Two-dimensional thermal analysis of organic materials by micro-scale thermography

by J. Morikawa*, E. Hayakawa***, T.Eto**, T. Hashimoto*

*Tokyo Institute of Technology, O-okayama, Meguro-ku,Tokyo 152-8550, Japan
** Eto Denki,Co. Ltd., Shinkawa, Mitaka, Tokyo 181-0004, Japan
*** ai-Phase, Co. Ltd., Osaki, Shinagawa, Tokyo 141-0061, Japan

Abstract

.

The time development of the spatial temperature distribution during the phase transitions of organic and polymeric materials under a temperature scan was observed with a method of micro-scale two-dimensional thermal analysis by using a high-speed IR camera with an InSb FPA. The advantage of this technique is (i) a high-speed, (ii) a non-contact method, (iii) a two-dimensional temperature image (320x256), and (iv) a micro-scale spatial resolution (3μm). The forerunning phenomenon of phase transition was visualized as the spatial temperature fluctuation by a three-dimensional differential calculus. The differences of the spatial inhomogeneity of proceeding speed of crystallization and rotator phase transitions were analyzed in the cooling scan of *n*-alkanes.

1. Introduction

Polymorphic phase behaviour of organic molecular crystals has been investigated in detail by various measuring techniques for its importance in oil chemistry and biophysical sciences. However, the heat transport properties such as thermal diffusivity and thermal conductivity in the polymorphic occurrence and crystallization under the latent heat generation have not yet been sufficiently studied.

Two-dimensional micro scale thermal analysis [1,2] for the measurement of latent heat released from the organic and polymeric materials during phase transition are presented in detail by use of a high-speed infrared focal plane arrays. The thermo graphically observed latent heat spreading over the homogeneous or the inhomogeneous structures developed in the polymorphic phase transitions allow estimating the forming process of higher-order structure. The anisotropic thermal properties in the developed structures further affect the heat transfer in the succeeding processes. This study introduces a new insight in the analysis of the early stage of polymorphic phase transitions of organic materials from the experimental viewpoint of heat transfer and its relationships with the development of the structure.

2. Experimental

2.1. IR thermography

A high-speed IR camera, Phoenix (Indigo), having an indium-antimony (InSb) sensor array of 320x256 pixels with the optimum wavelength between 3μm and 5μm, was used for taking the micro-scale thermography with the originally designed silicon germanium made microscopic lens with a magnification of x10, x7 and x1, corresponding to the area size of 0.96 mm x 0.77mm, 1.28 mm x 1.02 mm, and 14mm x 11mm, with the spatial resolution of 3.0 μm x3.0 μm, 4.0 μm x 4.0 μm, 43 μm x 43 μm, respectively. The frame rate for taking an image was selected 60 ~ 1000 frames/s (16.7msec~1msec per one picture) in this study. The length and distortion are calibrated by using a standard micro-scale of USAF 1951. The intensity was calibrated with the 82ch data logger by measuring the electric current of temperature sensor.

2.2 A precision temperature control of a micro alignement specimen stage

Temperature control of a micro precision alignment xyz stage with a pitch of 1μm was electronically designed by using a FPGA (Xilinx) technology. A constant rate of heating and cooling, 0.1°C/min-100°C /min is routinely used for thermal analysis in a thermo-graphical view.

2.3 Organic materials

Polymorphism is examined from the standpoint of the latent heat release of the specimens as follows.

1. *n*-alkane, the rotator phase and the odd-even effect of carbon number,
2. Fatty acids and alcohol, the effect of terminal groups,
3. Triacylglycerol, the polymorphic occurrence and transformation,
4. Fatty acid metallic salts, the different ions and the additive solvent effect,
5. Polycyclic aromatic hydrocarbons, the number of π electrons.

3. Analytical procedure

The time resolved IR images were analyzed with the procedures in the following.

i) Time differential images calculated from

$$I'(t) = \frac{\partial I}{\partial t} = \lim_{\Delta t \to 0} \frac{I(t) - I(t - \Delta t)}{\Delta t}$$

where I (t) is intensity, t is time, Δt is time interval between the capturing.

ii) Phase and amplitude image by Fourier transform,

$$G(\frac{n}{N}) = \frac{1}{N} \sum_{K=0}^{N-1} g(k) \exp\left(-j 2\pi nk / N\right)$$

where G(n/N) is a discrete Fourier transformed function, and N is a sample number in one cycle.

4. Results and discussion

Fig.1 shows a differential thermal analysis (DTA) curve in a cooling scan from the molten state (60°C) to the solid state (20°C) of *n*-alkane $C_{24}H_{50}$. The exothermic heat is observed at the crystallization (b, c, d) and the rotator phase transitions (f). The time indicated by each arrow in Fig. 1 corresponds to the thermo graphic images (b, c, d, f) and the time differential three-dimensional images (a, e) in Fig.2, in which the position for DTA analysis is indicated as a black arrow. The developing process of crystalline lamellae is observed in Fig.2b-d, succeeded by the rotator phase transitions in Fig.2f. On the other hand the 3D differential images in Fig.2a, e show the spatial temperature fluctuations just before the occurrence of crystallization and rotator phase transitions, which affect the structure developing process. For example, in the liquid-solid phase transition in Fig. 2a the temperature fluctuation is localized in contrast to the rapid and homogeneous fluctuations observed in solid-solid phase transition in Fig.2e. With an advantage of the small amount of specimen, the time and spatial differential analysis of high-speed thermography gives the precise information of the structure developing process in view of the heat transfer and thermal properties.

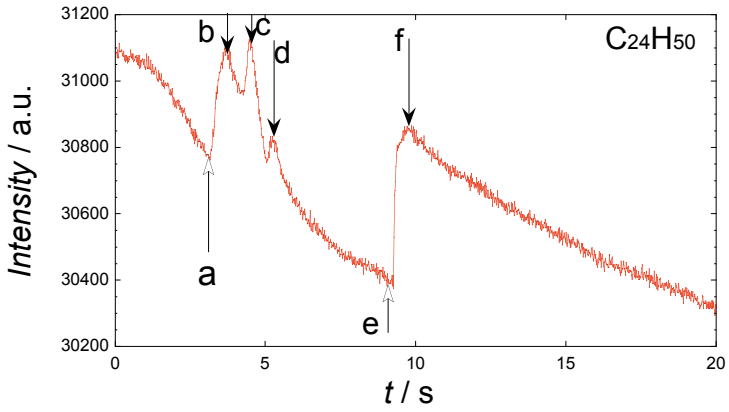

Fig. 1. Time development of a photon count intensity detected on a selected pixel (shown as a black arrow in Fig.2) of IR-FPA in the process of crystallization and rotator phase transition of $C_{24}H_{50}$ in a rapid cooling measurement.

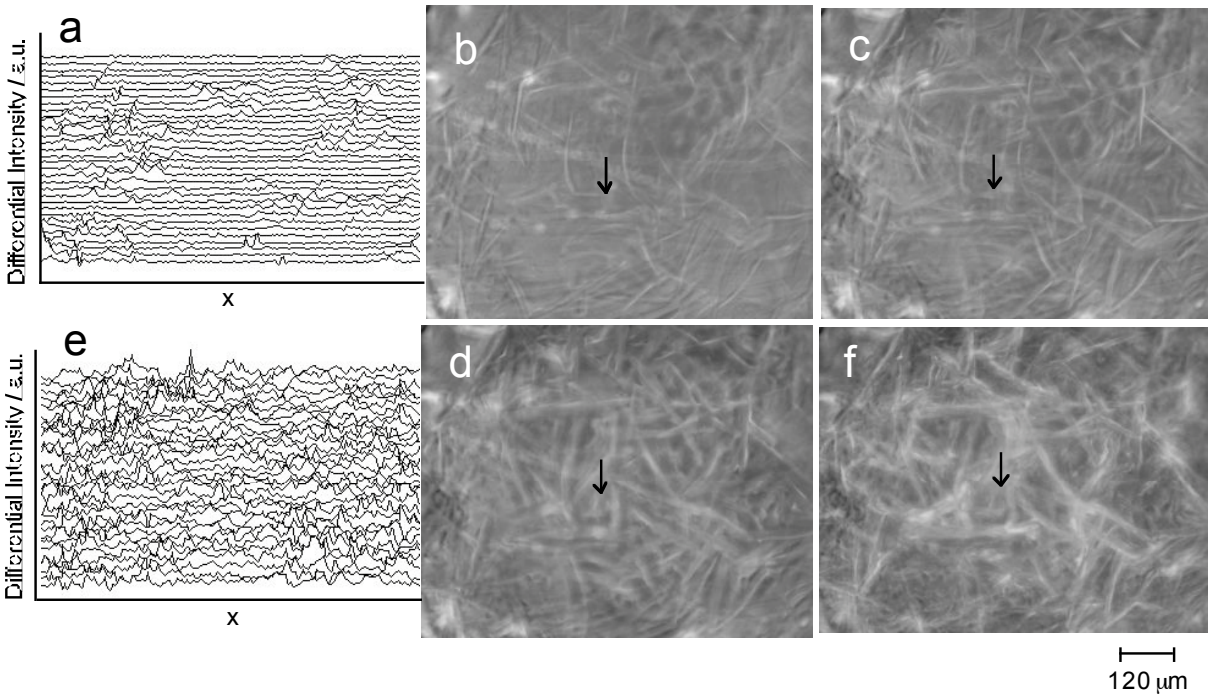

Fig. 2. Differential images of temperature distribution at the moment of (a) crystallization and (e) rotator phase transition, with the IR microphotographs in the process of crystallization (b, c, d) and rotator phase transition (f) of $C_{24}H_{50}$ in a rapid cooling measurement. Alphabets correspond to the arrows in Fig.1.

REFERENCES

[1] T. Hashimoto, and J. Morikawa, Two-dimensional thermal analysis on freezing of onion epidermal cell by high-speed infrared microscopic camera, *Jpn. J. Appl. Phys.*, 42 (2003) L706-L708.