or solid) phase stops before the phase transition is completed, is considered that the driving force of the phase growth is gone because of the balance between the decrease of the Gibbs free energy and the increase of the elastic energy which could not consume as the wrinkles.

#### 4.3. Comparison of the results of the dynamic specific heat and the area fractional change of the rotator phase

The reversible changes were measured in this study and the previous studies [3,4]. In this study, the area of the rotator phase changes reversibly. In the previous studies, we showed that the sample temperature changes reversibly. Such reversible phenomena are very special in the phenomena of occurring in first-order phase transitions. Therefore, we expect that the area fractional change have relevance to the dynamic specific heat.

The specific heat of  $n\text{-C}_{36}\text{H}_{74}$  becomes the dynamic specific heat in  $72.60\text{--}73.89^\circ\text{C}$  [3]. The end of

<sup>5</sup> In this measurement, we used the small crystal crystallized from melt. The sample is smaller than that used by Nozaki and Hikosaka [9,10]. Their sample is the single crystals prepared from *p*-xylene solution by evaporation of the solvent. However, our results show that the wrinkles and two-phase coexisting state are observed in both samples.

this temperature region corresponds to the temperature region in which the two-phases coexisting state is observed ( $T = 73.68\text{--}73.89^\circ\text{C}$ ). That is, the temperature region in which the specific heat becomes the dynamic specific heat includes that in which the two-phase coexisting state is observed. Furthermore, the dynamic specific heat and  $C_t^*$  defined in Eq. (1), are described by the Debye relaxation function (see Eq. (2)). Fig. 4c and d show the relaxation parameters of the dynamic specific heat in the temperature region ( $73.68\text{--}73.89^\circ\text{C}$ ). The relaxation strength of the dynamic specific heat increases as the temperature is raised. The relaxation strength of  $\Delta C_t$  also increases. Furthermore, the relaxation time of the dynamic specific heat and that of  $C_t^*$ , that is  $\tau_t$ , agree well with each other. Therefore, we consider that the dynamic specific heat measured in the end of the rotator phase transition temperature region is due to the area fractional change of the rotator phase.

The time dependence of the thermistor temperature  $T_t(t)$  is not equal to that of the sample temperature  $T_s(t)$ . This means that the heat contact of the sample and the heat bath (the slide) differs from the heat contact of the thermistor and the heat bath. Fig. 5 is the schematic representation of the temperature control attachment shown in Fig. 1. The thermistor put on the cover glass, in which the sample is inserted. Because the sample is sufficiently well in contact with the cover glasses, it is considered that the temperatures

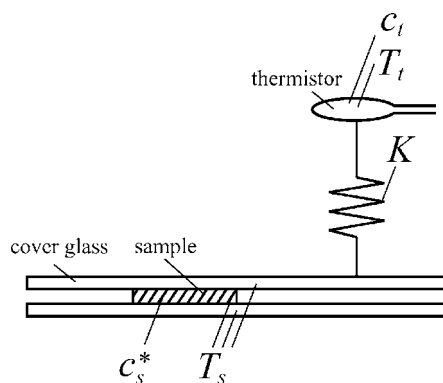


Fig. 5. The relation between the thermistor and the sample. The sample is inserted in the cover glasses. We assumed that the temperature of the sample and of the cover glasses are the same. On the other hand, the thermistor contacts with the cover glasses through grease.  $K$  is the thermal conductance and  $c_t$  is the specific heat of the thermistor.



of the sample and the cover glasses are the same,  $T_s(t)$ . Therefore, the simplest description of the heat transfer between the sample and the thermistor is

$$c_t \frac{dT_t(t)}{dt} = K(T_s(t) - T_t(t)), \quad (3)$$

where  $c_t$  is the specific heat of the thermistor and  $K$  is the thermal conductance between the cover glasses and the thermistor. When  $K$  is independent of  $T_t(t)$  and  $T_s(t)$ , we can derive the equation from Eq. (3):

$$\Delta T_t(\omega) = \frac{1}{1 + i\omega\tau_K} \Delta T_s(\omega), \quad (4)$$

where  $\tau_K$  is  $c_t/K$ . If the area change of the rotator phase  $\Delta A(\omega)$  is proportional to the temperature change of the sample  $\Delta T_s(\omega)$ ,  $\Delta A(\omega)$  is written as

$$\Delta A(\omega) = C_s^* \Delta T_s(\omega), \quad (5)$$

$$= C_s^* (1 + i\omega\tau_K) \Delta T_t(\omega), \quad (6)$$

where  $C_s^*$  is defined in Eq. (5). In Eq. (6),  $C_s^* (1 + i\omega\tau_K)$  corresponds to  $C_t^*$  defined in Eq. (1). When  $C_s^*$  is written as the Debye relaxation function:

$$C_s^* = \frac{\Delta C_s}{1 + i\omega\tau_s}, \quad (7)$$

the final form of  $\Delta A(\omega)$  is written as

$$\begin{aligned} \Delta A(\omega) &= \Delta C_s \frac{\tau_K}{\tau_s} + \Delta C_s \left(1 - \frac{\tau_K}{\tau_s}\right) \\ &\quad \times \frac{1}{1 + i\omega\tau_s} \Delta T_t(\omega). \end{aligned} \quad (8)$$

We can fit the curve calculated using Eq. (8) to the data shown in Fig. 3. The values of the relaxation time,  $\tau_s$ , is shown in Fig. 4e.<sup>6</sup>  $\tau_s$  decreases as the temperature  $T$  is raised. Compared with  $\tau_t$ ,  $\tau_s$  is near the relaxation time of the dynamic specific heat  $\tau_d$ . Therefore, it is expected that Eq. (8) is the more exact expression than Eq. (2).

Since the rotator phase coexists with the solid phase, it is assumed that the internal energy of the sample  $U(T, a)$  is written by addition of the independent term

of the area fraction  $a$  of the rotator phase,<sup>7</sup>  $U_0(T)$ , and the dependent term,  $U(a)$ , as [11,16]

$$U(T, a) = U_0(T) + U(a). \quad (9)$$

This assumption is based on the suggestion by Ubbelohde [11]. The time derivative of the internal energy is written as

$$\frac{\partial U(T, a)}{\partial t} = \frac{\partial T}{\partial t} \frac{\partial U}{\partial T} + \frac{\partial a}{\partial t} \frac{\partial U}{\partial a}, \quad (10)$$

$$\cong c_\infty \frac{\partial T}{\partial t} + B \frac{\partial a}{\partial t}, \quad (11)$$

where

$$c_\infty = \left. \frac{\partial U_0}{\partial T} \right|_{T-T_0 \rightarrow 0} \quad \text{and} \quad B = \left. \frac{\partial U}{\partial a} \right|_{a-a_0 \rightarrow 0}.$$

$T_0$  and  $a_0$  are the equilibrium values of  $T$  and  $a$ . Thus, we obtain the equation:

$$c_\infty \frac{\partial T}{\partial t} + B \frac{\partial a}{\partial t} = \kappa \operatorname{div} \operatorname{grad} T, \quad (12)$$

where  $\kappa$  is the thermal conductivity. When the area fractional change  $a(t)$  is described by the Debye relaxation:

$$\frac{\partial a(t)}{\partial t} = -\frac{1}{\tau_s} (a(t) - a_0(T)). \quad (13)$$

This equation was already introduced by Claudy and Vignon [16]. The dynamic specific heat  $c^*$  can be derived from Eqs. (12) and (13). Consequently, we get:

$$\begin{aligned} c^* &= c_\infty + \frac{T}{T_c} L \left. \frac{\partial a_0(T)}{\partial T} \right|_{T-T_0 \rightarrow 0} \frac{1}{1 + i\omega\tau_s} \\ &\equiv c_\infty + \frac{\Delta c_d}{1 + i\omega\tau_d}, \end{aligned} \quad (14)$$

where  $\Delta c_d$  and  $\tau_d$  are the relaxation strength and the relaxation time of the dynamic specific heat,  $T_c$  and  $L$  are the phase transition point and the latent heat determined from the Ginzburg–Landau theory. Soon, we will show the concrete expression of  $B$  in another paper. Eq. (14) shows that the relaxation times of the dynamic specific heat,  $\tau_d$ , and the coefficient of the area fraction,  $\tau_s$ , agree with each other when the

<sup>6</sup> The relaxation time of the heat connection between the cover glasses and the thermistor,  $\tau_K$ , is determined to be 15 s by the fitting. The value of the relaxation time is independent of  $\Delta T_t(\omega)$  and  $T$ .

<sup>7</sup> We consider that the area fraction  $a$  is equal to the volume fraction of the phase, because the phase growth in the vertical direction to the slide is so fast that  $a(x)$  is the same at any value of  $x$ , where  $x$  is the depth of the small crystal in the vertical direction.

dynamic specific heat relates to the area fractional change. Our result provides the experimental confirmation of the theories shown in [11,16], in which Eqs. (9) and (13) is assumed.

From Eq. (13), we can derive:

$$\Delta a(\omega) = \frac{1}{1 + i\omega\tau_s} \Delta a_0(T), \quad (15)$$

when the high frequency response can be negligible where  $\Delta a_0(T)$  is the relaxation strength. In Eq. (14),  $T_c$  is in 73.23–73.68 °C. Temperature 73.23 °C (346.38 K) is the temperature at which the rotator phase returns to the solid phase, when  $T$  is gone down (see Section 2 (result 3)). Temperature 73.68 °C (346.83 K) is the temperature at which the rotator phase appears in the solid phase when  $T$  is raised. In the temperature region in which the two-phase coexisting state is observed, the temperature most apart from  $T_c$  is the end of the phase transition temperature 73.89 °C (347.04 K). Therefore, in Eq. (14),  $T/T_c$  is almost one ( $1.000 \leq T/T_c < 1.002$ ) in the case of the sample used in this study. Considering the significant figure of the dynamic specific heat is two figures [3], the relaxation strength  $\Delta c_d$  is rewritten as

$$\Delta c_d = L \left| \frac{\partial a_0(T)}{\partial T} \right|. \quad (16)$$

From Eq. (16), Eq. (17) is derived:

$$\Delta a_0(T) = \frac{1}{L} \int_{T_0}^T \Delta c_d(T') dT'. \quad (17)$$

When  $T - T_0 \equiv \Delta T \rightarrow 0$ , we can derive:

$$\Delta a(\omega) = \frac{1}{1 + i\omega\tau_s} \frac{\Delta c_d(T)}{L} \Delta T, \quad (18)$$

from Eqs. (15) and (17). Therefore, comparing with Eqs. (7) and (18), (2) and (18), the relaxation strengths of  $\Delta C_s$  and  $\Delta C_t$  are expected to be related with  $\Delta c_d$  as

$$\Delta c_d = \frac{\Delta C_s}{L} \frac{1}{A_{\text{total}}} \equiv \Delta c_s, \quad (19)$$

and

$$\Delta c_d \approx \frac{\Delta C_t}{L} \frac{1}{A_{\text{total}}} \equiv \Delta c_t, \quad (20)$$

where  $A_{\text{total}}$  is the total area of the small crystal. Fig. 4f and g show the temperature dependences of  $\Delta c_s$  and

$\Delta c_t$ .  $\Delta c_s$  and  $\Delta c_d$ ,  $\Delta c_t$  and  $\Delta c_d$  agree well with each other. This supports the consideration that the origin of the dynamic specific heat is the area fractional change of the phase which coexists in the first-order phase transition temperature.

## 5. Conclusions

We observed the state of  $n\text{-C}_{36}\text{H}_{74}$  by polarizing microscope in the rotator phase transition temperature region, which is the first-order phase transition temperature region. In this region, the two-phase coexisting state is observed. This state was already observed in  $n\text{-C}_{25}\text{H}_{52}$  [9,10]. Therefore, we expect the two-phase coexisting state is the common phenomenon in alkanes. The area fraction of the coexisting phase changes reversibly when the temperature changes. We showed that the area fractional change can be described by the Debye relaxation. The relaxation parameters and those of the dynamic specific heat agree well. Therefore, we consider that the dynamic specific heat measured in the end of the rotator phase transition temperature region is due to the area fractional change of the rotator phase.

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