Detailed observations of dynamic changes such as phase transitions, melting and crystallization using an XRD-DSC with a high-speed, high-sensitivity two-dimensional PILATUS detector

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1. Introduction

X-ray diffractometry (XRD) and differential scanning calorimetry (DSC) are widely used to measure changes in the physical and chemical states (e.g., phase transition, crystallization, dehydration, decomposition) of solid substances. Rigaku Corporation's instrument for simultaneous measurements of XRD and DSC (hereafter referred to as the XRD-DSC) is configured with a general purpose X-ray powder diffractometer to which a DSC is attached. As an instrument capable of providing information on thermal and structural changes from a single measurement of samples weighing on the order of a mere several mg to less than 20 mg, it has earned a good reputation in research and development involving pharmaceuticals, complexes, liquid crystals, catalysts, high polymers, and electronic materials. The features of the XRD-DSC and the data obtained using a high-speed one-dimensional X-ray detector were presented last year in this journal⁽¹⁾. This article introduces the features of an XRD-DSC on which a PILATUS 100K/R high-speed, high-sensitivity two-dimensional detector is mounted, as well as the latest data obtained with this device.

2. Features of the PILATUS 100K/R

With pixels arranged on an X and Y grid within an area measuring approximately 34 mm by 84 mm, the PILATUS 100K/R boasts noise levels less than 1/1,000 those of Rigaku's standard CCD detector, as well as high



Fig. 1. External view of the PILATUS 100K/R.

data read-out speeds (3 ms) approximately 1,000 times faster than Rigaku's standard CCD detector.

The PILATUS 100K/R offers the following features:

- Allows visual observations of Debye rings for at-aglance grasp of the effects of coarse grains and the presence/absence of orientation.
- Captures two-dimensional diffracted images in several minutes.
- Performs high-speed in situ measurements.
- Evaluates micro regions.
- Absence of dark current issues associated with CCDs allows hours of measurement with no increase in background noise.
- In addition to using the PILATUS in a fixed position, a TDI (Time Delay Integration) mode is available for simultaneous scanning, as found in scintillation counters and one-dimensional detectors.
- Design allows easy adjustments; maintenance-free.

Figure 2 shows typical applications of the PILATUS 100K/R.

The XRD-DSC with the PILATUS 100K/R offers the following features:

- Performs both reflection and transmission measurements.
- Provides fast read-out speeds (3 ms) for detailed observations of changes in X-ray diffraction patterns at intervals of several seconds.
- Shows changes in X-ray diffraction patterns with moving images while simultaneously displaying changes in the DSC curve.
- Shows appearance/disappearance of coarse grains and orientation during phase transitions.
- 3. Examples of measurement with the XRD-DSC using the PILATUS 100K/R
- 3.1. Crystallization and melting behavior of tripalmitin crystalline fat

A type of triacylglycerol having a chain and sublattice structure, tripalmitin occurs as a wide range of structural polymorphs. It readily undergoes structural changes when subjected to environmental factors such as temperature and pressure. Understanding its crystallization and melting behavior requires

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Fig. 3. Tripalmitin structures.

information on both small-angle and wide-angle regions. Figure 3 shows a schematic diagram of tripalmitin structures. The speed of cooling from the molten state is known to affect the structure of tripalmitin deposits. Shown here are the results of measurements obtained by filling an aluminum transmission measurement container with a sample and performing measurements at a heating/cooling rate of 5°C/min and exposure times of 5 sec/shot. A combination of the Rigaku NANO-Viewer, nano-scale X-ray structure analysis equipment and a transmission-type DSC was used. Figure 4 shows the data obtained during heating. Figure 5 shows the data obtained during after melting.

In tripalmitin, the sublattice structure changes first



⑦ 69.7°C: Sublattice structure disappears completely.

Total and dissolves.
Total and diterative.
Total and dissolves.
Total and di

Fig. 4. DSC curve and change in two-dimensional image (inner rings correspond to chain length structure at small-angle region peak; outer rings correspond to sublattice structure) during heating of tripalmitin.

during the phase transition in a heating process. In the melting process, we first confirm the disappearance of the sublattice structure, followed by the disappearance of the chain structure. In the crystal deposition process, we observe the formation of a chain structure and sublattice structure, in that order, as shown in Fig. 5.

3.2. Crystallization and melting behavior of amorphous terfenadine

As shown in Fig. 6, the DSC curve for amorphous terfenadine, an anti-allergy drug, shows an exothermic peak in a heating process between 95 and 120°C, suggesting crystallization. We see two adjacent endothermic peaks in the temperature range of 143°C to 155°C. It is difficult to determine the type of reaction occurring at these two endothermic peaks based on the DSC curve alone. The results of measurements performed using the XRD-DSC with a high-speed one-

dimensional X-ray detector mounted confirm that crystal phases A and B form at the exothermic peak and that crystal phases A and B melt in sequence at the endothermic peaks⁽¹⁾.

Figure 6 shows measurements of the same reaction obtained by the XRD-DSC with the PILATUS 100K/R mounted. A sample measuring was placed in an aluminum container 7 mm by 7 mm and 0.2 mm in depth. Measurement was performed by the reflection method (DSC heating rate: 2° C/min, XRD measurement angle range: 5 to $21^{\circ}/2\theta$, PILATUS measurement system: fixed mode, exposure time: 10 sec/shot).

In this example, the Debye ring resulting from the crystal deposition is continuous, indicating that the crystals lack orientation.



Fig. 5. DSC curve in cooling process of tripalmitin and changes in two-dimensional image during early stage of crystal deposition process.

3.3. DSC curve and phase transition of straightchain hydrocarbon (n-C₂₃H₄₈) during cooling and heating

Straight-chain hydrocarbon phase transitions are known to vary, depending on whether the carbon number is even or odd. In particular, the structural changes that occur in a rotational phase during heating/cooling have attracted much interest. Professor Toshimasa Hashimoto and Assistant Professor Junko Morikawa at the Graduate School of Tokyo Institute of Technology have studied thermal diffusivity measured by alternating-current methods using temperature waves and by a combination of the XRD-DSC (reflection-method measurement) with PILATUS 100K/R. They examined the relationship between structural changes in a rotational phase and thermal diffusivity⁽²⁾. Figure 7 shows the DSC curve and changes in a two-dimensional image (DSC heating/cooling rate: 0.5°C/min, XRD measurement angle range: 2.6 to $33^{\circ}/2\theta$, PILATUS measurement:

fixed mode, exposure time: 10 sec/shot). I will limit my comments here and mention only that the PILATUS, as a two-dimensional detector, permits easy detection of coarse grains. As seen in ① in Fig. 7, coarse grains are deposited in the early stages of hexagonal crystal deposition, but the grains are of uniform size when deposition is complete.

4. Conclusions

Performing simultaneous measurement for X-ray diffractometry and DSC measurement simultaneously makes it possible to observe a specific reaction process and structural changes with remarkable clarity during heating/cooling in small sample amounts, even if a scintillation counter is used as an X-ray detector.

Using the PILATUS 100K/R, two-dimensional detector as an X-ray detector allows us to easily acquire detailed information not readily obtained in the past on structural and thermal changes in laboratory settings,





95°C: Crystallization begins.



148.0°C: Crystal phase A melts.

 $120^{\circ}\mathrm{C}$: Crystallization ends.



150.5°C: Crystal phase B melts.





Fig. 7. XRD-DSC measurement of straight-chain carbon hydride $(n-C_{23}H_{48})$.

including rapidly occurring structural changes, multiple reactions occurring within a narrow temperature range, and the relationship between temperature conditions (heating, cooling) and size and orientation of crystal grains.

This enables the rapid acquisition of information essential for understanding the physical properties of

materials and the mechanisms underlying the various functions of a material, which in turn accelerates advanced research and development activities in your own research laboratory and improves process management.

References

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