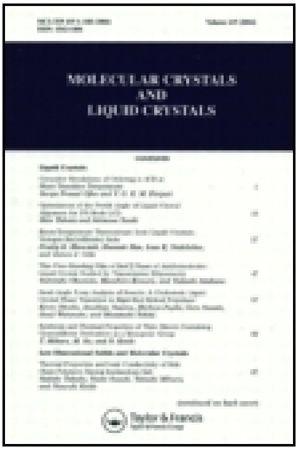

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Three-Dimensional Structural Study using Micro FT-IR Spectrometer on Polymorphism of Long-Chain Dicarboxylic Acids

Fumitoshi Kaneko [a] , Eiichi Ishikawa [a] , Masamichi Kobayashi [a] & Masao Suzuki [b]

[a] Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka, 560, Japan

[b] Oleochemical Research Laboratory, NOF Corporation, Amagasaki, Hyogo, 660, Japan

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Three-Dimensional Structural Study using Micro FT-IR Spectrometer on Polymorphism of Long-Chain Dicarboxylic Acids

FUMITOSHI KANEKO,[a] EIICHI ISHIKAWA,[a] MASAMICHI KOBAYASHI,[a] and MASAO SUZUKI[b]
[a]Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560, Japan; [b]Oleochemical Research Laboratory, NOF Corporation, Amagasaki, Hyogo 660, Japan.

Polymorphism and higher order structures of even-number dicarboxylic acid (C_{16}-C_{20}) have been studied with micro-FT-IR spectroscopy. There were at least four polymorphs. Single crystals were an assemblage of lamellas, whose thickness reaches to 0.1μm order. The surfaces of each lamella are composed of folded hydrocarbon-chain segments. Dicarboxylic acids form a lamellar crystal like polymers. Two lamellar stacking modes were found in polymorph C.

Keywords: dicarboxylic acid; polymorphism; higher order structure; lamella; micro-FT-IR spectroscopy

INTRODUCTION

Dicarboxylic acids are interesting material from a viewpoint of structural chemistry. An infinite one-dimensional chain can be formed with hydrogen bonding of carboxyl groups at both ends. Indeed the melting point of octadecanedioic acid is 124.7°C, which is closer to that of polyethylene (136.5°C) rather than that of stearic acid (69.6°C) having the same eighteen carbon atoms. It is inferred that strong intermolecular interactions would exist in the longitudinal direction and that the structure and physical properties of dicarboxylic acids would have a strong resemblance to polymers.

Dicarboxylic acids are attracting interest in the field of information industry. Recently the research and development for thermoreversible recording media becomes active. In particular, polymeric films involving dispersed crystals of long-chain molecules already have been put to practical use, as rewritable recording media. The addition of dicarboxylic acids to the rewritable polymeric films improves thermal resistance.

The information about the solid-state structure of dicarboxylic acids is a basic knowledge for various fields. We have found various crystalline phases and large scaled higher order structures. In this paper we treat the higher order structures mainly. Polymorphism and a micro-FT-IR technique for structural study are discussed also.

EXPERIMENTAL

High purity samples(more than 99%) of hexadecanedioc, octadecanedioic, and eicosanedioic acids were provided by NOF Corporation. Single crystals were grown from solutions by cooling. Solvents employed were methanol, acetone, and methyl acetate. Polarized transmission IR spectra were measured with a JASCO Janssen FT-IR spectro-meter and a wire-grid polarizer.

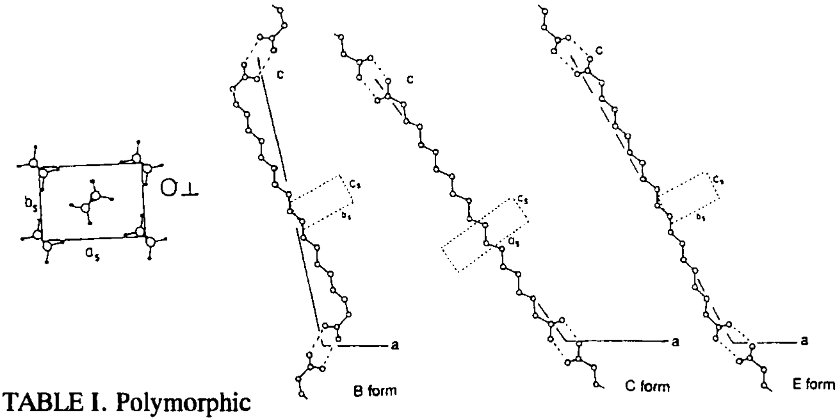

FIGURE 1. Crystal Structures of Dicarboxylic Acid

TABLE I. Polymorphic Phases

di-C20	A	B	C	E
di-C18	A		C	
di-C16			C	

RESULTS

Polymorphism

We have found at least four polymorphs. Roughly speaking, each polymorph shows almost the same IR spectra as the solid phases of n-saturated fatty acids do, except the bands due to methyl groups[1]. We named the four polymorphs according to the nomenclature of fatty acids[2], as summarized in Table 1. Polymethylene chains adopt the T// subcell in the A form, and O⊥ subcell in the B, C, and E forms. From the IR spectra, we infer the crystal structures of B, C and E forms as shown in Fig. 1.

Two Crystal Morphologies of C and Oblique Transmission Spectra

There are two types of crystal morphologies in the C form; lozenge shaped crystals with an acute interedge angle of 55° and leaf shaped crystals. There was no difference in normal transmission IR spectra between the two types of single crystals, but in the oblique transmission spectra a large difference was observed; the principle of this technique is depicted in Fig. 2. We can measure the oblique transmission spectra without changing sample setting by masking some area of the entrance Cassegrain type condenser. A sample was set on a rotary stage. By changing the setting angle of this rotary axis θ, the incident direction of IR radiation can be freely altered. In this case, the polarization of the incident radiation is parallel to the a_S axis of the O⊥ subcell at θ=0° and 180°. The leaf crystal shows a significant intensity change between θ=0° and 180°, while in the lozenge crystals there is no large intensity change between the two settings.

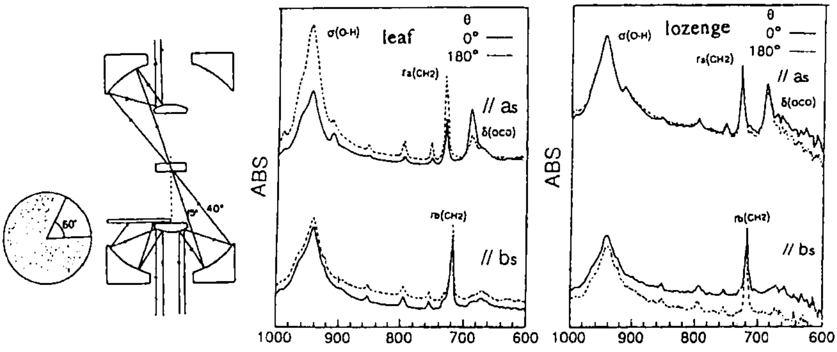

FIGURE 2.
IR spectra of two types of crystal of C taken with oblique transmission method

Water Wettability, Chemical Etching and SEM

Two structures can be expected for the flat face of single crystals of dicarboxylic acids; one is composed of free carboxyl groups and the other is covered with folded hydrocarbon segments. We investigated the water wettability of the flat face in the C form, and found that a drop of water on a flat face exhibits a contact angle of about 100°, which is the almost same as that of n-alkanes and n-fatty acids whose flat faces consist of hydrophobic methyl groups. This result strongly suggests that the flat crystal face is covered with hydrophobic folded hydrocarbon segments.

We performed also chemical etching on the crystal faces. Several steps observable with an optical microscope appeared on dissolution process, which suggests a layered structure. This layered structure was confirmed with scanning electron microscopy. Lamellas were clearly observed at the cross section as shown in Fig. 3. The thickness reaches to 0.1μm order.

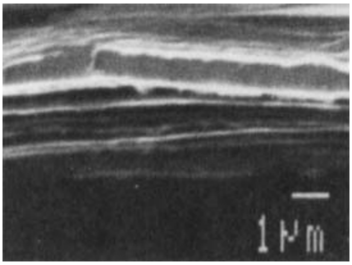

FIGURE 3
SEM image of a cross section

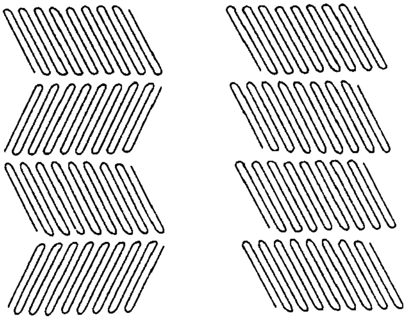

FIGURE 4
Stacking modes of lammelas in leaf and lozenge crystals.

DISCUSSION

A single crystal of dicarboxylic acids can be regarded as an assemble of lamellae, whose thickness greatly exceeds the molecular scale. We infer that very long linear chains of dicarboxylic acids connected with hydrogen bonds are folded in the lamellae as in the case of polymers. The oblique IR transmission spectra suggested two stacking modes of lamellae in the C form. In a leaf crystal the chain inclination is uniform (Fig. 4 left), while in a lozenge crystal two inclination directions coexits at equal ratio. Fig. 4 right shows a possibility; an inversion of tilting direction occurs at every stacking.

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