SUPPORTING INFORMATION

Solid-State Low Temperature → Middle Temperature Phase Transition of Linoleic Acid Studied by FTIR Spectroscopy

Fuwei Pi, Fumitoshi Kaneko, [†*] Makio Iwahashi,[ξ] Masao Suzuki,[§] and Yukihiro Ozaki[*]

Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan

[†] Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

[ξ] Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Minami-ku, Sagamihara, Kanagawa-ken, Japan 252-0373

[§] Research Institute of Biological Materials, Keihanna Research Laboratory, Hikaridai 1-7, Seika, Soraku, Kyoto 619-0237

Schematic unit cell structures of oleic acid and linoleic acid

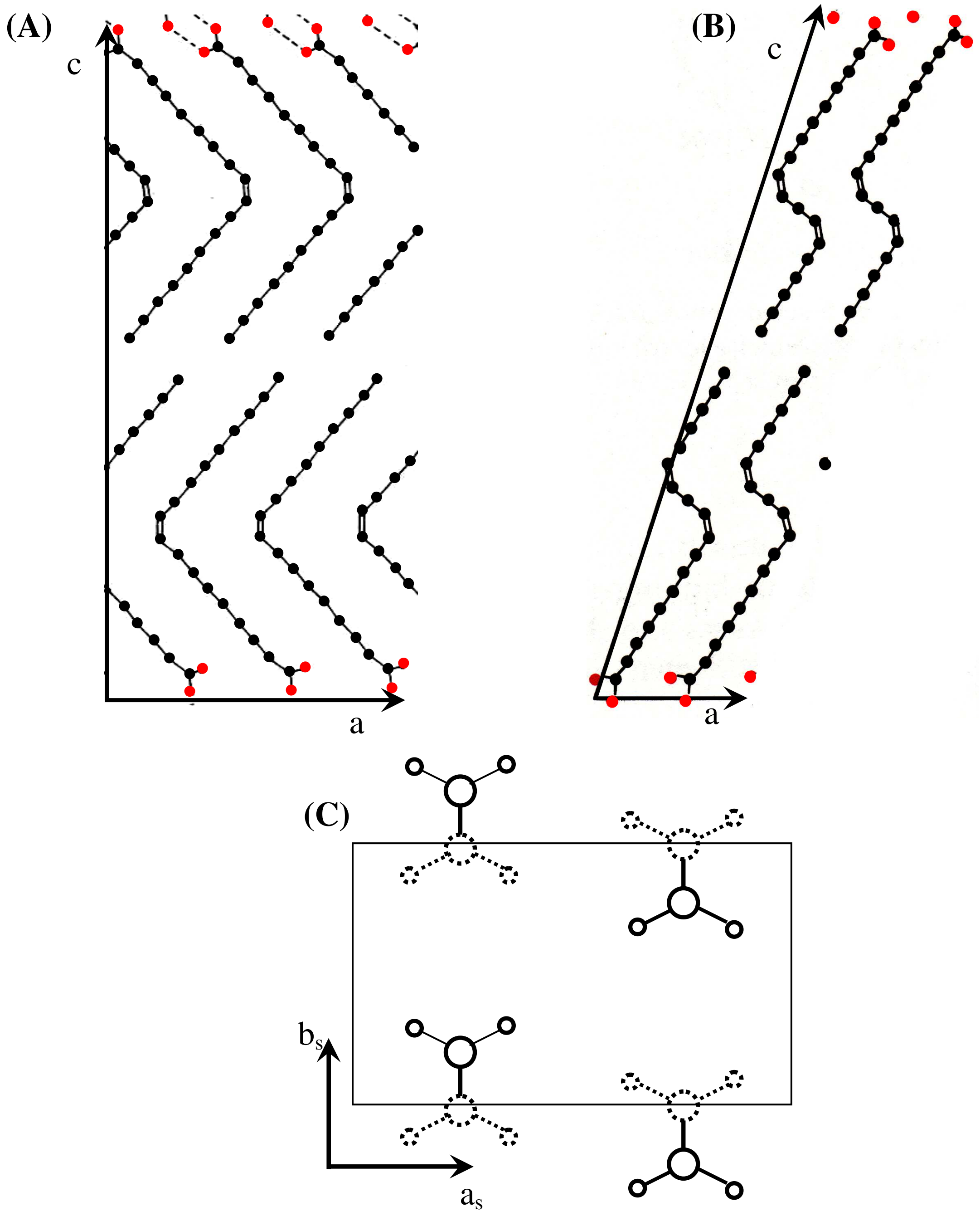


Figure S1. Schematic representations of crystal structures of (A) oleic acid and (B) linoleic acid viewed along the *b*-axis and (C) O'// subcell structure. (Reproduced from the reports of Abrahamson, et al. and Ernst, et al.)

Reference:

Ernst, J.; Sheldrick, W. S.; Fuhrhop, J. H. *Z. Naturforsch.* **1979**, *34b*, 706.

Abrahamson, S.; Nahringbauer, I. R. *Acta Crystallogr.* **1962,** *15*, 1261.

Allowed phase angles for simple coupled oscillator models with fixed-fixed and free-fixed boundary conditions

Most of the features of the vibrational spectra of long-chain compounds can be interpreted on the basis of vibrational modes of the infinite polyethylene chain. The characteristics of the infinite chain are shown in the frequency-phase angle relationship, which shows that the frequencies of normal modes in polyethylene significantly depend on the phase angle (the phase difference between neighboring methylene groups).

The phase angle can take any value within 0 ~ π for the infinite chain, whereas only limited numbers of phase angles are allowed for long-chain compounds with a finite hydrocarbon chain. The allowed phase angles can be estimated with the simple coupled oscillator model where each oscillator interacts only with two nearest neighbor oscillators. Here, we consider a system composed of *n* oscillators at positions 1 to *n* with the following two cases;

(a) Fixed-fixed boundary condition, where the displacements of two ends (positions 0 and n+1), A_0 and A_{n+1}, are both zero,

○—●—●—● ··· ●—●—○

0 1 2 3 n-1 n n+1

and

(b) Free-fixed boundary condition, where A_0 equals zero and A_{n+1} is at maximum.

○—●—●—● ··· ●—●

0 1 2 3 n-1 n

It is supposed that the standing waves of simple coupled oscillators have a form

$$A_i = B\cos(\phi \bullet i) + C\sin(\phi \bullet i) \qquad (1)$$

where A_i is the oscillator's displacement at position *i*.

From the condition $A_0 = 0$, equation (1) can be simplified as

$$A_i = C \sin(\phi \bullet i). \qquad (2)$$

When the condition of another end for (a), $A_{n+1} = 0$, is applied to equation (2),

$(n+1)\phi = k\pi$ is obtained, where k is integer.

Seeking the answers in the range of $0 < \phi \leq \pi$, the allowed phase angles for (a) can be described as:

$$\phi = k\pi / (n+1) \qquad k = 1,2,3, ..., n. \qquad (3)$$

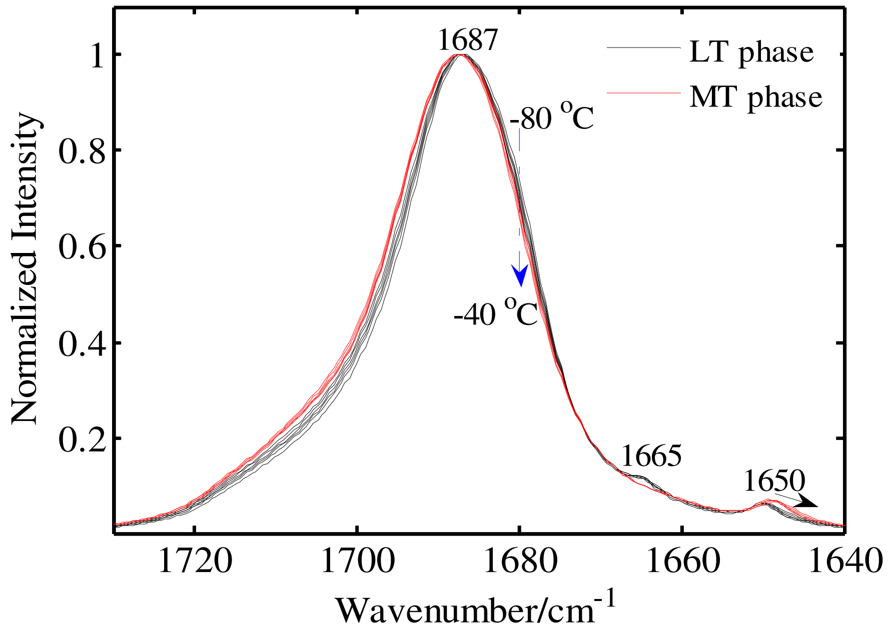
Similarly, from the condition of another end for (b) that A_n is at maximum,

$n\phi = (2k-1)\pi/2$ is obtained.

Hence, the allowed phase angles for (b) can be described as:

$$\phi = (2k-1)\pi / 2n \qquad k = 1,2,3, ..., n. \qquad (4)$$

(A)



(B)

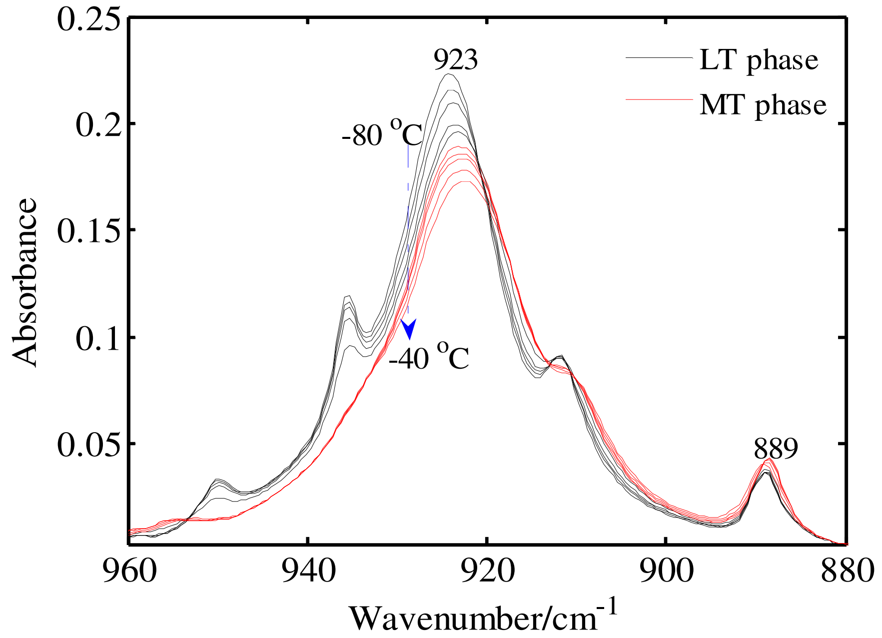


Figure S2. Spectral changes of linoleic acid in the region regarding the bands of (A) 1687 cm^{-1} and (B) 923 cm^{-1} from the LT phase to MT phase.

There are not remarkable changes occur in the frequency at the bands of 1687 and 923 cm^{-1} with increasing temperatures from the LT phase to the MT phase as explained in the manuscript (see the section 4.3).