

THERMAL BEHAVIORS OF VINYL ESTERS OF LONG-CHAIN FATTY ACIDS AND THEIR COMBLIKE POLYMERS

Y. SHIBASAKI and K. FUKUDA

Department of Chemistry, Faculty of Science, Saitama University
255 Shimo-okubo, Urawa 338 (Japan)

ABSTRACT

Phase transition behaviors of vinyl esters of long-chain fatty acids (C₁₂-C₁₈) and their comblike polymers have been investigated by the thermal analysis combining with X-ray diffraction and infrared spectroscopy. Effect of the length of hydrocarbon chain on the thermal behaviors of both monomers and polymers have been elucidated. Vinyl stearate exhibits three crystalline modifications, α (hexagonal), β_1 (monoclinic, M_{II}) and β_2 (monoclinic, O_I) forms. With shortening of the alkyl chain the polymorphic behaviors become simpler. The thermal behaviors of the resultant polymers are influenced by the packing mode of monomer molecules and the polymerization temperature.

INTRODUCTION

Long-chain esters of acrylic and methacrylic acids crystallize in layered structures similar to the monolayer assemblies and exhibit characteristic polymorphisms, depending on the chemical structure of functional groups and chain length (ref.1,2). The structure of the resultant comblike polymers are influenced by the packing mode of monomer molecules (ref.3). In this study, the thermal behaviors of vinyl esters of long-chain fatty acids (C₁₂-C₁₈) and their comblike polymers have been investigated together with X-ray and infrared (IR) analysis, in relation to the mechanisms of the solid-state polymerizations. The polymorphic behavior of vinyl stearate has been reported in a separated article (ref.4).

EXPERIMENTAL

Materials

The monomers used are commercial reagents from Tokyo Kasei Co., which were purified by recrystallizations from acetone. Abbreviations and their melting points are given in Table 1. The polymers were obtained by the postpolymerization at various temperatures after the γ -ray irradiation of 1 Mrad at -196°C.

Methods for studying thermal behaviors

Thermal analysis was carried out with a Perkin-Elmer model DSC-1 differential scanning calorimeter. The sample weights of 5-15 mg and scanning rates ranging

TABLE 1

Vinyl esters of lauric to stearic acids

Compound	Abbreviation	mp. (°C)
Vinyl stearate	VC18	36.0 - 36.5
Vinyl palmitate	VC16	25.5 - 26.4
Vinyl myristate	VC14	15.0 - 15.8
Vinyl laurate	VC12	2.5 - 3.8

from 0.5 to $8^{\circ}\text{Cmin}^{-1}$ were adopted. X-Ray diffraction patterns were obtained by the powder method with a Rigaku Denki X-ray diffractometer. IR spectra were taken by KBr disk method with a Nihon Bunko model IR-G spectrophotometer.

RESULTS AND DISCUSSION

Polymorphic behaviors of long-chain vinyl monomers

The DSC curves of vinyl stearate (VC18) are shown in Figure 1. The results with highly purified sample (Fig. 1a) indicate the existence of at least two crystalline modifications, which we refer to as β_1 and β_2 forms on the basis of the nomenclature proposed by Larsson (ref.5). The β_2 form crystal with higher melting point (36.5°C) is a stable state at any temperature below its melting point, while the β_1 form crystal with lower melting point (33.2°C) is a metastable state. The enthalpy (ΔH) and entropy (ΔS) for fusion of the β_2 form crystal are $81.6 \text{ kJ mole}^{-1}$ and $264 \text{ JK}^{-1}\text{mole}^{-1}$, respectively, while those of the β_1 form are smaller by about 15%.

On the other hand, the DSC curves of VC18 with minute impurity (Fig. 1b) are somewhat different. From these results it has been found that the α form ($\Delta H = 46.5 \text{ kJ mole}^{-1}$ and $\Delta S = 153 \text{ JK}^{-1}\text{mole}^{-1}$) appears transiently in the cooling process

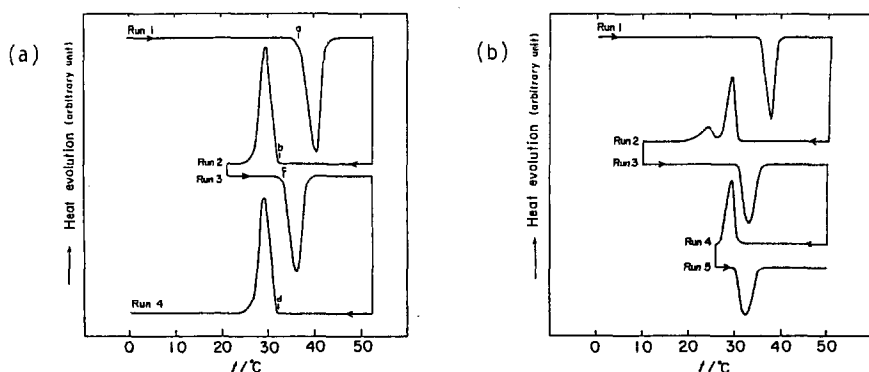


Fig. 1. DSC curves of vinyl stearate: Scanning rate $2^{\circ}\text{Cmin}^{-1}$.
 (a) Highly purified sample. (b) Impurity sample.

of the melt by the aid of impurities. The α form transforms to the β_1 form rather quickly, although the rate of transition from α to β_1 depends on the content of impurities. Further, the metastable β_1 form is stabilized by impurities and the transition from β_1 to β_2' is practically forbidden.

The X-ray pattern (ref.4) for the α form shows one short spacing of 4.18 Å, and the long spacing diffractions corresponding to the fully extended molecular length of 29.4 Å. Therefore, the α form is a hexagonal packing with perpendicular orientation. The β_1 form shows two short spacings of 3.70 and 4.15 Å together with the long spacing diffractions of 26.4 Å. The β_2' form shows no diffraction peak for the short spacing, although the long spacing is nearly equal to that of β_1 form. In addition, in the IR spectra of the β_1 form the scissoring and rocking bands of methylene groups (1470 and 720 cm^{-1}) are both single, whereas these two bands for the β_2' form split into doublets (ref.4). Thus, the crystal structures of the β_1 and β_2' forms of VC18 can be assigned to the monoclinic crystals with M_{11} and O_1 subcells, respectively.

Polymorphic behaviors of VC18 can be expressed as shown in Figure 2. The β_2' form is obtained by the crystallization from common solvents such as acetone and also from the molten state through the β_1 form. The β_1 form crystal is obtained by the cooling of molten sample and also by the crystallization from methanol or acetone-water (1:1) mixture. The schematic diagrams for Gibbs free energy-temperature and the entropy-temperature curves of VC18 are shown in Figure 3. The β_2' form is only stable state below the melting point and the β_1 form is a metastable form. The α form, which is unstable, can be appeared only transiently by the aid of impurities.

Next, the effect of the alkyl chain length on the polymorphic behavior of vinyl esters has been examined. The DSC curves of vinyl palmitate (VC16) are

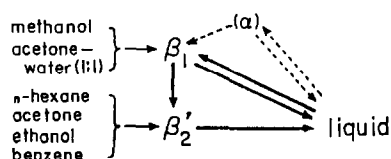


Fig. 2. Polymorphic behavior of vinyl stearate.

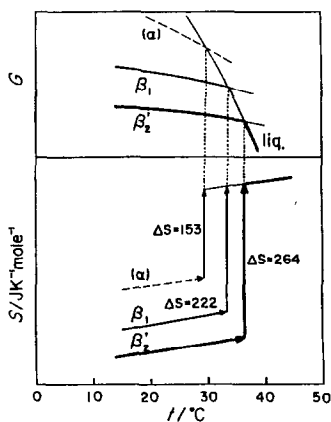


Fig. 3. Schematic diagrams for the Gibbs free energy-temperature and the entropy-temperature curves of vinyl stearate.

shown in Figure 4. VC₁₆ exhibits both the β_1 and β_2 forms. On immediate heating of the β_1 form crystal obtained from the melt two peaks appeared (Fig. 4a). The ratio of these peak areas depends on the limit of cooling temperature, the holding time, and the scanning rate. The fraction of higher peak increased with decreasing of the scanning rate (Fig. 4b). The lower and the higher peaks correspond to the melting of the β_1 and β_2 form crystals, respectively. The DSC curves of vinyl myristate (VC₁₄) and laurate (VC₁₂) with shorter alkyl chains are shown in Figure 5. These compounds also exhibit the β_1 and β_2 forms, although the double peaks could not be observed in the reheating curve. In these cases, the β_1 form crystal grown in the cooling process of the melt may transform quickly into the β_2 form, because of the cohesive energy per molecule become smaller with the shortening of alkyl chain.

Thermal behaviors of the comblike polymers obtained from long-chain vinyl esters

The comblike polymers obtained by the polymerization of long-chain vinyl

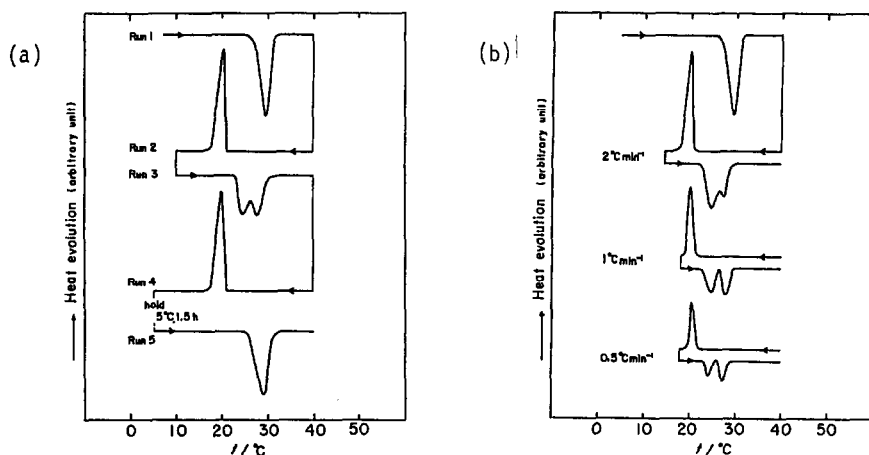


Fig. 4. DSC curves of vinyl palmitate. (a) Effect of thermal treatment. (b) Effect of scanning rate.

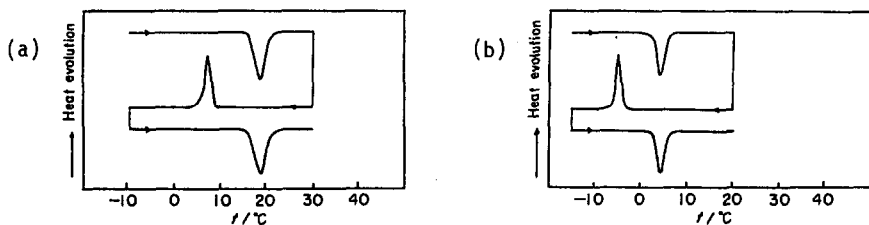


Fig. 5. DSC curves of long-chain vinyl esters. (a) Vinyl myristate. (b) Vinyl laurate.

esters crystallize in the layered structure, predominantly owing to the cohesive forces between long side chains. The thermal behaviors of these polymers should be dependent on their stereoregularities. The DSC curves of poly(vinyl stearate) (PVC₁₈) are shown in Figure 6. With the PVC₁₈ sample obtained by the postpolymerization in the β_1 form monomer at 30°C (Fig. 6a) the shape of every peak is sharp and the melting peak tends to sharpen by the annealing. On the other hand, with the PVC₁₈ samples obtained from the β_2 form monomer at 20 and 30°C (Fig. 6b) the melting peaks are somewhat lower and double peaks appear on their cooling curves, whereas the polymer obtained by the polymerization at 0°C exhibits the higher melting point than that of the polymer obtained from the β_1 form and shows a single peak on cooling. From the X-ray diffraction measurements it has been found that the PVC₁₈ sample obtained from the β_2 form at 0°C crystallizes in the most closely packed hexagonal mode. These results indicate that the melting point of the comblike polymer is dependent on the stereoregularity. In the two dimensional polymerization of the monomers with sufficiently long alkyl chain, a syndiotactic rich polymer may be obtained at a lower temperature, because the topochemical reaction in the crystal effectively controls the stereoregularity of the resultant polymer (ref.2). With the increase of polymerization temperature the propagation reaction is activated and the selectivity of reaction may decrease. Therefore, the content of atactic polymer is increased, and hence the lowering of melting point occurs. It seems that the increase of these tendency at the later stage of polymerization results in the double peaks on the cooling curve (Fig. 6b). It is interesting to note that this phenomenon was observed only with the monomer

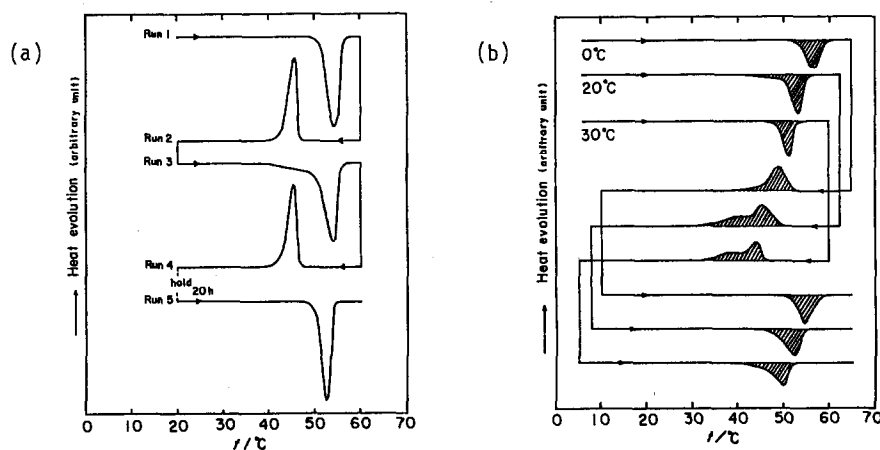


Fig. 6. DSC curves of poly(vinyl stearate): Scanning rate $2^{\circ}\text{C min}^{-1}$. (a) Obtained from the β_1 form at 30°C. (b) Obtained from the β_2 form at 0-30°C.

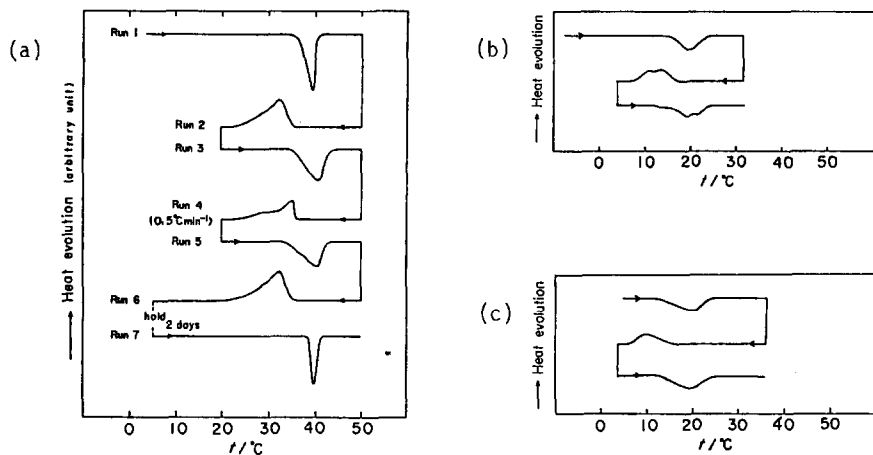


Fig. 7. DSC curves of the comblike polymers: Scanning rate $2^{\circ}\text{C min}^{-1}$.
 (a) Poly(vinyl palmitate). (b) Poly(vinyl myristate). (c) Poly(vinyl laurate).

in β_2' form crystal (monoclinic, O_1 subcell). Thus, it can be concluded that the stereoregularity of the resultant polymer is controlled by the arrangement and packing mode of the monomer molecules and also by the polymerization temperature.

As shown in Figure 7, the DSC curves of the comblike polymers change with the decrease of side chain length. The thermal behavior of poly(vinyl palmitate) (PVC_{16}) is rather similar to that of PVC_{18} (Fig. 7a), whereas those of poly(vinyl myristate) (PVC_{14}) and poly(vinyl laurate) (PVC_{12}) (Fig. 7b and 7c) are remarkably different. For instance, the peaks become broad and the enthalpy changes for fusion per gram are markedly decreased. These results, which are in well agreement with the other comblike polymers (ref. 3, 6, 7), are attributable to the fact that the comblike polymers of vinyl esters of long-chain fatty acids crystallize in a hexagonal packing with respect to the side chains but eight or nine methylene units of the side chains in the vicinity of main chain are amorphous.

REFERENCES

- 1 Y. Shibasaki, H. Nakahara and K. Fukuda, *J. Polym. Sci. Polym. Chem. Ed.*, **17** (1979) 2387-2400.
- 2 Y. Shibasaki and K. Fukuda, *J. Polym. Sci. Polym. Chem. Ed.*, **17** (1979) 2947-2959; *ibid.*, **18** (1980) 2437-2449.
- 3 Y. Shibasaki and K. Fukuda, *Thermal Analysis, Proceedings of the 7th ICTA, Vol. 2*, Wiley, New York, 1982, pp. 1517-1523.
- 4 Y. Shibasaki and K. Fukuda, *Thermochimica Acta*, in press.
- 5 K. Larsson, *Ark. Kemi*, **23** (1964) 35-56.
- 6 E.F. Jordan, Jr., D.W. Feldeisen and A.N. Wrigley, *J. Polym. Sci. A-1*, **9** (1971) 1835-1852.
- 7 H.W.S. Hsieh, B. Post and H. Morawetz, *J. Polym. Sci. Polym. Chem. Ed.*, **14** (1976) 1241-1255.