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Surface effects on phase transition behaviour and thermal polymerisation of long-chain compounds in micro DSC measurements *

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Abstract

The surface effects of the aluminium sample pan on the melting behaviour of stearic acid and also on the phase transition behaviour and thermal polymerisation of *N*-octadecyl acrylamide during differential scanning calorimetry (DSC) were investigated. The surface effects in the micro DSC measurements can be classified into two types. In the case of stearic acid, when the weight of sample was smaller than 0.01 mg, the molar heat of fusion estimated from the peak area in the first heating curves increased abruptly up to two or three times the normal value (64.3 kJ mol^{-1}); however, in the second heating curves obtained with samples stored for a long time after the first heating at room temperature, the molar heat of fusion tends to decrease. In contrast, in the DSC curves for *N*-octadecyl acrylamide with sample weights of around a milligram, an endothermic peak for melting appeared at 75 °C, followed by a broad exothermic peak for thermal polymerisation ranging from 115 to 155 °C; when the sample weight is smaller than a critical value of around 0.2 mg, the thermal polymerisation and also the polymorphic transition are suppressed strongly. The surface effects are attributed to the strong interaction, such as chemisorption, of the polar head group with the surface of the pan which restricts the conformational freedom of the functional groups.

INTRODUCTION

In recent years much attention has been paid to the aggregation states and thermal properties of long-chain compounds in thin solid films, such as Langmuir–Blodgett films and vacuum-deposited films. Because the sample weight in these thin solid films is extremely small and the surface-area to bulk-volume ratio is very high, their thermal properties are different from those of the bulk phase, and quantitative DSC measurements become less accurate. However, only minute samples are available under certain condi-

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tions, such as in the thermal analysis of specific biomaterials. Therefore, it is desirable that the effect of sample weight on DSC should be elucidated.

As reported previously [1,2], we have found that the polymorphic behaviour of long-chain vinyl compounds and the heat of fusion of stearic acid are influenced by the surface effects of the aluminium sample pan as the sample weight decreases. Recently, Takamizawa and Urabe observed a type of surface effect in the micro DSC measurements of heptacosane crystallised from dilute solution: the total transition enthalpy observed in the second and third runs decreased rapidly when the sample weight was smaller than 0.1 mg [3].

In order to clarify those phenomena of primary importance to micro DSC measurements, this paper examines the surface effects of the aluminium sample pan on the melting behaviour and heat of fusion of stearic acid, and also on the phase transition behaviour and thermal polymerisation of *N*-octadecyl acrylamide which has a polymerisable group at the top of the polar head.

EXPERIMENTAL

Stearic acid (SA, m.p. 68.4–69.0 °C) was bought from Asahi Denka Kogyo and purified by recrystallisation from methanol eleven times. *N*-Octadecyl acrylamide (ODAAm, m.p. 74.3–74.5 °C) was synthesised by the reaction between octadecylamine and acryloyl chloride at 0–5 °C for 10–15 h in toluene, and purified by recrystallisation from methanol five times.

Thermal analysis was performed using Seiko Denshi Kogyo models DSC20 and DSC100 differential scanning calorimeters. The linearity of the sensitivity of the DSC apparatus was checked using indium. Scanning rates of 5–10 °C min^{-1} were used, and sample weights were varied in the range 0.0056–5 mg. Powdered samples were sealed tightly in aluminium pans (50 μl), the sample weight being measured on a Mettler micro-balance AE163 and a Sartorius ultra microbalance 4504MP8.

RESULTS AND DISCUSSION

Melting behaviour and heat of fusion of stearic acid

Firstly, the effects of sample weight on the melting behaviour and heat of fusion of SA were studied more precisely than in our previous paper [2]. The DSC curves for SA samples of 0.0056–0.0410 mg measured by the highly sensitive DSC100 are shown in Fig. 1. In the case of first heating (Fig. 1(A)), the onset temperatures for fusion are relatively low and are distributed in the range 50–55 °C, although the peak temperatures are almost constant

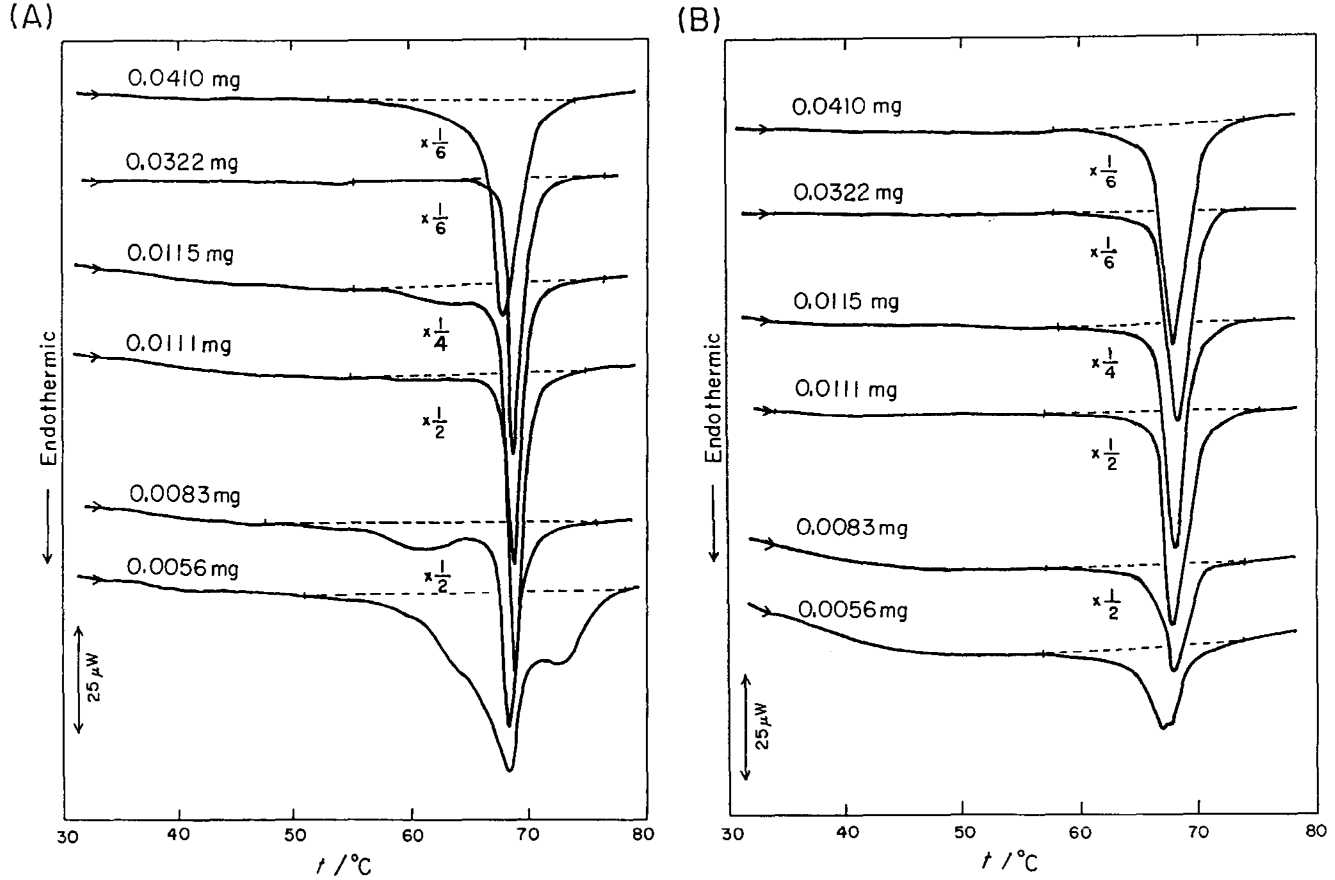

Fig. 1. DSC curves for stearic acid of various weights: (A) first heating curves; (B) second heating curves of samples stored at room temperature for nine months after the first heating. DSC 100, Al pan, 5 °C min^{-1}, N_2 gas flow.

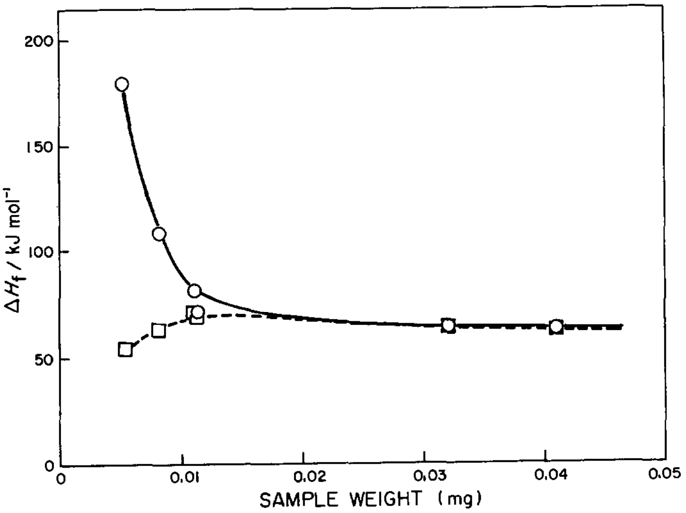

Fig. 2. Effect of sample weight on the molar heat of fusion of stearic acid: (o) first heating; (□) second heating.

(68.0–68.6 °C) irrespective of sample weight. When the weight of sample is smaller than 0.01 mg, a broad peak or shoulder frequently appears at around 60 °C. In addition, to investigate the effect of contact between the sample molecules and the aluminium surface on the melting behaviour, DSC measurements were carried out on the same samples stored for nine months at room temperature following the first heating (Fig. 1(B)). Under these conditions, both the onset and peak temperatures are almost constant. The differences between the first and the second heating curves increase with decreasing sample weight.

The effect of sample weight on the molar heat of fusion obtained from the peak areas of the DSC curves is shown in Fig. 2. With samples less than 0.01 mg, the molar heat of fusion obtained from the first heating curves increases abruptly up to two or three times the normal value (64.3 kJ mol^{-1}). Even if the endothermic peaks above the melting peaks are omitted, the values for the molar heat of fusion were anomalously large. These results give further confirmation of the surface effect of the sample pan on the melting behaviour of SA, as reported previously [2]. In contrast, the molar heat of fusion of the samples stored for nine months at room temperature decreased slightly with the decrease in sample weight; this seems to suggest another type of surface effect.

Figure 3 shows the DSC curves for the 0.0056 mg sample at different time intervals. In the first and second heatings (Runs 1 and 2), rather broad endothermic peaks are observed at 72.2 and 75.9 °C above the melting peak, respectively. The melting behaviour on the second heatings carried out immediately after the first cooling, is similar to that of the first run.

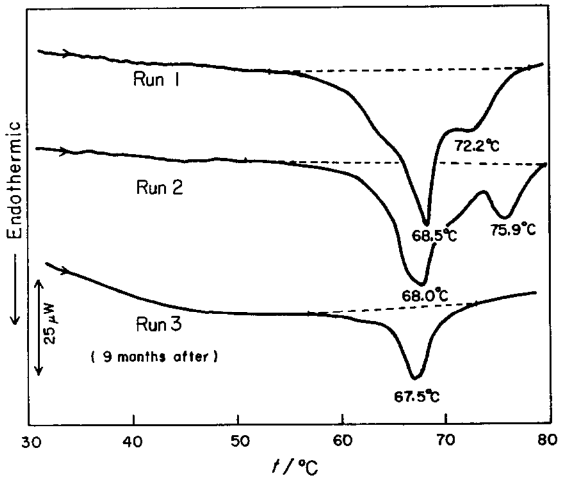

Fig. 3. DSC curves for 0.0056 mg stearic acid at different time intervals: Run 1, a first heating curve for a powdered sample; Run 2, a second heating curve measured immediately after the first heating; Run 3, a third heating curve of the sample stored at room temperature for nine months after the second heating. DSC 100, Al pan, 5 °C min^{-1}, N_2 or Ar gas flow.

However, the shape of the melting peak for the third heating (Run 3), obtained after nine months, is not unusual and the value of the molar heat of fusion is somewhat smaller than normal.

The extraordinarely large heat of fusion obtained for the ultra-micro SA sample can be observed only when SA molecules are in contact for the first time with the surface of an aluminium pan covered with an oxide layer. Here aluminium stearate may be forming on the surface of the pan. If this is the case, the lower and higher temperature peaks around the melting point in Fig. 3 can be assigned to the formation and polymorphic transition of aluminium stearate, respectively, although the latter peak is considerably lower than the phase transition temperature of aluminium stearate (approx. 100 °C) [4]. Thus, the unusual melting behaviour and the larger molar heats of fusion of SA involve the chemisorption of SA molecules on the surface of the pan, which has been covered with a thin oxide layer.

However, the chemisorption of SA molecules on the surface of the aluminium seems to be achieved rather slowly and is accompanied by a rearrangement of the molecules to form a close-packed monolayer. The surfaces of the aluminium sample pan and cover are somewhat abraded, as shown in the SEM photographs, Fig. 4(a) and (b), respectively. Both surfaces are striped by shallow ridges and furrows 0.2–0.3 μm wide and have many pits 0.1–2 μm in diameter. Therefore, the real surface area of the sample pan is much larger than the areas estimated by simple geometrical calculation. With the sample stored for a long time following heating sufficiently higher than the melting point, another type of surface effect,

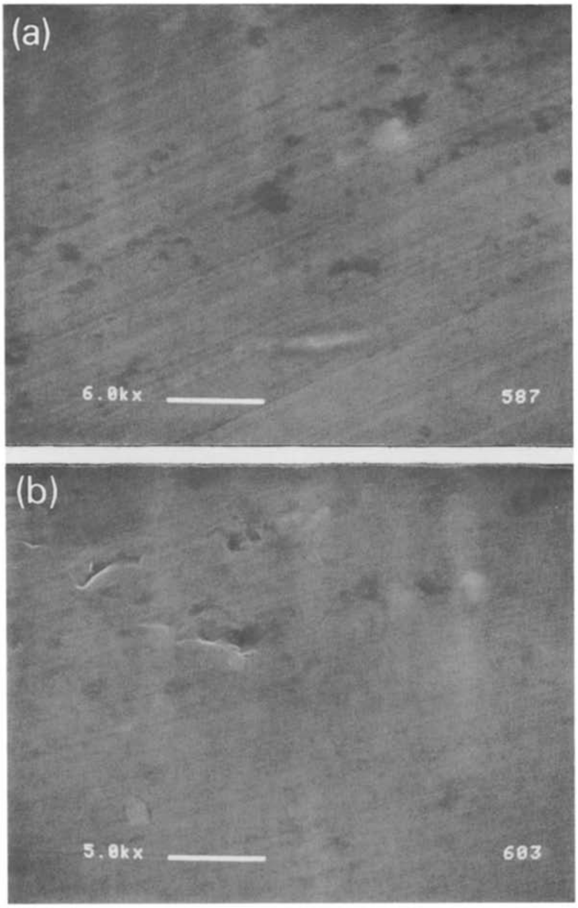

Fig. 4. SEM photographs of aluminium sample pan: (a) surface of pan, originally ×6000, bar equals 2.5 μm; (b) surface of cover, originally ×5000, bar equals 3 μm.

similar to that mentioned by Takamizawa and Urabe [3], can be expected. In the monolayer in direct contact with the surface of the pan, the head groups are anchored strongly on the surface and the hydrocarbon tails will be arranged in a somewhat loose hexagonal packing, as reported with the first monolayer in the L–B film of SA deposited on a Ge plate [5]. Thus, in the extreme case of one monolayer, we should detect only the melting of the hydrocarbon tail. As the sample weight decreases, the ratio of surface monolayer to bulk phase is increased. This seems to be the main reason why the heats of fusion for the ultra-micro SA sample tend to decrease.

From these results, it is concluded that the surface effects in the micro DSC measurements can be classified into two types.

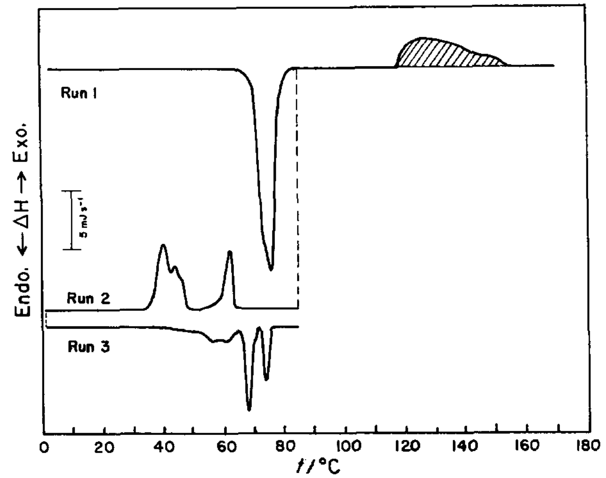

Fig. 5. DSC curves for 1.70 mg *N*-octadecyl acrylamide; DSC 20, Al pan, 5 °C min^{-1}.

Phase transition behaviour and thermal polymerisation of N*-octadecyl acrylamide*

Next, the surface effects of the aluminium pan on the phase transition behaviour and thermal polymerisation of ODAAm were studied using the DSC20 apparatus. In the DSC measurements of ODAAm of milligram order, an endothermic peak for melting appears at 75 °C, followed by a broad exothermic peak for thermal polymerisation (hatched peak), as shown in Fig. 5. On the other hand, in the cooling curve returned at 85 °C (Run 2), two exothermic peaks frequently appear, which correspond to two endothermic peaks in the reheating curve (Run 3). The higher peak is assigned to the stable crystalline form (the β_2 form) [1] and the lower peak can be attributed to a metastable crystal, although the reproducibility of this peak is somewhat poor. After thermal polymerisation, only a small peak for crystallisation of unreacted monomer molecules was observed in the cooling curve returned at 160 °C. This result indicates that thermal polymerisation of ODAAm can occur effectively in the relatively narrow temperature range of 115–155 °C. Furthermore, as shown in Fig. 6, we have found that when the sample weight is smaller than a critical value, the metastable crystal with lower melting point cannot be observed and thermal polymerisation is suppressed remarkably. The exothermic peaks for the thermal polymerisation of ODAAm are not smooth, as shown in Fig. 7. The onset temperatures for polymerisation seem to increase with decreasing sample weight, whereas the temperatures indicating completion of polymerisation all fall around 150 °C. On the other hand, the molar heats of polymerisation estimated from the peak areas are almost constant with samples of milligram order, as

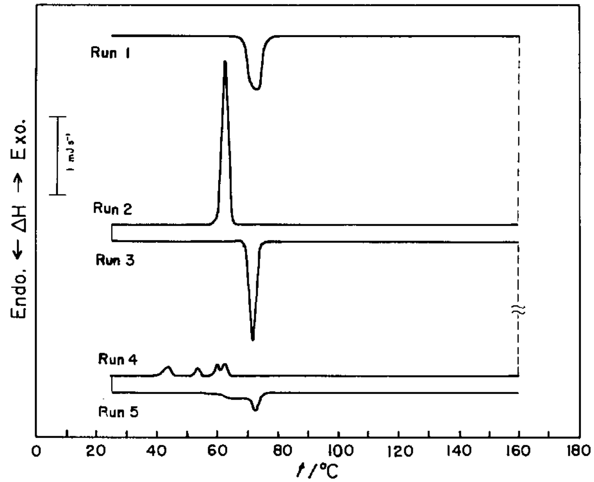

Fig. 6. DSC curves for 0.22 mg *N*-octadecyl acrylamide; DSC 20, Al pan, 5 °C min^{-1}.

shown in Fig. 8. The molar heat of polymerisation decreases sharply in the range 0.2–0.5 mg, and becomes undetectable with samples smaller than 0.2 mg.

From these results it can be deduced that both the thermal polymerisation and polymorphic transition of ODAAm are strongly suppressed by the surface effect of the aluminium pan. The strong interaction between the aluminium surface and the amide group, on which the terminal C=C group is linked, may be caused by a hydrogen bond between the C=O group and

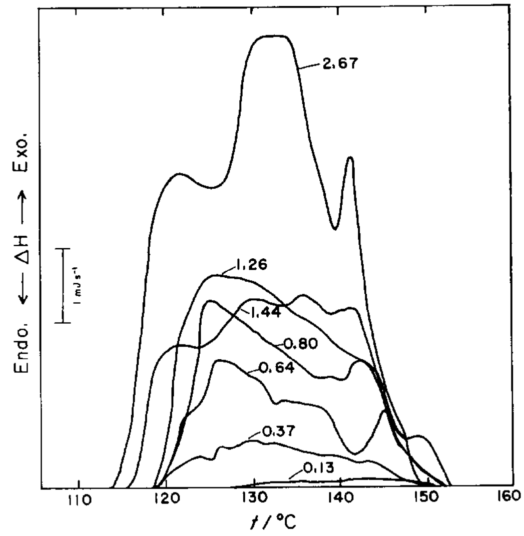

Fig. 7. DSC curves for thermal polymerisation of *N*-octadecyl acrylamide of various weights; DSC 20, Al pan, 5 °C min^{-1}.

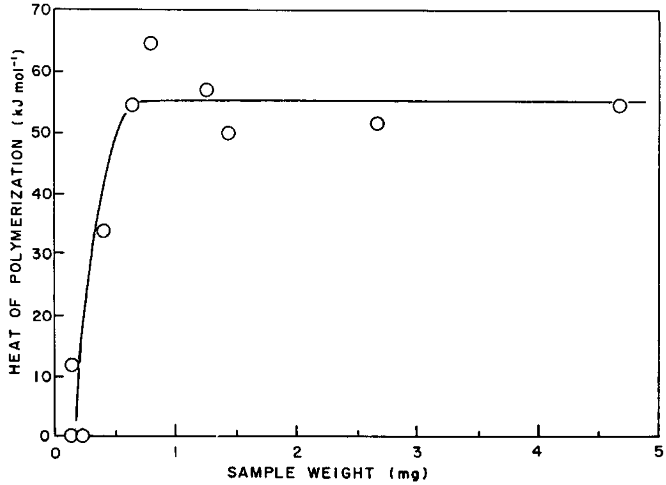

Fig. 8. Effect of sample weight on the molar heats of polymerisation of *N*-octadecyl acrylamide.

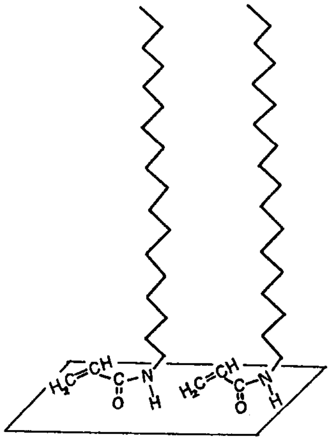

Fig. 9. Schematic representation of the arrangement of *N*-octadecyl acrylamide molecules on the surface of the aluminium pan.

the HO group on the thin oxide layer of the aluminium pan. Thus, the C=C groups seem to be oriented nearly parallel to the solid surface, as shown in Fig. 9. This orientation of the C=C groups should be unfavourable and their conformational freedom is not sufficient for thermal polymerisation.

CONCLUDING REMARKS

A strong interaction between the polar head group of amphiphilic compounds and the thin oxide layer of the aluminium pan seems to cause surface effects in micro DSC measurements which can be classified into two types: one surface effect is due to chemisorption of stearic acid on the surface of the aluminium sample pan which is covered with a thin oxide layer; and the other is attributed to the anchoring of the polar head group on the surface of the pan, which restricts the conformational freedom of the head groups.

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