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POLYMORPHIC BEHAVIOR OF VINYL STEARATE

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ABSTRACT

The polymorphic behavior of vinyl stearate has been elucidated by thermal analysis combined with X-ray diffraction and infrared spectroscopy. Vinyl stearate exhibits three crystalline modifications, α (hexagonal), β_1(monoclinic, $M_{\parallel}$) and β_2'(monoclinic, $O_{\perp}$) forms. The packing mode of this compound is influenced by the thermal history and also by the nature of the solvent used for crystallization.

INTRODUCTION

Long-chain vinyl compounds, such as octadecyl acrylate and methacrylate, crystallize in a layered structure similar to monolayer assemblies and exhibit characteristic polymorphisms [1–5]. The polymerizabilities of these long-chain monomers in bulk states and Langmuir–Blodgett films are remarkably influenced by the mode of molecular packing and the conformational freedom of the functional group [6–8]. From this point of view the polymorphic behavior of vinyl stearate is of much interest, because the C=C bond is not conjugated with the C=O bond, differing from octadecyl acrylate, and hence the conformational freedom of the polar head group is expected to be large. Although Morosoff et al. [9] have elucidated the crystalline structure of vinyl stearate by X-ray diffraction, the phase transition behavior of this compound has not yet been revealed. In this study, the polymorphism of vinyl stearate has been examined by differential scanning calorimetry (DSC), combined with analyses by X-ray diffraction and infrared (IR) spectroscopy.

EXPERIMENTAL

Materials

Vinyl stearate was prepared by the transesterification of vinyl acetate with stearic acid in the presence of 100% sulfuric acid or methane sulfonic acid as

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a catalyst and mercury acetate as a masking agent for the C=C bond at 70°C for 3 h under a nitrogen atmosphere. The crude vinyl stearate obtained by distillation under reduced pressure (b.p. 166–168°C/2 mmHg) was purified by repeated recrystallizations from acetone. The melting point of the final product is 36.0–36.5°C. Commercial vinyl stearate (m.p. 35.5–36.5°C), from Tokyo Kasei Co., was also used for comparison.

Methods for studying polymorphism

Thermal analysis was performed with a Perkin-Elmer (model DSC-1) differential scanning calorimeter. The sample weight was about 5 mg, and scanning rates ranging from 1 to 4°C $\min^{-1}$ were adopted. X-ray diffraction patterns were obtained by the powder method with a Rigaku Denki X-ray diffractometer, using Cu$K\alpha$ radiation ($\lambda = 1.5405$ Å) under the conditions of 30 kV and 20 mA. IR spectra were recorded by the KBr disk method at different temperatures with a Nihon-Bunko (model IR-G) spectrophotometer.

RESULTS AND DISCUSSION

Thermal analysis

The DSC curves of vinyl stearate are shown in Fig. 1. Only one endothermic peak appears on the heating curve (run 1) of the sample crystallized from a solution in usual solvents (acetone, *n*-hexane, ethanol, etc.). The melting peak begins at 35.5°C and reaches a maximum at 40.0°C. In this case the extrapolated onset temperature (point a) is 36.5°C, while the melting point, determined by direct observation of the melting behavior of the sample with a thermometer under a microscope, is 36.0–36.5°C. On the cooling curve of the molten sample (run 2) a crystallization peak appears at b (31.7°C), and on immediate heating (run 3) an endothermic peak appears at c (33.2°C). Point c is lower than point a. These results indicate the existence of at least two crystalline modifications with a different packing mode, which we refer to as the β_1 and β_2' forms, respectively, on the basis of the nomenclature proposed by Larsson [10]. The β_2' form crystal, with higher melting point, is in a stable state at any temperature below its melting point, while the β_1 form crystal, with lower melting point, is in a metastable state. The enthalpy and entropy changes for fusion of various crystalline forms estimated from peak area are given in Table 1; these enthalpy changes, obtained from DSC curves, were calibrated using the literature value of $\Delta H = 56.7$ kJ mol^{-1} (47.6 cal g^{-1}) for stearic acid [11]. ΔH and ΔS for fusion of the β_1 form are about 85% of those for the β_2' form. Since the energy difference between β_1 and β_2' is relatively small ($\Delta H = 13$ kJ mol^{-1}

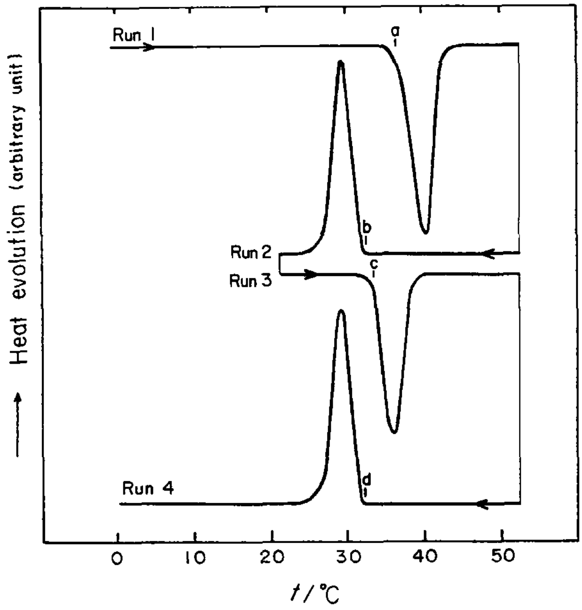

Fig. 1. DSC curves of vinyl stearate. Scanning rate: 2°C min^{-1}.

and $\Delta S = 42$ J K^{-1} mol^{-1}) the β_1 crystal transforms very slowly to the β_2' form; for example, it requires several days at room temperature.

On the other hand, the polymorphic behavior of long-chain compounds is remarkably influenced by impurities. DSC curves of vinyl stearate with a minute impurity are shown in Fig. 2. The enthalpy change of fusion in the first run (77.8 kJ mol^{-1}) corresponds to that of a highly purified sample (β_2' form), but two peaks appear in the cooling curve (run 2). The higher peak ($\Delta H = 46.5$ kJ mol^{-1} and $\Delta S = 153$ J K^{-1} mol^{-1}) can be assigned to crystallization into the α form, and the lower peak ($\Delta H = 18.3$ kJ mol^{-1} and $\Delta S = 61.2$ J K^{-1} mol^{-1}) may correspond to the transformation from the α to the β_1 form. The total changes of enthalpy and entropy are almost equivalent to those for a single exothermic peak (run 3, $\Delta H = 65.4$ kJ mol^{-1} and $\Delta S = 214$ J K^{-1} mol^{-1}). However, even when the sample is reheated

TABLE 1

Thermodynamic prameters for fusion of various crystalline forms of vinyl stearate

Crystal form	T (K)	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
α[a]	303.2	46.5	153
β_1	306.4	68.6	222
β_2'	309.7	81.6	264

[a] The α form is an extrinsic crystal form, which is caused by minute impurities.

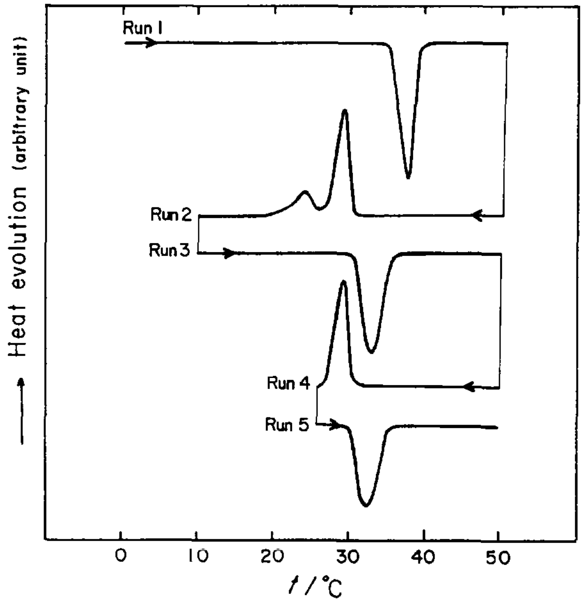

Fig. 2. DSC curves of vinyl stearate with minute impurities. Scanning rate: 2°C $\min^{-1}$.

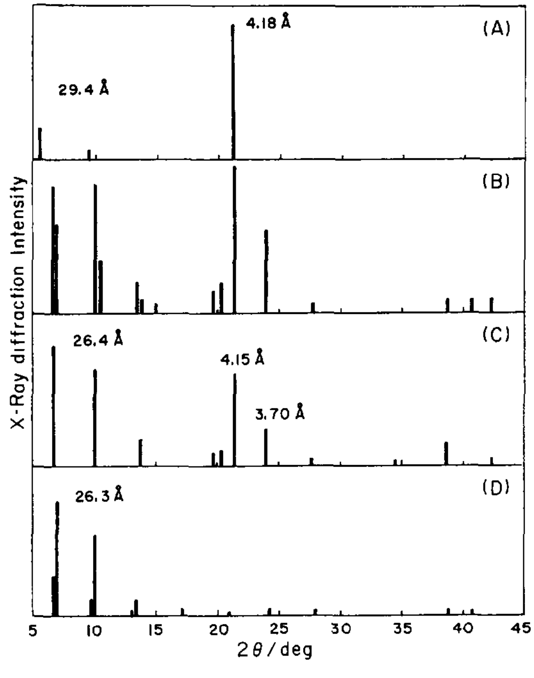

Fig. 3. X-ray diffraction patterns for various crystalline modifications of vinyl stearate: (A) α form crystallized from molten sample with some more impurities; (B) β_1 form crystallized from the melt of highly purified sample; (C) β_1 form crystallized from methanol solution; (D) β_2' form crystallized from acetone solution.

(run 5) immediately after the appearance of the α form (run 4), the ΔH value of melting (59.9 kJ mol^{-1}) is similar to the total enthalpy change in the cooling process (run 2, $\Delta H = 64.8$ kJ mol^{-1}) rather than the heat of fusion of the α form. From these results its can be concluded that the vinyl stearate sample containing minute impurities transiently exhibits the α form crystal in the cooling process of the melt, although with highly purified vinyl stearate the α form could not be detected by the DSC measurement at any scanning rate. The α form transforms to the β_1 form quickly, but the rate of transition from α to β_1 strongly depends on the impurity content. Further, the metastable β_1 form is stabilized and the transition from β_1 to β_2' is retarded by the presence of minute impurities; sometimes it requires several months at room temperature.

X-ray diffraction

X-ray diffraction patterns for vinyl stearate in the different crystalline forms are shown in Fig. 3. In the α form crystal, obtained by cooling the molten sample with some more impurity to room temperature (Fig. 3A), a single intense diffraction, that corresponds to the spacing of 4.18 Å, and the distinct diffraction peaks for the long spacing of 29.4 Å, which is comparable to the fully extended molecule, are observed. These features are characteristic of the hexagonal packing of long hydrocarbon chains. With the β_1 form crystal (Fig. 3B) obtained from the melt of a highly purified sample, two diffraction peaks at the 4.15 and 3.70 Å spacings together with the long spacing peaks of 26.4 Å are observed. These results indicate that the β_1 form can be assigned to a monoclinic crystal. In addition, the β_1 form crystal can be obtained from an acetone–water (1 : 1) mixture [9] and also from methanol solution (Fig. 3C). This is a case where the polymorphism of long chain esters is influenced by the polarity or dissolving power of the solvent. With the β_2' form crystal (Fig. 3D) a series of sharp diffraction peaks corresponding to the second and higher orders of the spacing of 26.3 Å (nearly equal to that of the β_1 form) appears, but no diffraction peak for the short spacing which reflects the packing mode of long hydrocarbon chains can be observed. Therefore, the feature of arrangement of the monomer molecules in the β_2' form crystal cannot be estimated from the result of X-ray diffraction alone.

Infrared spectra

In order to obtain some precise information on the packing modes of vinyl stearate molecules in various crystalline forms, the IR spectra at different temperatures were examined. The sample embedded in a KBr disk was thermally treated and the spectra were obtained at various temperatures. The results are shown in Fig. 4. With the molten sample (Fig. 4A) the characteristic bands are assigned as follows: C=O stretching at 1760 cm^{-1}, C=C stretching at 1648 cm^{-1}, CH_2 scissoring at 1470 cm^{-1}, C–O–C stretching at 1150 cm^{-1}, H–C out-of-plane deformation at 950 and 870 cm^{-1}, and CH_2 rocking at 720 cm^{-1}, respectively. The IR spectrum for the α form (not shown) resembles that for the molten state quite well.

Bands for the scissoring and rocking vibrations of $-CH_2-$ groups can be closely correlated with the packing mode of the long hydrocarbon chains. In the crystals with hydrocarbon chains packed in the orthorhombic manner ($O_{\perp}$ subcell), in which every second chain plane is approximately perpendicular to neighboring planes [12], these two bands split into doublets; for example, at 1473 and 1463 cm^{-1} for scissoring and at 727 and 719 cm^{-1} for rocking [13,14]. On the contrary, in the monoclinic ($M_{\parallel}$) and triclinic ($T_{\parallel}$) packings with parallel chain planes or in the hexagonal packing, these bands should be single at 1470 and 720 cm^{-1}, respectively. With the β_1 form (Fig. 4B), splitting of these bands cannot be observed. On the other hand, in the spectrum of the β_2' form (Fig. 4C) these two characteristic bands split into doublets and, moreover, nine progression bands caused by the wagging vibration of the $-CH_2-$ groups appear distinctly. These results indicate that only in the β_2' form does the C=O bond lay in the plane of *trans* zig-zag

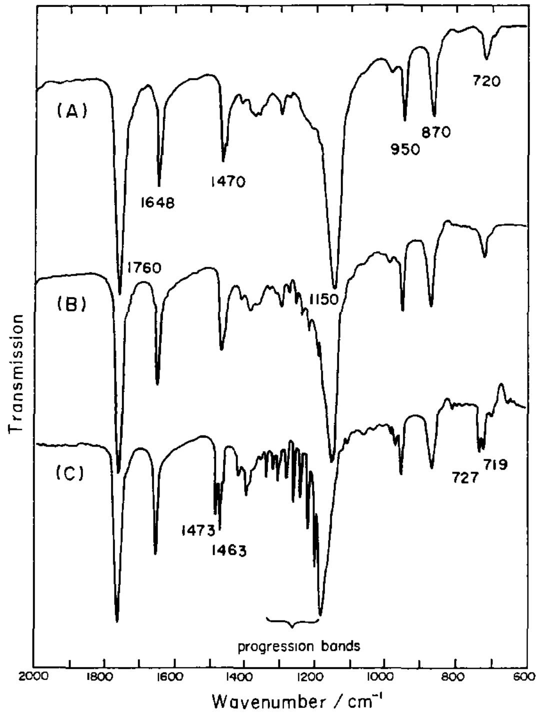

Fig. 4. Infrared spectra for various states of vinyl stearate: (A) molten state; (B) β_1 form (at 25°C) crystallized from the melt; (C) β_2' form (at 12°C) crystallized from acetone solution.

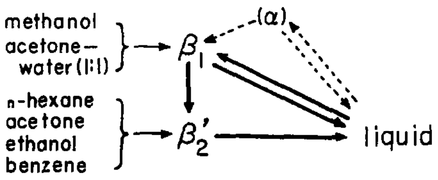

Fig. 5. Polymorphic behavior of vinyl stearate. ( ) and broken lines express the extrinsic properties.

hydrocarbon chain and the deviation of the ester group from the chain plane is within 17° [15]. Thus, the crystal structures of the β_1 and β_2' forms of vinyl stearate can be assigned to the monoclinic crystals with $M_{\parallel}$ and $O_{\perp}$ subcells, respectively. In these two crystal forms the packing mode of long alkyl chains and the conformation of ester groups differ from each other, although the inclination of the molecules is nearly the same.

Polymorphic behavior

The polymorphic behavior of vinyl stearate can be expressed as shown in Fig. 5. The β_2' form crystal (monoclinic with $O_{\perp}$ subcell, stable state with higher melting point) can be obtained by crystallization from common solvents such as acetone, and from the molten state through the β_1 form. With highly purified samples, the β_1 form crystal (monoclinic with $M_{\parallel}$ subcell, metastable state with lower melting point) is obtained by the cooling

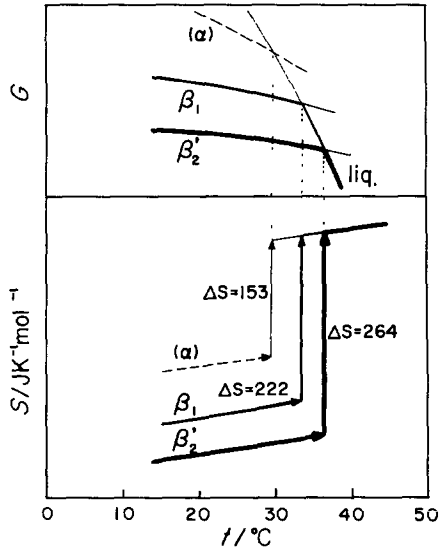

Fig. 6. Schematic diagrams for the Gibbs free energy–temperature and the entropy–temperature curves of vinyl stearate.

of molten sample and also by crystallization from methanol or an acetone–water (1 : 1) mixture. The β_1 form crystal transforms gradually into the β_2' form at room temperature. On the other hand, the α form crystal (hexagonal, unstable state with lowest melting point) can be obtained in the cooling process of the molten sample containing minute impurities. The α form crystal transforms quickly into the β_1 form, while with the sample of low purity, the $\beta_1 \rightarrow \beta_2'$ transition is practically forbidden.

The schematic diagrams for Gibbs free energy–temperature and the entropy–temperature curves of vinyl stearate are shown in Fig. 6. Below the melting point, only the β_2' form is stable and the β_1 form is a metastable form. Since the energy difference between β_1 and β_2' is relatively small, the $\beta_1 \rightarrow \beta_2'$ transition proceeds very slowly. On the contrary, the α form is an unstable state and can appear only transiently with the aid of impurities. Since the energy difference between α and β_1 is relatively large, the $\alpha \rightarrow \beta_1$ transition seems to occur rapidly.

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REFERENCES

1 Y. Shibasaki, H. Nakahara and K. Fukuda, J. Polym. Sci., Polym. Chem. Ed., 17 (1979) 2387.

2 Y. Shibasaki and K. Fukuda, J. Polym. Sci., Polym. Chem. Ed., 17 (1979) 2947.

3 Y. Shibasaki and K. Fukuda, J. Polym. Sci., Polym. Chem. Ed., 18 (1980) 2347.

4 Y. Shibasaki and K. Fukuda, in W. Hemminger (Ed.), Thermal Analysis, Proc. 6th, ICTA, Bayreuth, Vol. 2, Birkhaeuser Verlag, Basel, 1980, p. 399.

5 Y. Shibasaki and K. Fukuda, Thermal Analysis, Proc. 7th ICTA, Kingston, Ont., Vol. 2, Wiley, New York, 1982, p. 1517.

6 Y. Shibasaki and K. Fukuda, Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem., 20 (1) (1979) 427.

7 K. Fukuda and T. Shiozawa, Thin Solid Films, 68 (1980) 55.

8 K. Fukuda, Y. Shibasaki and H. Nakahara, Thin Solid Films, 99 (1983) 87.

9 N. Morosoff, H. Morawetz and B. Post, J. Am. Chem. Soc., 87 (1965) 3035.

10 K. Larsson, Ark. Kemi, 23 (1964) 35.

11 E.M. Barrall, II and J.F. Johnson, in P.E. Slade, Jr. and L.T. Jenkins (Editors), Thermal Characterization Techniques, Marcel Dekker, New York, 1970, p. 9.

12 D. Chapman, The Structure of Lipids by Spectroscopic and X-Ray Techniques, Methuen, London, 1965, p. 237.

13 R.G. Snyder, J. Mol. Spectrosc., 7 (1961) 116.

14 M. Tasumi and T. Shimanouchi, J. Chem. Phys., 43 (1965) 1245.

15 I. Fischmeister, Progress in the Chemistry of Fats and Lipids, Vol. 14 Part 3, Infrared Absorption Spectroscopy of Normal and Substituted Long-Chain Fatty Acids and Esters in the Solid State, Pergamon Press, New York, 1975, p. 118.