# STRUCTURE RELAXATION OF *n*-ALKANES OBSERVED BY THE SIMULTANEOUS DSC-FTIR METHOD

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## Abstract

Phase transitions of hexatriacontane (C36) and octacosane (C28), both as the solution grown single crystal (SGC) and polycrystalline aggregates (MCC) prepared by cooling at 1 K min$^{-1}$ from the isotropic liquid state, were measured by the simultaneous DSC-FTIR method. MCC of C36 showed the freezing of the high temperature stable phase, which had a slight lower order of the lattice vibration mode comparing with the room temperature stable phase. MCC of C28 demonstrated thermo-reversible phase transition, however, had a binomial distribution of crystal stability of the monoclinic phase.

**Keywords:** conformational disorder, phase transition, simultaneous DSC-FTIR, structural disorder

## Introduction

As polymer crystals are in the quasi equilibrium state, a melting of polymers occurs in a wide temperature range accompanying with complex phenomena such as re-crystallization, re-organization of molecules and so on. Generally, polymer crystals contain structural or conformational disorders caused by the restriction of long chains. Complex phenomena following the melting of polymers are expected to be a result of stabilization of conformational and structural disorders. Thermal behaviors of *n*-alkanes are investigated as a model compound of polymers, especially for polyethylene [1]. In this study, the structure relaxation of *n*-alkane crystal containing structural or conformational disorders was investigated by the newly developed simultaneous differential scanning calorimetry and Fourier transform infrared spectroscopy method (DSC-FTIR).

Thermal analysis, especially DSC is a convenient tool to observe phase transitions, however, DSC gives only a total thermodynamic information of samples, and another measurements are necessary to obtain structural information. We have developed the simultaneous DSC instrument [2], in order to measure DSC and another method, such as X-ray diffraction (XRD), FTIR, Raman spectroscopy and light scattering [3], at the same time. The application of the simultaneous DSC-XRD [4] and DSC-FTIR [5, 6] methods were reported in order to analyze the mechanism of melting and crystallization of polymers. In this study, we have focused on the conforma-

tional change of *n*-alkanes during phase transitions as a model compound of polyethylene observed by the DSC-FTIR.

## Experimental

### *Sample*

Two kinds of *n*-alkanes, hexatriacontane (C36) and octacosane (C28) were used through the experiments. The single crystals (SGC) of C36 and C28 were obtained by the re-crystallization from *p*-xylene solution. The polycrystalline aggregates (MCC) of C36 and C28 were prepared by cooling at 1 K min$^{-1}$ from the isotropic liquid state. The single crystal mat of SGC was prepared by hand press. Sample (about 2 mg), sandwiched between two KBr disks with 1 mm thickness, was clumped in the aluminum sample vessel for DSC-FTIR measurement.

### *Instruments*

The simultaneous DSC-FTIR measurement was carried out by setting the simultaneous DSC instrument [2] on the JASCO FTIR 620 with MCT (Mercury Cadmium Telluride) detector in the wavelength range between 400 and 2.000 cm$^{-1}$. Under the rapid scan FTIR mode, the accumulation of one spectra and the wavelength resolution were 36 times and 4 cm$^{-1}$, respectively. Under this condition, the time resolution of FTIR spectra was 1.5 s. The scanning velocity and the time resolution of DSC were 1 K min$^{-1}$ and 0.5 s, respectively. Temperature and enthalpy calibrations were carried out using indium, sandwiched with thin KBr disks and clumped in an aluminum sample vessel, at 1 K min$^{-1}$. XRD measurement was carried out using a Mac Science MXP18 operating at 40 kV and 300 mA with 0.1518 nm of wavelength.

## Results and discussion

Figure 1 shows DSC heating curves for SGC (solid line) and MCC (dotted line) of C36 (a) and C28 (b) measured by the simultaneous DSC-FTIR method at 1 K min$^{-1}$. XRD analysis suggested that SGC of C36, SGC and MCC of C28 were the monoclinic phase (M phase), however, MCC of C36 was the monoclinic system with orthorhombic type sub-unit (C′ phase). SGC of C36 shows three endothermic transitions such as the transition from the M phase to the C′ phase, the transition from the C′ phase to the H phase (hexagonal) and the melting of the H phase. The endothermic peak temperatures of these transitions of C36 are 346, 347.5 and 349.9 K, respectively. The C36 chain slips along the *c* axis at the M-C′ transition, in order to form the orthorhombic sub-unit. The tilt angle between the end methyl group and the molecular axis changes at the M-C′ transition of C36 (Tilt transition [7]). The C′-H transition is known as the rotational transition [7].

The heating DSC curve for MCC of C36, in which the C′ phase of C36 was frozen under the cooling condition of 1 K min$^{-1}$, showed the C′-H and the H-isotropic liquid transitions. The peak temperatures of C′-H transition and the melting of H
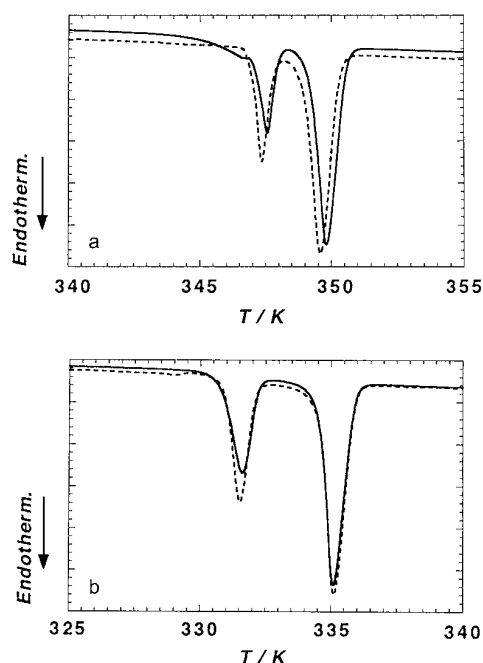
**Fig. 1** DSC heating curves for SGC (solid line) and MCC (dotted line) of C36 (a) and C28 (b) measured by the simultaneous DSC-FTIR method at 1 K min$^{-1}$

phase of MCC were slightly lower (about 0.5 K) than those of SGC because of the higher heat conduction of MCC comparing with the single crystal mats of SGC. The total heat of the M-C′ and the C′-H transitions for SGC of C36 was almost equal to that of the C′-H transition for MCC of C36.

DSC heating curves for SGC and MCC of C28 (Fig. 1b) measured by the simultaneous DSC-FTIR method at 1 K min$^{-1}$ shows the M-H transition and the melting of the H phase at around 331.5 and 335 K, respectively. Adding with both transitions, MCC of C28 shows a small endothermic transition at around 329 K. Both peak temperatures of the M-H transition and the melting of SGC were same with those of MCC. The heat of the M-H transition and the melting for both samples were almost the same.

From the simultaneous DSC-FTIR measurement, the conformational and thermal changes were monitored in real time of the transitions. Figure 2 shows FTIR results for SGC (a) and MCC (b) of C36 measured by the simultaneous DSC-FTIR method at 1 K min$^{-1}$. IR band at 720 cm$^{-1}$, assigned to the rocking vibration mode of methylene units ($\gamma_{CH}$), was observed as a doublet with the absorption peaks at 730 and 720 cm$^{-1}$ in the M phase. The splitting of the $\gamma_{CH}$ mode into two components at 730 and 720 cm$^{-1}$ arises from interactions between adjacent molecules in the crystalline phase, which results in both an in-phase and an out-of-phase rocking mode [8]. Therefore, the splitting of IR band suggested the symmetrical molecular align-

ment and the symmetrical direction of molecular vibration in the crystal lattice. In the M and C′ phases of SGC, FTIR spectra showed the doublet $\gamma_{CH}$ absorption band at 730 and 720 cm$^{-1}$ due to the symmetric direction of vibration which are parallel to the *a* axis and *b* axis of the crystal [8], respectively. In other word, C36 molecules with trans conformation aliened symmetrically (the order trans conformation) in the M and C′ phases. Following to the C′-H transition, the doublet $\gamma_{CH}$ absorption band changed to the single peak at 720 cm$^{-1}$. Allowing the rotational molecular motion in the H phase, C36 molecules with trans conformation aliened asymmetrically (the disorder trans conformation) in the H phases. Therefore, the IR absorption peaks at 730 and 720 cm$^{-1}$ indicated the order and the disorder trans conformations, respectively. The ratio of the order trans conformation to the disorder trans conformation of the M phase of SGC was larger than that of the frozen C′ phase of MCC. This result suggested that the order of the lattice vibration mode of the M phase of C36 was higher than that of the frozen C′ phase due to the conformational and structural disorders. The absorption peak at 730 cm$^{-1}$ varnished in the H phase, and the absorbance at 720 cm$^{-1}$ decreased in the isotropic liquid state.
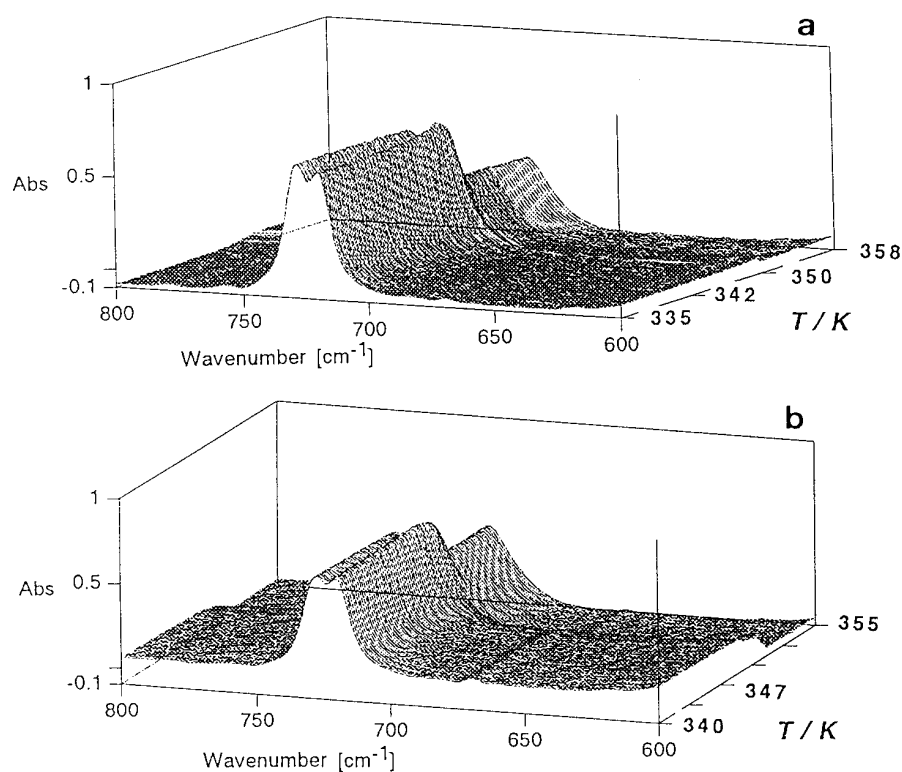


**Fig. 2** FTIR results for SGC (a) and MCC (b) of C36 measured by the simultaneous DSC-FTIR method at 1 K min$^{-1}$

Figure 3 shows changes of the relative absorbance at 720 and 730 cm$^{-1}$ for SGC (a) and MCC (b) of C36 observed on heating at 1 K min$^{-1}$ compared with DSC curve. The relative absorbance was obtained by normalizing its maximum and minimum values. For SGC (Fig. 3a), the absorbance at 730 cm$^{-1}$ started to decrease at 345.0 K and the slow decreasing continued until 346.5 K, the absorbance at 720 cm$^{-1}$ increased in this stage which corresponded to the M-C′ transition. As molecules moved along the *c* axis in the crystalline state in the M-C′ transition, the kinetic process of molecular diffusion in the solid state governed in this transition. Therefore, the broad M-C′ transition was observed between 345.0 and 347.5 K. The absorbance at 730 cm$^{-1}$ decreased steeply between 347.0 and 347.5 K for SGC of C36 which corresponded to the C′-H transition. From the conformational view point, the C′-H transition was finished completely at the DSC peak temperature. At the melting of the H phase, the disordering of trans conformation finished at the DSC peak temperature.

For MCC of C36 (Fig. 3b), the slow decrease of the absorbance at 730 cm$^{-1}$ observed in the M-C′ transition of SGC scarcely observed. The absorbance at 730 cm$^{-1}$ decreased extremely in the C′-H transition between 346.5 and 347.2 K. The confor-
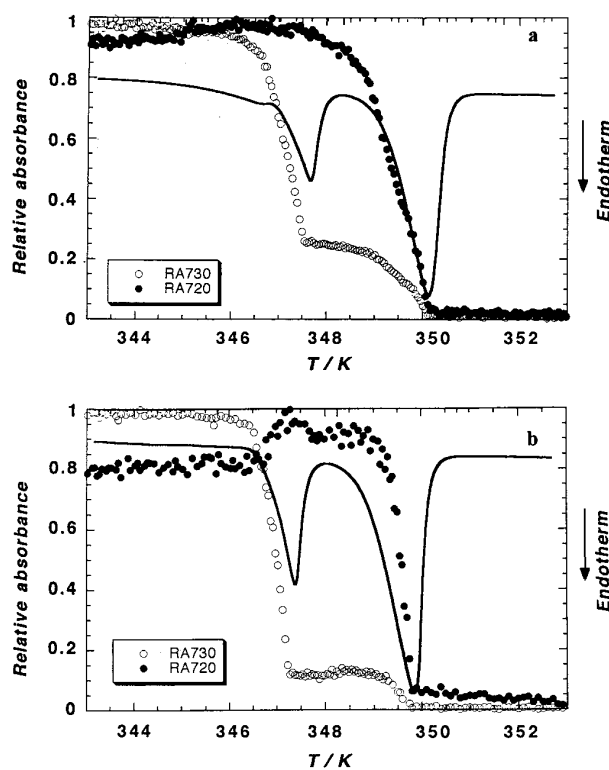


**Fig. 3** Changes of absorbance at 720 cm$^{-1}$ (black) and 730 cm$^{-1}$ (white) for SGC (a) and MCC (b) of C36 observed on heating at 1 K min$^{-1}$ compared with DSC curve

mational and thermal changes occurred at the same time at the C′-H transition. In the temperature range below this transition, the absorbance at 720 cm$^{-1}$ increased gradually, and then increased during the C′-H transition. Both absorbances at 730 and 720 cm$^{-1}$ increased slightly at the initial stage of melting of the H phase. These results suggested that the frozen C′ phase of MCC contained not only structural disorder but also conformational disorder. The relaxation of conformational disorder occurred during the C′-H transition and the initial stage of melting due to allow molecular motions.

Figure 4 shows changes of absorbance at 720 and 730 cm$^{-1}$ for SGC (a) and MCC (b) of C28 observed on heating at 1 K min$^{-1}$ compared with DSC curve. The absorbance at 730 cm$^{-1}$ started to decrease at 329 K for SGC and at 328.5 K for MCC. The small step decrease of the absorbance at 730 cm$^{-1}$ was observed between 328 and 329.5 K for MCC, which corresponded to the small endothermic peak at around 329 K shown in Fig. 1b. In this temperature range, the absorbance at 720 cm$^{-1}$ increased slightly. For SGC of C28, the absorbance at 730 cm$^{-1}$ started to decrease at 329 K, in other word, the rotational vibration mode started at around 329 K. The behavior of the absorbance change of MCC at 329 K was similar to that observed at
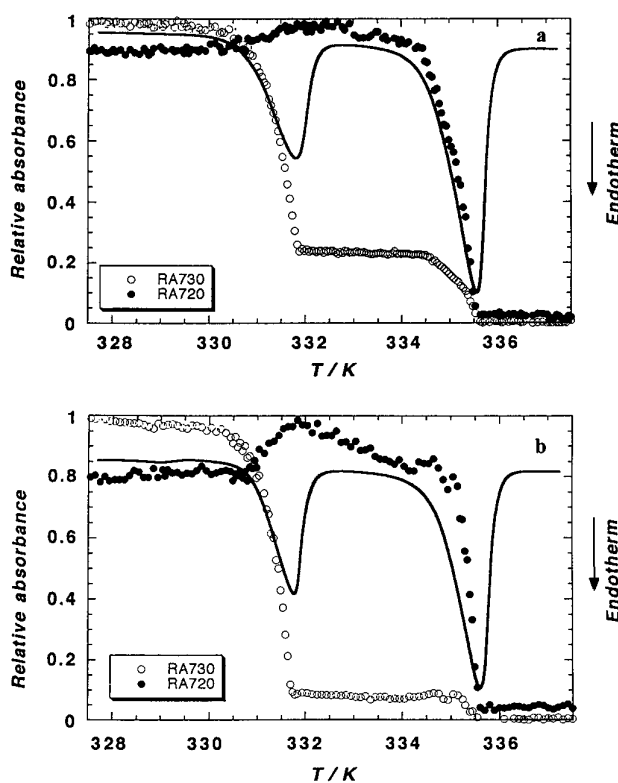


**Fig. 4** Changes of absorbance at 720 cm$^{-1}$ (black) and 730 cm$^{-1}$ (white) for SGC (a) and MCC (b) of C28 observed on heating at 1 K min$^{-1}$ compared with DSC curve

the M-H transition. Therefore, the small endothermic peak of MCC at 329 K is expected to be the M-H transition of the M phase with structural or conformational disorders. This result suggested that MCC had binomial distribution of crystal stability in the M phase. During the M-H transition, the absorbance at 720 cm$^{-1}$ increased for both SGC and MCC. However, the increment for MCC was larger than that for SGC. This result indicated that the M phase of MCC contained small amount of conformational disorder.

The C′ phase containing disorders in the molecular position and in conformation was frozen by cooling at 1 K min$^{-1}$ due to the kinetic effect. Probably, the C′-M transition occurred slowly accompanying molecular diffusion in the solid state. Conformational change corresponded to thermal change in the M-C′, the C′-H transition and the melting for both samples of C36. The increase of absorbance at 720 cm$^{-1}$ during the C′-H transition indicated that the C36 crystal obtained by cooling at 1 K min$^{-1}$ contained not only structural but also conformational disorders. Although the phase transitions observed for SGC and MCC of C28 were thermo-reversible similar conformational disorder was observed for the C28 crystal obtained by cooling at 1 K min$^{-1}$.

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