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Simultaneous X-ray diffraction and differential scanning calorimetry in the study of phase transitions ☆

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Abstract

Regarding phase transitions, it is important to study both the thermodynamic behavior and the microscopic structure. To learn about the detailed mechanism of phase transitions, it is highly desirable to make clear the correlation between the thermodynamic behavior and the microscopic structure. For this purpose, we developed the simultaneous measurement of X-ray diffraction and differential scanning calorimetry, using synchrotron X-rays.

Keywords: DSC; Phase transition; Synchrotron X-ray; XRD

1. Introduction

A differential scanning calorimeter is a powerful tool in the study of phase transitions, because DSC is usually sufficiently sensitive to detect even the small anomalies at phase transitions. Furthermore, we can investigate thermodynamic behavior from DSC results. In addition, the structure of each phase is another important factor in the study of phase transitions. We have found that in such cases simultaneous measurement of X-ray diffraction and DSC at the phase transition

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may be necessary. When there is thermal hysteresis, the thermodynamic state of a material should be considered, based on the corresponding microscopic structure. When there are many DSC anomalies in a narrow temperature range, we need to clarify the structure of each phase between successive anomalies. Furthermore, for a precise comparison between the thermodynamic behavior and the structural parameters, it is important to measure them under the same conditions. Simultaneous measurement of X-ray diffractometry and differential scanning calorimetry have been reported by several authors [1–3]. In all of these, the measurements were performed using a synchrotron source of X-rays. Furthermore, they used a commercially available DSC apparatus (model FP84, Mettler Instrument Corp.) which had originally been developed for use in optical microscopy. Therefore, the apparatus has a 2.5 mm hole through which the optical beam can pass and which, in this application, lets the X-ray beam through. Among the above measurements, Russell and Koberstein [1] used a sample cell supplied commercially from Mettler Instrument Corp., Ungar and Feijoo [2] used a sample pan and a lid made of graphite or boron nitride, and Chung and Caffrey [3] used a sample pan formed from a thin aluminum plate and a lid cut from aluminum foil.

In the present study, based upon the above knowledge, we constructed an apparatus for the simultaneous measurements of X-ray diffractometry and DSC, using a synchrotron source in the Photon Factory, Laboratory for High Energy Physics, Japan.

2. Setup of apparatus

In this measurement, a differential calorimeter (Mettler Instrument Corp., model FP84) was used because the former measurements had been done using the same calorimeter. The two glass plates on either side of the sample cell that served for thermal insulation were replaced by polyimide films with a thickness of 7.5 μm (see No. 3 in Fig. 1). This does not affect the performance of the DSC apparatus. The absorption of an X-ray beam by a pair of the polyimide films is not significant. The sample cell was made of aluminum which has the advantage of both high thermal conductance and low absorption of X-rays. The sample cell was 100 μm thick at the bottom of the pan and 12.5 μm thick at the lid (see Nos. 4 and 5 in Fig. 1, respectively). On transmission through the sample cell, the X-ray beam of wavelength 0.15 nm is decreased by 80%. Thus, using the sample cell, a sufficiently intense X-ray beam could be obtained.

The sample cell was sealed, using pressure. On the side of the lid, a cap supplied by Mettler Instrument Corp. was applied so that the cell was the correct size when placed in a vertical position (see No. 6 in Fig. 1). On the top of the cap, a hole 2 mm in diameter was made to allow the X-ray beam to pass through. A silicone gum ring held the cap in place (see No. 7 in Fig. 1).

3. Experimental

The experiments were performed at the phase transition of fully hydrated dipalmitoylphosphatidylcholine (DPPC). Phospholipid molecules of DPPC dis-

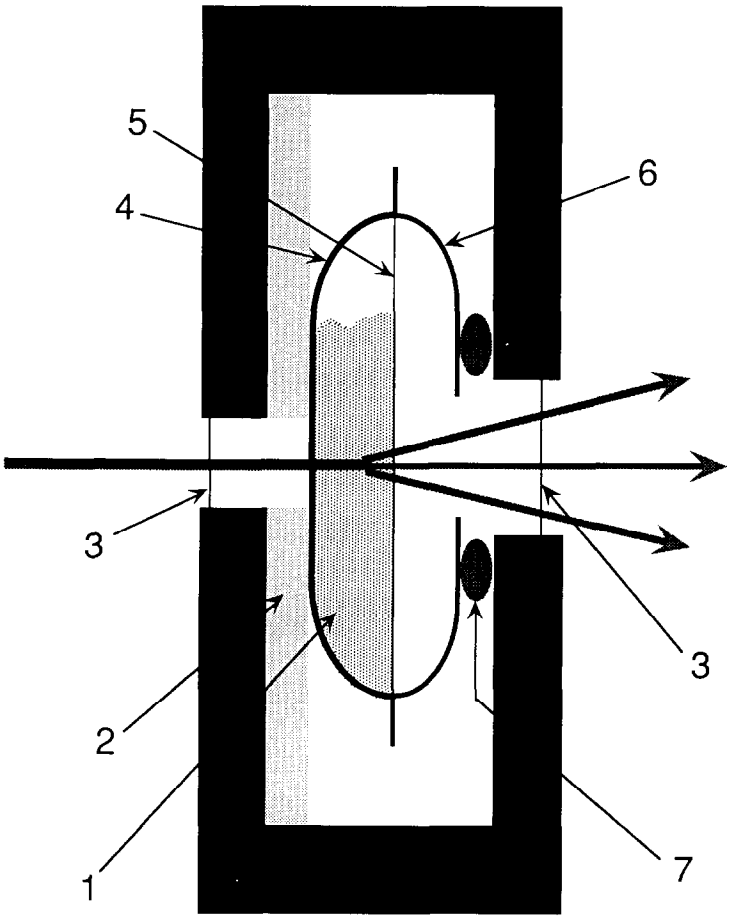
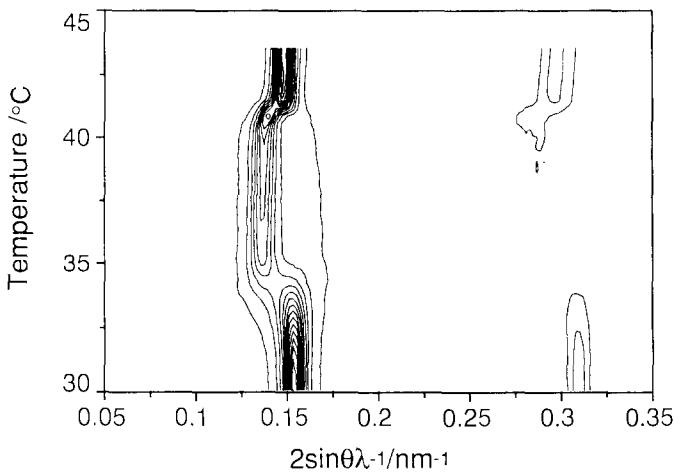


Fig. 1. The sample cell and its surroundings for the simultaneous measurement of X-ray diffraction and differential scanning calorimetry. An X-ray beam is applied on the left side and the diffracted X-rays are emitted from the right side: 1, sample; 2, base plate on which thermocouples are deposited; 3, polyimide films; 4, pan of the sample cell; 5, lid of the sample cell; 6, cap of the sample cell; 7, silicone gum ring.

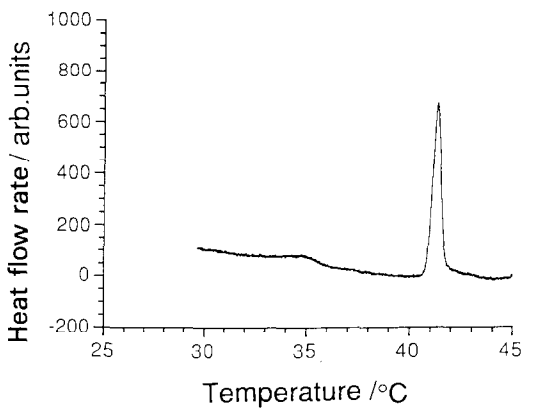
persed in excess water usually forms multilamellar vesicles. Therefore, we can observe the Debye–Scherrer rings due to the lamellar spacing by X-ray diffractometry. In fully hydrated DPPC, there are the gel $L_{\beta'}$ phase, the ripple $P_{\beta'}$ phase and the liquid-crystalline L_{α} phase in the heating sequence. The transition from the $L_{\beta'}$ phase to the $P_{\beta'}$ phase is the pre-transition and the transition from the $P_{\beta'}$ phase to the L_{α} phase is the main transition. From X-ray diffraction studies on cooling [4–6], the metastable $P_{\beta'}$ phase has been found, in which the secondary ripple structure is formed. In fact, in cooling through the main transition the X-ray diffraction profile is composed of complex multipeaks and then is disentangled by the superposition of peaks partly due to the normal primary ripple structure and partly due to the secondary ripple structure. Therefore, at the main transition some part of the

secondary ripple structure converts into the primary ripple structure; in other words, the metastable $P_{\beta'}$ phase and the normal $P_{\beta'}$ phase coexist. We have made simultaneous XRD and DSC measurements to investigate this complex behavior at the main transition.

Small-angle X-ray diffraction experiments were carried out using a monochromatic synchrotron X-ray beam with the wavelength of 0.15 nm at Station BL15A of the Photon Factory. The optical X-ray system was similar to that previously used



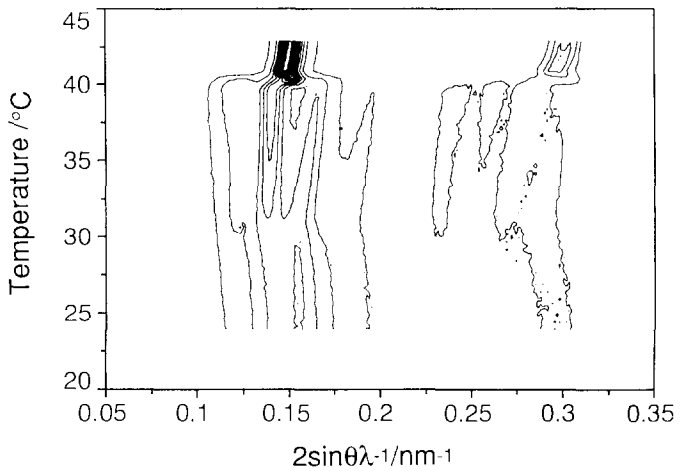
(A)



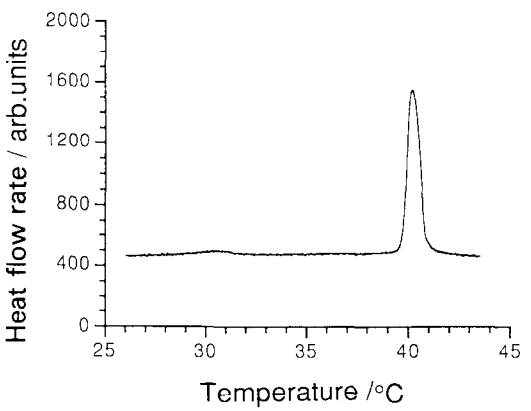
(B)

Fig. 2. A. Intensity contour map of first-order and second-order lamellar reflections observed by X-ray diffraction on heating fully hydrated dipalmitoylphosphatidylcholine. The reflections for the $L_{\beta'}$ phase occur below about 35°C, for the $P_{\beta'}$ phase between about 35 and about 41°C, and for the L_{α} phase above about 41°C. B. Measured curve obtained simultaneously by differential scanning calorimetry on heating. In relation to the XRD result, the pre-transition is at about 35°C and the main transition at about 41°C. The background was not stable in this measurement in comparison with the scan of Fig. 3B. The scale and the origin of the ordinate are drawn arbitrarily as a matter of convenience of the data analyses of X-ray diffraction and differential scanning calorimetry.

[4]. The diffraction patterns were recorded using a one-dimensional position-sensitive proportional counter (Rigaku, Tokyo). In the present study, the DSC sample cell was set at a similar position as the sample in the former study, in such a way that the X-ray beam was applied to the bottom of the sample cell. Both XRD and DSC data was gathered simultaneously at a scan rate of ± 0.5 K min^{-1}.



(A)



(B)

Fig. 3. A. Intensity contour map of first-order and second-order lamellar reflections observed by X-ray diffraction on cooling fully hydrated dipalmitoylphosphatidylcholine. There is a clear transition at about 41°C. However, the change near about 31°C is gradual. Furthermore, there are multipeaks, which indicate the coexistence of the metastable $P_{\beta'}$ phase the normal $P_{\beta'}$ phase, in the temperature range between about 31 and about 41°C, and the intensity profile, which indicates the incomplete formation of the $L_{\beta'}$ phase, below about 31°C is broader than that on heating. B. Measured curve obtained simultaneously by differential scanning calorimetry on cooling. In relation to the XRD result, there are two anomalies at about 41 and about 31°C. The scale and the origin of the ordinate are drawn arbitrarily as a matter of convenience of the data analyses of X-ray diffraction and differential scanning calorimetry.

The water concentration in a fully hydrated DPPC sample was 65 wt%. The thickness of the sample part of the sample cell was about 1 mm. In heating, we observed normal behavior in XRD and DSC as shown in Fig. 2A and 2B, respectively. In Fig. 2A, in heating, the intensity contour of the first-order lamellar reflection exhibits a broad transition from the $L_{\beta'}$ phase to the $P_{\beta'}$ phase at about 35°C, and a sharp transition from the $P_{\beta'}$ phase to the L_{α} phase at about 41°C. The second-order lamellar reflection is seen in Fig. 2A. In relation to the above behavior at the phase transitions, the DSC result shows a broad peak at the pre-transition and a sharp peak at the main transition as seen in Fig. 2B. It should be noted that this coincidence was shown much more clearly as a result of the simultaneous measurements. In Fig. 3A, in cooling, however, the intensity contour of the first-order lamellar reflection exhibits a sharp transition from the L_{α} phase to the coexistence region of the normal $P_{\beta'}$ phase and the metastable $P_{\beta'}$ phase at about 41°C. The X-ray diffraction profile in the coexistence region is similar to that observed under similar conditions in the former study [6]. On further cooling, the intensity contour of the first-order lamellar reflections changes but does not reach that of the stable $L_{\beta'}$ phase. The second-order lamellar reflections are also seen in Fig. 3A. In the DSC curve shown in Fig. 3B, the anomaly takes place at about 31°C, but it is considerably smaller than that at the pre-transition on heating. At this temperature, the lamellar reflections indicate a separation between the high and low temperature regions as seen in Fig. 3A. However, their change is not remarkable in comparison with that at the pre-transition on heating.

It is concluded that the DSC anomalies at the main transition, on heating and on cooling, are not significantly different, as pointed out in our previous paper [4], although the existence of the metastable $P_{\beta'}$ phase is obvious in the XRD results. Furthermore, the smaller DSC anomaly at the pre-transition on cooling than on heating is due to the incomplete formation of the stable $L_{\beta'}$ phase on cooling, in agreement with the XRD results. However, the existence of the metastable $P_{\beta'}$ phase is clear by XRD, although there is no marked indication of it in the DSC result. Finally, it should be pointed out that simultaneous XRD and DSC measurements are useful in the study of phase transitions, especially in the detailed study of correlation between microscopic structure and thermodynamic behavior.

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