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THERMOANALYTICAL STUDY ON THE POLYMORPHIC BEHAVIOUR OF LONG-CHAIN VINYL COMPOUNDS *

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ABSTRACT

The polymorphic behaviour of long-chain vinyl compounds such as vinyl stearate, octadecyl acrylate and methacrylate was studied by differential scanning calorimetry. These long-chain monomers, except *N*-octadecyl acrylamide, exhibit characteristic polymorphism depending on the chemical structure of the functional groups. From the entropy changes for fusion $\Delta_f S$ and transformation $\Delta_t S$, the molecular packing and mobility of functional groups are discussed in relation to the polymerizability. In addition, the effect of minimization of sample weight on the phase transition has been examined.

INTRODUCTION

Long-chain vinyl compounds, such as vinyl stearate, crystallize in the layered structure and exhibit characteristic polymorphism which depends on the chemical structure of the functional groups and the length of the alkyl chain [1,2]. Two-dimensional polymerization in the monolayer assemblies and in the bulk crystal with layered structures is influenced by the arrangement or packing modes of the monomer molecules and also by the conformational freedom of the functional groups [3–6].

In this study, the polymorphic behaviour of five long-chain vinyl compounds with different functional groups or hydrocarbon chain lengths has been studied by differential scanning calorimetry (DSC). The effects of the chemical structure of the functional groups on the phase transition behaviour were elucidated on the basis of thermodynamical data such as enthalpy and entropy changes (ΔH and ΔS). The packing modes of long-chain monomer molecules in the layered structure, the rotational freedom around the molecular axis and the conformational freedom of the

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TABLE 1

Long-chain vinyl compounds

Compound	Abbreviation	Melting point (° C)
Octadecyl acrylate	$C_{18}Acr$	32.5–33.0
Octadecyl methacrylate	$C_{18}MAcr$	28.7–29.7
N-Octadecyl acrylamide	$C_{18}AAm$	72.3–72.8
Vinyl stearate	VC_{18}	36.0–36.5
Vinyl palmitate	VC_{16}	25.5–26.4

functional groups, which were estimated from the entropy changes for fusion $\Delta_f S$ and transformation $\Delta_t S$, can be related to the polymerizability. In addition, changes in phase transition behaviour caused by an epitaxial effect at the surface of the sample pan have been examined by the minimization of the sample weight in the DSC measurements.

EXPERIMENTAL

For the monomers, except *N*-octadecyl acrylamide, commercial products from Tokyo Kasei Co. were used after purification by recrystallization from acetone or methanol. *N*-octadecyl acrylamide was synthesized from octadecylamine and acryloyl chloride by reaction at 0–15°C for 10–15 h in toluene. Abbreviations and melting points of the long-chain vinyl compounds are given in Table 1. Thermal analyses were carried out with a Perkin–Elmer model DSC-1b or a Seiko Denshi Kogyo model DSC-20 differential scanning calorimeter. Sample weights of 0.1–5 mg and scanning rates ranging from 0.5 to 4°C min^{-1} were adopted. The observed values of ΔH were calibrated using the heat of fusion of stearic acid, 56.7 kJ mol^{-1} (47.6 cal g^{-1}) [7]. X-ray diffraction patterns were obtained by the powder method with a Rigaku Denki X-ray diffractometer. γ-Ray-initiated post-polymerization in the different crystalline modifications was investigated with regard to the polymerization rate and the saturated conversion.

γ-Ray irradiations were carried out at the Japan Atomic Energy Institute at Takasaki.

RESULTS AND DISCUSSION

Polymorphic behaviour

DSC curves of $C_{18}Acr$ ($CH_3(CH_2)_{17}OCOCH{=}CH_2$) are shown in Fig. 1(A). These results indicate that $C_{18}Acr$ exhibits at least five crystalline modifications with different packing modes, which we refer to as α, sub α,

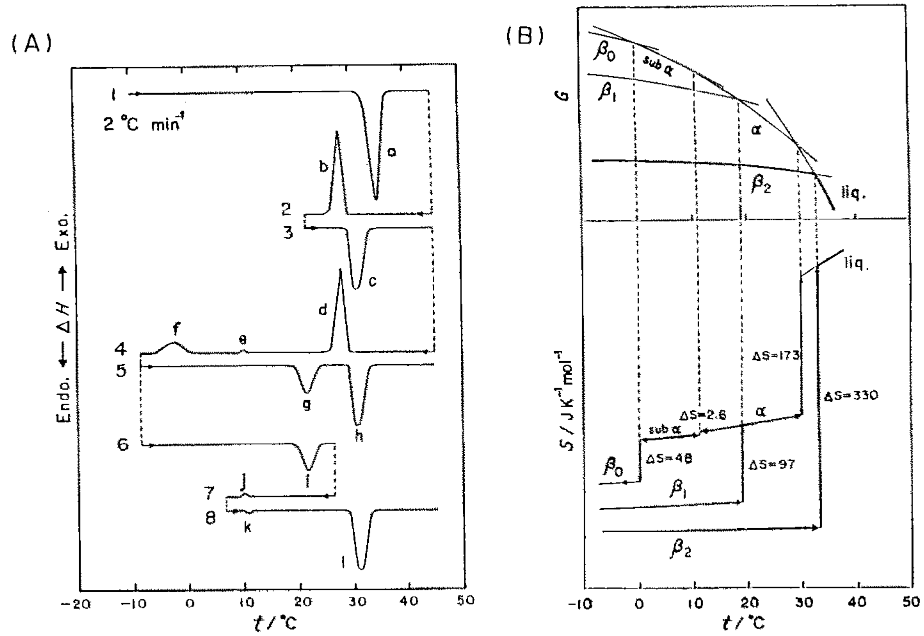


Fig. 1. (A) DSC curves (scanning rate, 2° C min^{-1}) and (B) schematic diagrams for the Gibbs energy–temperature and entropy–temperature relationships of octadecyl acrylate.

β_0, β_1 and β_2 forms respectively on the basis of the nomenclature proposed by Larsson [8]. An endothermic peak a on run 1 corresponds to the melting of the β_2 form crystal (triclinic); $\Delta_f H = 101$ kJ mol^{-1}. Endothermic peaks c, h and l are attributed to the melting of the α form crystal (hexagonal); $\Delta_f H = 53$ kJ mol^{-1}. The exothermic peaks d, e and f are assigned to the phase transitions liquid $\rightarrow \alpha$, $\alpha \rightarrow$ sub α and sub $\alpha \rightarrow \beta_0$ respectively. The endothermic peaks g and i can be attributed to the $\beta_1 \rightarrow \alpha$ transition. The values of $\Delta_t S$ were calculated from the values of $\Delta_t H$ which were estimated from the peak areas on the DSC curves. The entropy–temperature curves and schematic Gibbs free energy–temperature diagrams for C_{18}Acr are shown in Fig. 1(B). The entropy changes for fusion of the β_2 form and the α form are 330 J K^{-1} mol^{-1} and 173 J K^{-1} mol^{-1} respectively. It can be seen from Fig. 1(B) that only the β_2 form is stable and the α, β_0 and β_1 forms are all metastable throughout the whole temperature range. Although the monotropic phase transitions $\beta_0 \rightarrow \beta_1$ and $\beta_1 \rightarrow \beta_2$ could not be observed by the DSC measurements, we can estimate these transitions from the energetics.

DSC curves of C_{18}MAcr ($CH_3(CH_2)_{17}OCOC(CH_3){=}CH_2$) are shown in Fig. 2(A). The DSC curves for runs 1–4 are very similar to those of C_{18}Acr, but the heating curves 5–7 differ in appearance from those of exothermic peaks. The peak g is attributable to the $\beta_1 \rightarrow \beta_2$ transition, whereas peak 1

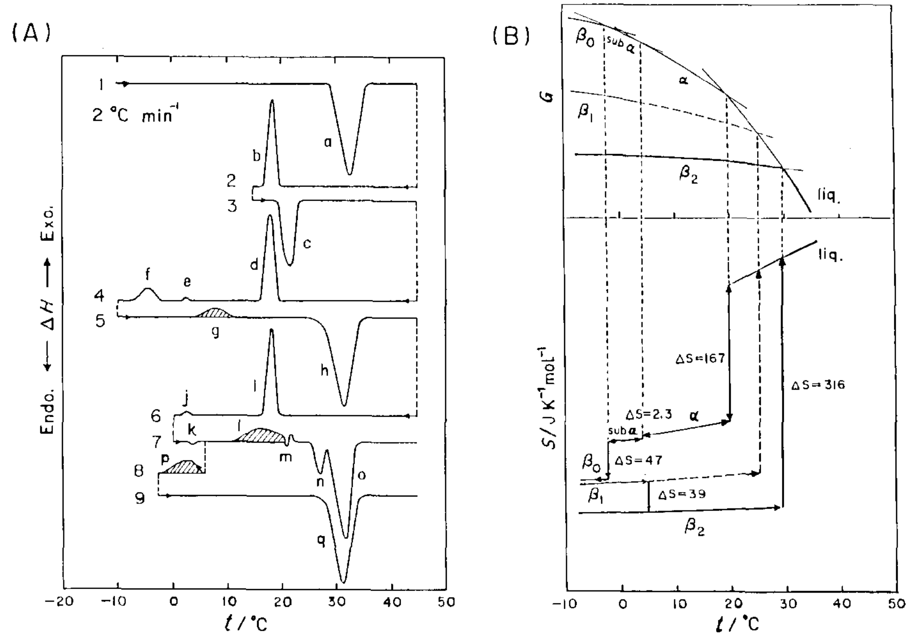


Fig. 2. (A) DSC curves (scanning rate, 2 °C min^{-1}) and (B) schematic diagrams for the Gibbs energy–temperature and entropy–temperature relationships of octadecyl methacrylate.

on run 7 seems to be caused by the successive transitions $\alpha \rightarrow \beta_1 \rightarrow \beta_2$. From the results of the DSC measurements we estimated the entropy–temperature curves and the schematic diagrams for the Gibbs free energy–temperature relation of C_{18}MAcr as shown in Fig. 2(B). Thermodynamic parameters for fusion of the β_2 and α form crystals are $\Delta_f H = 95.6$ kJ mol^{-1}, $\Delta_f S = 316$ J K^{-1} mol^{-1} and $\Delta_f H = 48.9$ kJ mol^{-1}, $\Delta_f S = 167$ J K^{-1} mol^{-1} respectively. From these results it can be deduced that C_{18}MAcr also exhibits the α, sub α, β_0, β_1 and β_2 forms similar to those of C_{18}Acr, although the phase transition behaviour is slightly different.

As reported previously [1], VC_{18} ($CH_3(CH_2)_{16}COOCH{=}CH_2$) shows dimorphism. A highly purified sample exhibits the β_1 and β_2' forms, which can be assigned to the monoclinic crystals with a monoclinic parallel ($M_{\parallel}$) subcell and an orthorhombic perpendicular ($O_{\perp}$) subcell respectively. Thermodynamic parameters for fusion of β_2' and β_1 crystals are $\Delta_f H = 81.6$ kJ mol^{-1}, $\Delta_f S = 264$ J K^{-1} mol^{-1} and $\Delta_f H = 68.6$ kJ mol^{-1}, $\Delta_f S = 222$ J K^{-1} mol^{-1} respectively.

From the DSC curves shown in Fig. 3, C_{18}AAm ($CH_3(CH_2)_{17}NHCO$-$CH{=}CH_2$) seems to exhibit no polymorphism. The heat of fusion $\Delta_f H$ is 65.7 kJ mol^{-1} and the entropy change $\Delta_f S$ is 190 J K^{-1} mol^{-1}. The crystal structure of this monomer may be assigned to the β_2 form, whereas recently Miyashita et al. [9] have proposed a somewhat different form in which the

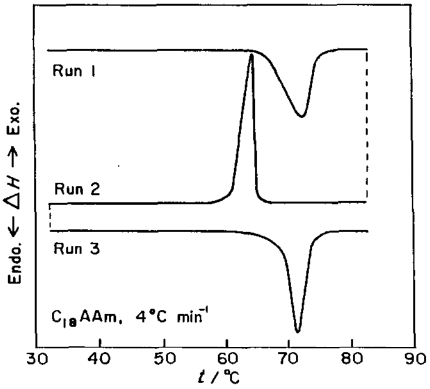


Fig. 3. DSC curves of *N*-octadecyl acrylamide (scanning rate, 4 ° C min^{-1}).

functional group is slightly twisted. In either case, a relatively low value of $\Delta_f S$ is characteristic of C_{18}AAm.

The polymorphic behaviour and entropy–temperature diagrams for fusion of the four kinds of long-chain vinyl compounds are shown together in Fig. 4. Combining the results of DSC, X-ray diffraction and IR spectra the crystal structures of the α, β_1, β_2' and β_2 forms can be assigned as hexagonal, monoclinic with $M_{\parallel}$ and $O_{\perp}$ subcells and triclinic with $T_{\parallel}$ subcells respectively [3,4]. Molecular arrangements and subcell dimensions in the α, β_1, β_2' and β_2 forms are shown in Fig. 5. The diagrams of the subcells of the α and β_1 forms correspond to VC_{18} and that of the β_2 form to C_{18}Acr. Subcell dimensions of the β_1 forms of C_{18}Acr, C_{18}MAcr and VC_{18} are slightly different from each other reflecting the chemical structure of the functional groups. Crystal structures of the sub α and β_0 forms have not yet been clarified.

Relationship between polymerizability and thermodynamic parameter

The polymerization of long-chain vinyl compounds is markedly accelerated in the hexagonal packing (α form) of monomer molecules with perpendicular orientation in the layered structure and rotational freedom around the molecular axis, together with conformational freedom of the functional group. Contrary to this, the polymerization of C_{18}Acr and C_{18}MAcr in the triclinic (β_2 form) and monoclinic (β_1 form) crystals is forbidden [3,4]. In the cases of VC_{18} and C_{18}AAm, however, the monomer molecules in the β_1, β_2' and β_2 forms can polymerize without difficulty [1,10]. As an example, results of the postpolymerization of VC_{18} in the β_1 and β_2' forms at 20 ° C are shown in Fig. 6 in comparison with the result for C_{18}MAcr in the β_2 form ($\Delta_f S = 316$ J K^{-1} mol^{-1}) at 26 ° C and that of C_{18}Acr in the α form ($\Delta_f S = 173$ J K^{-1} mol^{-1}) at 20 ° C. In the case of

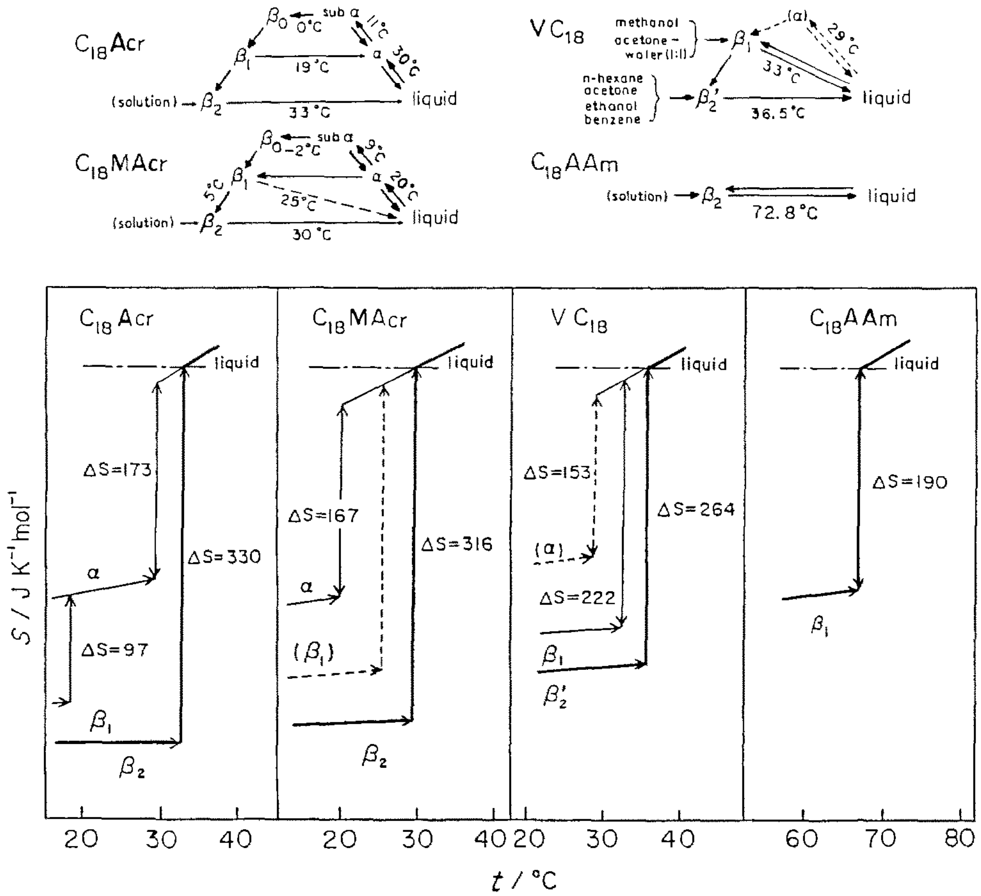
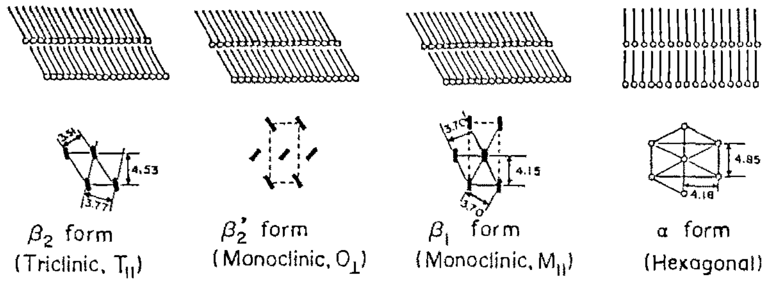


Fig. 4. Polymorphic behaviour and entropy changes for fusion of long-chain vinyl compounds.

VC$_{18}$, although the initial rate of polymerization of the β_1 form crystal with $M_{\parallel}$ subcell ($\Delta_f S = 222$ J K^{-1} mol^{-1}) is slightly higher than that of the β_2' form with $O_{\perp}$ subcell ($\Delta_f S = 264$ J K^{-1} mol^{-1}), the saturated conversions



β_2 form (Triclinic, $T_{\parallel}$)
β_2' form (Monoclinic, $O_{\perp}$)
β_1 form (Monoclinic, $M_{\parallel}$)
α form (Hexagonal)

Fig. 5. Packing modes and subcell dimensions of long-chain vinyl compounds.

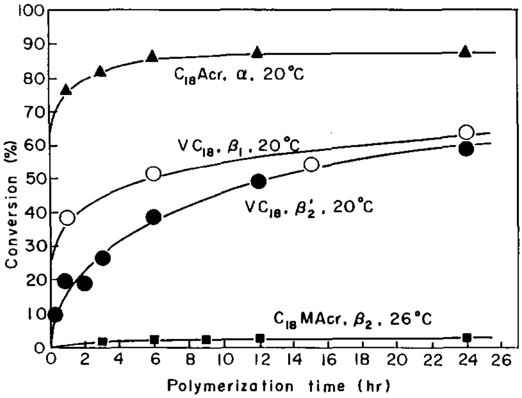


Fig. 6. Postpolymerization of vinyl stearate in the β_1 and β_2' forms at 20 °C after γ-ray irradiation of 1 Mrad at -196 °C, in comparison with those of octadecyl acrylate in the α form at 20 °C and octadecyl methacrylate in the β_2 form at 26 °C.

in both crystal forms are nearly equal, showing relatively high polymerizability. The difference in the polymerizability in the layered structure should be attributable to the difference in packing modes and mobility of the functional groups, which is represented by some thermodynamic parameters. It was found that the entropy change for fusion $\Delta_f S$ can be used as a measure of polymerizability in the solid state [2]. The values of $\Delta_f S$ for the stable crystalline forms of these long-chain monomers (Fig. 4) show a somewhat good correlation with the polymerizability. When the value of $\Delta_f S$ is smaller than a critical value ranging from 270 to 310 J K^{-1} mol^{-1}, solid state polymerization may be allowed, reflecting the conformational freedom of the functional groups.

Effect of sample weight

Finally, effects of sample weight on the phase transition of the vinyl esters of long-chain fatty acids were examined. In the case of VC_{18}, the rate of the $\beta_1 \rightarrow \beta_2'$ transition in the bulk state is so slow that this transition cannot be observed by normal DSC measurements as shown in Fig. 7(A), although the phase transition has been confirmed by the changes in X-ray diffraction or IR spectra after several weeks or months. When the sample weight is minimized to 0.43 mg (Fig. 7(B)), the $\beta_1 \rightarrow \beta_2'$ transition is accelerated and is confirmed by the DSC curve of a sample maintained at room temperature for 6 days. In contrast with this, the rate of the $\beta_1 \rightarrow \beta_2'$ transition of VC_{16} is relatively fast as shown in Fig. 8(A). The lower peak on the second heating curve can be assigned to the melting of the β_1 form crystal and the higher peak may be attributed to the melting of the β_2' form crystal. The ratio of the peak areas of the higher and lower peaks depends on the scanning rate

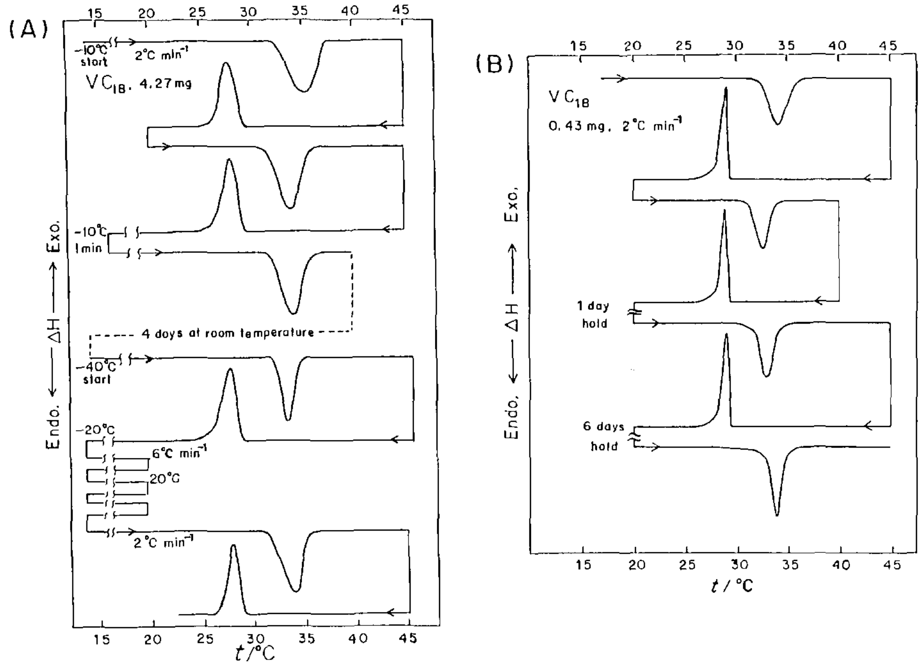


Fig. 7. Effect of sample weight on the phase transition behaviour of vinyl stearate.

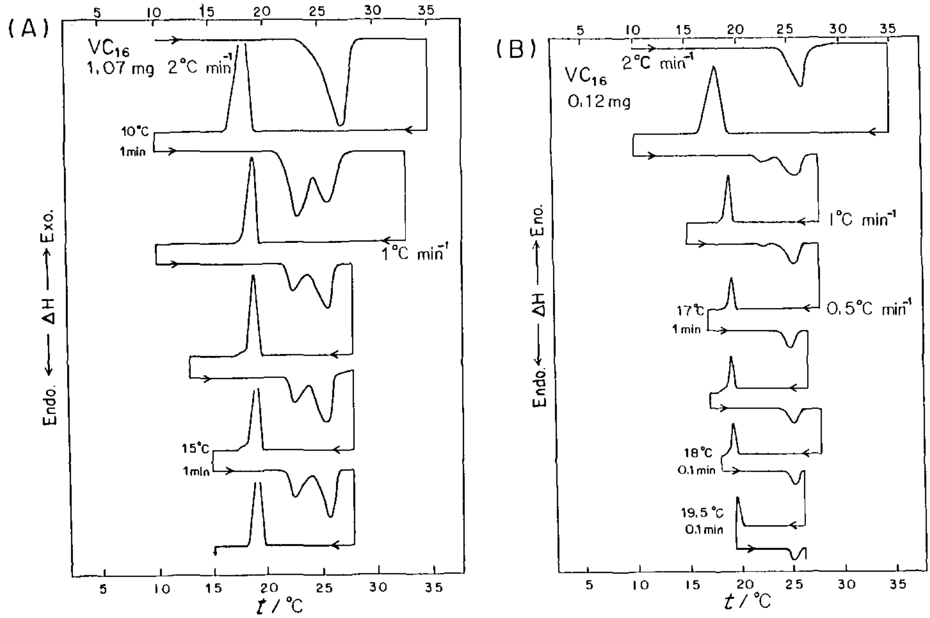


Fig. 8. Effect of sample weight on the phase transition behaviour of vinyl palmitate.

of the DSC measurements. After slow cooling the lower peak on the heating curve became smaller. Furthermore, when the sample weight is minimized to 0.12 mg and the scanning rate is reduced to 0.5 °C min^{-1} (Fig. 8(B)), the melting peak of the β_1 form cannot be observed, probably because almost all the β_1 form crystal is transformed into the β_2' form in the cooling process. From these results it can be deduced that the $\beta_1 \rightarrow \beta_2'$ transition of long-chain vinyl esters is accelerated by a surface effect of the aluminium pan, whose surface should be covered with a very thin film of Al_2O_3.

CONCLUDING REMARKS

The polymorphic behaviour of long-chain vinyl compounds is influenced markedly by the chemical structure of the functional groups and the length of the alkyl chains. The entropy changes for fusion can be related to the polymerizability of the long-chain monomers in layered structures in terms of the packing mode of the molecules and the mobility of the functional groups. In addition, a surface effect of the sample pan was observed by the minimization of the sample weight.

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