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Temperature Dependent Structure and Dynamical Properties of Oleic Acid at γ and α Polymorphic Phases Revealed by FTIR Spectroscopy

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Introduction

Oleic acid (*cis*-9-octadecenoic acid) has been attracting considerable attention from various fields of science and technology as one of the most abundant *cis*-monounsaturated fatty acids in nature. Unfortunately, the detailed dynamical properties at different portions at molecular level are unclear even it has been determined having three polymorphic phases, i.e., α (mp 13.3 ˚C), β (mp 16.2 ˚C), and γ phases. Several previous studies operated by using Raman spectroscopy and NMR indicate that the γ phase carries out a solid-state reversible transition with a selective conformational disordering in the methyl-sided hydrocarbon chain to the α phase at -2.2 ˚C on heating. Such a partial melting process at lamellar interfaces has not been found in other long-chain compounds consisting of saturated acyl chains. It can be regarded as a characteristic property of *cis*-monounsaturated acyl chains. Therefore, the comprehensive investigation on this phase transition is very essential for understanding the functional dynamics of oleic acid and elucidates the influence of *cis*-unsaturation on aggregation states and functions of fats and lipids in biological system.

To elucidate the detailed information about the transition mechanism and explore the dynamical properties of oleic acid at molecular level, the temperature dependent FTIR spectroscopy, which allows us to get a variety of structural information at once, was operated for investigating the dynamical features of the acyl chain and molecular ends in present study.

Experiment

Temperature-dependent FTIR spectra of oleic acid from -40 °C to melt were measured with a Thermo Nicolet Nexus 470 Fourier transform spectrometer equipped with a MCT detector through normal transmission IR measurement method. By sandwiching the liquid oleic acid between a pair of KBr plates, the measured specimens, the γ and α phase oleic acid, were obtained by controlling the temperature of the cryostat. The spectra were recorded with co-adding 128 scans at 1 cm^{-1} resolution.

Results and discussion

As shown in Figure1, the characteristic IR bands, particularly, those associated with the

cis-olefin group and the methyl end, show sudden and drastic changes at the γ → α transition point. For example, the =C-H out-of-plane bending at 703 cm^{-1} sharply smears after the phase transition point. The CH_2 rocking and CH_2 twisting progression bands in the region of 900-720 cm^{-1} exhibit characteristic spectral changes and the analysis by using the simple-coupled oscillator model shows that the methyl-sided chain carries out larger structural change than the carboxyl-sided chain on the transition point, which is consistent with the previous Raman and X-ray studies.

In the temperature ranges of the γ and α phases, there are no essential spectral variations that indicate some crucial structural changes, except several small spectral changes in the bands associated with the carboxyl group. The bands associated with carboxyl group carries out continuous structural changes in the γ phase, which suggests an equilibrium shift between certain two different states of the carboxyl group. In the α phase, the carboxyl group gradually begins to assume a character similar to that in the melt with temperature, as the temperature approaches to the melting point (Figure 2).

It is also shown that the molecular motion is activated more strongly in the methyl terminal than the rest of the molecule in the γ phase (Figure 3).

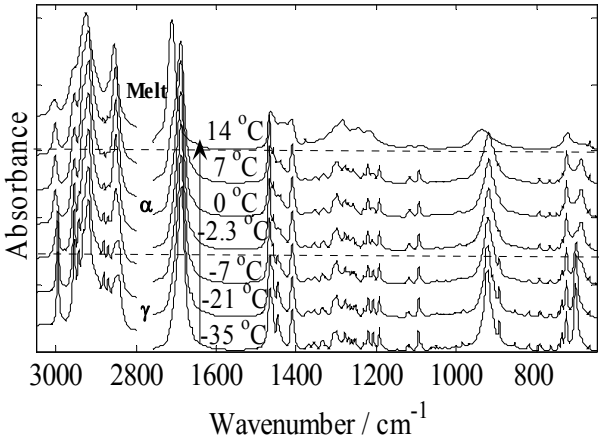

Figure 1. Temperature dependent FTIR spectra of oleic acid in the region of 3050-650 cm^{-1} at selective temperature.

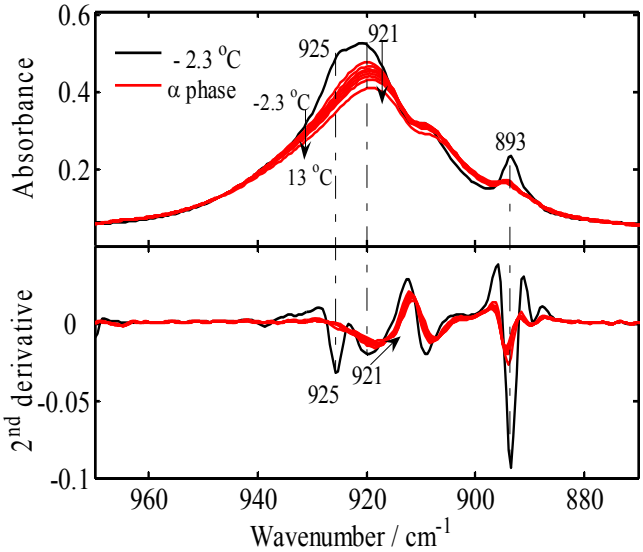

Figure 2. Spectral changes of the bands associated with the O-H out-of-plane band (upper part) and corresponding second derivatives (bottom part) in the γ → α phase transition.

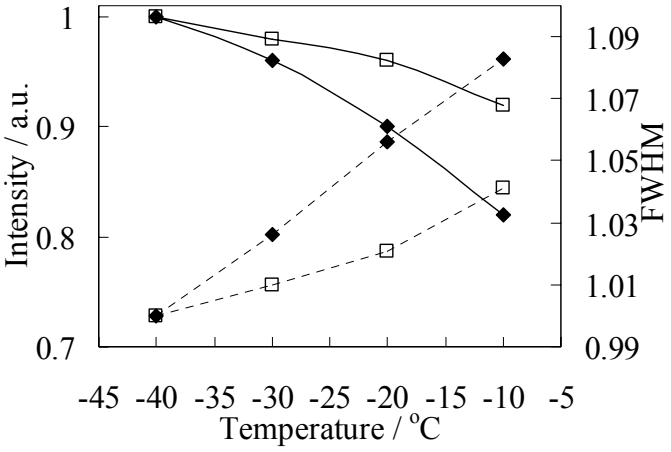

Figure 3. Changes of the intensity and full width at half maximum (FWHM) of the CH_3-C rocking (◆) and the =C-H out-of-plane bending (□) bands. Data are relative values compared with those at -40 °C.