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Crystalline phase transition with a large conformational change in a thiodicarboxylic acid

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A large conformational transition in a crystal of thiodipropionic acid is investigated by differential scanning calorimetry (DSC), X-ray diffraction, optical microscopy, and computer modeling. The room temperature phase (A-phase) was already known to be orthorhombic where the chains have largely zigzagged conformation with both S–C bonds in gauche conformation. A high temperature phase (C-phase) above 105 °C is found by DSC. By X-ray analysis, the crystal structure of the C-phase is found to be monoclinic with molecules having nearly extended conformation. Nucleation and growth of the C-phase are clearly observed by polarizing microscope. It is found that each C-phase domain grows very fast in a preferred direction which is nearly parallel to the {110} planes of the C-phase. Molecular dynamics simulation of the transition reveals that the largely zigzagged molecules in the A-phase readily transforms to the extended all trans form at higher temperatures. © *1999 Kluwer Academic Publishers*

1. Introduction

Long chain hydrocarbons, such as *n*-alkanes, *n*-alcohols, or aliphatic acids, are basic constituents of many biological systems. They are also very important materials in coating, cosmetics, detergents, and in future thin film devices [1, 2]. The long chain molecules are known to have various ways of self-assembly such as crystals, membranes, micelles, etc. Though the structures and the molecular dynamics in these systems are now the subjects of great interest [3], the structure of the crystal and the molecular behavior therein should be the basis of the arguments about more complicated structures. Indeed many studies on crystals of long chain molecules have been accumulated [1, 4–11].

Solid-solid transitions in the crystals of long chain molecules are mostly irreversible, since even slight changes in the relative positions or orientations of the molecules require large activation energy. However, reversible transitions are also observed near the melting points; these are the transitions between the low-temperature ordered phases and the high-temperature disordered phases, for example the rotator phase in *n*-alkanes [4–9] and *n*-alcohols [10, 11]. Large structural fluctuations present near the melting point may be the origin of such reversibility. Even in this case, the molecules nearly keep their original chain conformations through the transitions. Here we report a considerably different and rare transition, which is accompanied by a large conformational changes but still reversible. A chain molecule we consider here is a thiodipropionic acid (TDPA); HOOC-$(CH_2)_2$-S-$(CH_2)_2$-COOH.

Dicarboxylic-acid (DCA) is a hydrocarbon both chain-ends being replaced with carboxylic groups. The carboxylic groups connect the molecules, by hydrogen bonds, into an infinitely long chain. Being in effect infinitely long, the crystals of DCAs are much more stable and have melting points much higher than those of corresponding *n*-alkanes [1]. Though structural investigations of DCAs are still very scarce [12], an interesting crystalline transition, martensitic in nature, has been reported recently [13].

A sulfur atom in the backbone chain gives rise to a characteristic dipole-interaction, which results in a peculiar molecular conformation and a high thermal stability. For example, polyethylene-sulfide was found to have a molecular conformation typical of sulfur-containing chains and to have higher melting point, $T_m = 210\,^\circ\mathrm{C}$, than that of polyethylene, $T_m = 140\,^\circ\mathrm{C}$ [14]. Oligomers having thioethylene units were also investigated and an interesting crystalline transition with considerable conformational changes was observed [15].

TDPA is a short dicarboxylic-acid containing a sulfur atom in the main chain. An X-ray analysis of a single crystal at room temperature has already shown that the molecules have a largely zigzagged conformation, where both S–C bonds are in gauche state [16]. A crystalline phase transition near the melting point was also noticed by IR analysis [17]. However, the structure of the high temperature phase or the mechanism of the transition has not attracted any attention as far as the authors are aware. We here investigate these problems

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by use of various experimental techniques and a computer modeling.

2. Experimental

A powder sample of TDPA, which was obtained from Nitto Kagaku, went through a simple purification by recrystallization from aqueous solution. Single crystals were obtained from aqueous solution by slow cooling; they were rectangular thin plates of several mm width and several tens of micrometer thickness.

Differential scanning calorimetry (DSC) was made by Rigaku DSC-8230 at a heating and cooling rate of 2 °C/min; both powder and single crystalline samples were used without any appreciable difference in the thermograms being noticed. X-ray diffraction studies were made by a four-circle diffractometer (Rigaku-AFC). The temperature of the sample was controlled by blowing hot air.

Optical changes by the solid-solid transition were studied with a polarizing microscope equipped with a CCD camera and a hot stage. The image was stored in a conventional video tape with one frame 1/30 sec. Computer simulation of the transition was carried by use of a molecular simulation software Cerius2 (MSI)† [18]; the constant temperature-pressure (NTP) simulations were done on the basis of a consistent force field (CFF) where the electrostatic interactions were taken into account by Ewald method.

3. Results

3.1. Thermal analysis

Phase behaviors can be examined most conveniently by DSC. Samples of TDPA, powdered and single crystalline, were heated and cooled at 2 °C/min. A typical thermogram obtained (Fig. 1) shows clear endotherms at 105 and 128 °C; the temperatures are those of the departure from the base line. It will be shown that these endotherms correspond to the transition to a high temperature crystalline phase and its melting, respectively. By cooling we observed a very sharp crystallization at 126 °C and a transition back to the low temperature phase at 95 °C. Large undercooling observed is typical of the solid-solid transitions in such large molecules.

The presence of the two crystalline modifications is thus indicated. We hereafter refer to the low temperature and the high temperature crystalline phases as A and C, respectively, according to the notation adopted by Bland and Cudby [17]. The temperature T_c of the transition from the A-phase to the C-phase is 105 °C.

3.2. Single crystal analysis

Single crystals obtained were thin platelets of sufficient width. We investigated the crystal structures of the A- and the C-phases by a four circle diffractometer. The low temperature phase A was found to be orthorhombic with lattice constants $a = 5.065$ A, $b = 8.667$ A, $c = 18.096$ A (29 °C), and the space group Pcan (Pbcn). The molecules in the A-phase are largely zigzagged due to gauche conformation at both S–C bonds (Fig. 2a). This structure is just the same as that already reported by Prout [16]. Variation with temperature in the lattice constants of the A-phase was also studied (Fig. 3). The lattice constants a, b, and c gradually increase with temperature until they break at T_c.

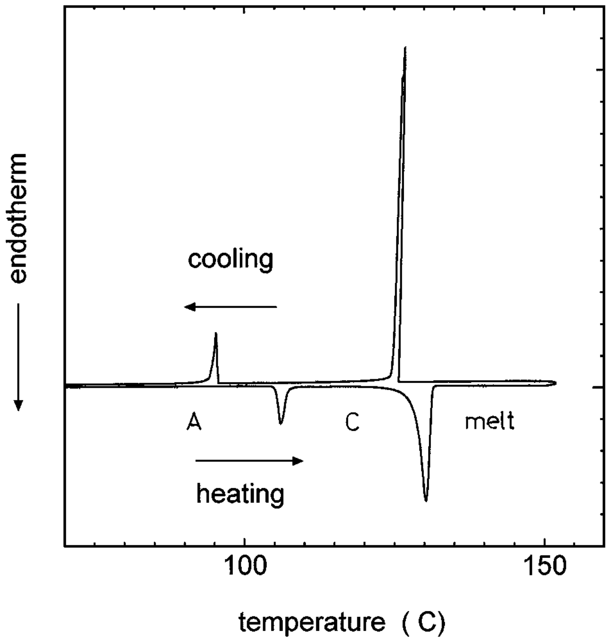

Figure 1 DSC thermograms of TDPA obtained by heating and cooling at 2 °C/min. The low and high temperature crystalline phases are denoted as A and C, respectively.

When heated above T_c, multiple-site nucleation and growth of the C-phase domains occur. The domains have slightly different orientations (see Section 4), which leads to breakup into crystallites of different orientations. Therefore it is not easy to prepare a single crystal of the C-phase, but by repeated trials using many crystals we could fortunately obtain a single crystalline C-phase. The structure of the C-phase was found to be monoclinic $a = 4.94$ A, $b = 8.68$ A, $c = 19.94$ A, $\gamma = 97.0^{\circ}$ with a possible space group $P2_1/n$ ($P2_1/c$). In this phase, Bragg reflections at higher angles are very weak and the number of significant Bragg reflections was greatly diminished probably due to large structural disorder present. Both direct structure analysis and a least square refinement of the initial trial structure were not successful. Very conspicuous in the structure of the C-phase is that the crystalline c-axis is much longer than that of the A-phase. Simple inspection of the possible chain conformation suggests that the chains are nearly extended planar-zigzag with all backbone bonds having trans conformation.

Relative orientations of the reciprocal lattice vectors of the crystallite against the diffractometer axes, the setting parameters, are give by the machine software. From the parameters for both the A-phase and the C-phase lattices, the orientation relation between these two lattice systems is determined. Fig. 4 shows the lattice translation vectors $(\mathbf{a}_{\mathrm{C}}, \mathbf{b}_{\mathrm{C}})$ for the C-phase depicted relative to those of the matrix A-phase $(\mathbf{a}_{\mathrm{A}}, \mathbf{b}_{\mathrm{A}})$; the c-axes

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[†] Cerius2 is a molecular simulation software by Molecular Simulations Inc. (MSI).

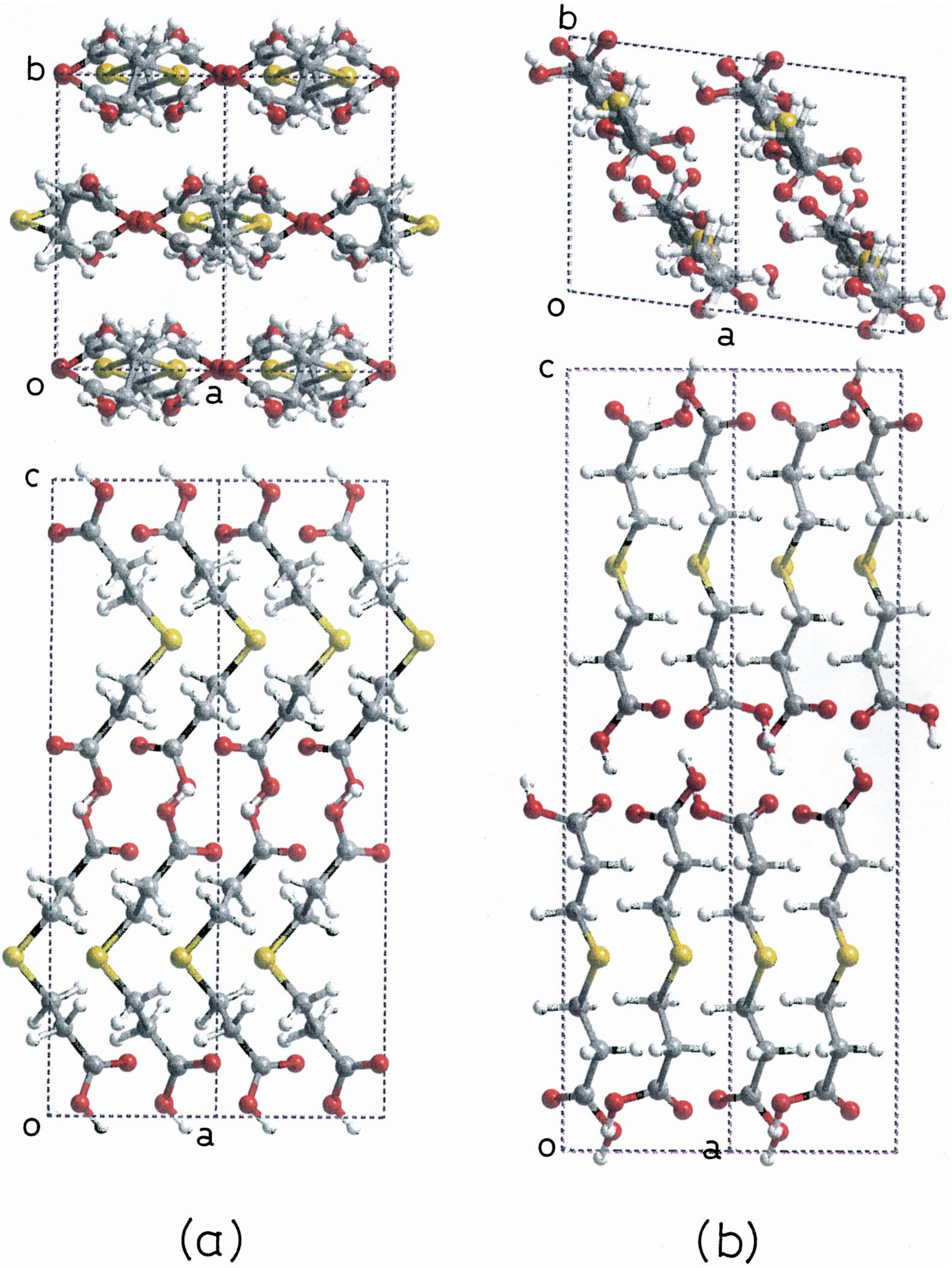

Figure 2 Crystal structures of TDPA: (a) the A-phase structure determined by X-ray, and (b) the possible C-phase structure. The atoms are depicted in colors: sulfur in yellow, oxygen in red, carbon in gray, and hydrogen in white.

of both phases are nearly parallel. The transformation from the A-phase to the C-phase seems to be induced by a slight lattice deformation along the (110) plane of the C-phase accompanied by a large conformational changes.

As will be described in the next section, the A-phase domain and the C-phase domain have a straight boundary parallel to one of the {110} planes of the C-phase, especially at the initial stage of transformation. In Fig. 4 is shown also the expected phase boundary (the left half is the A-phase lattice and the right half is the C-phase lattice); the A-phase molecules are depicted as circles and those of the C-phase as bars representing the average shape of the molecular cross section. Though detailed structure of the C-phase is still unknown, strong 110 reflection as well as results of computer modeling suggest that the directions of the molecular zigzag planes are nearly parallel to the (110) plane.

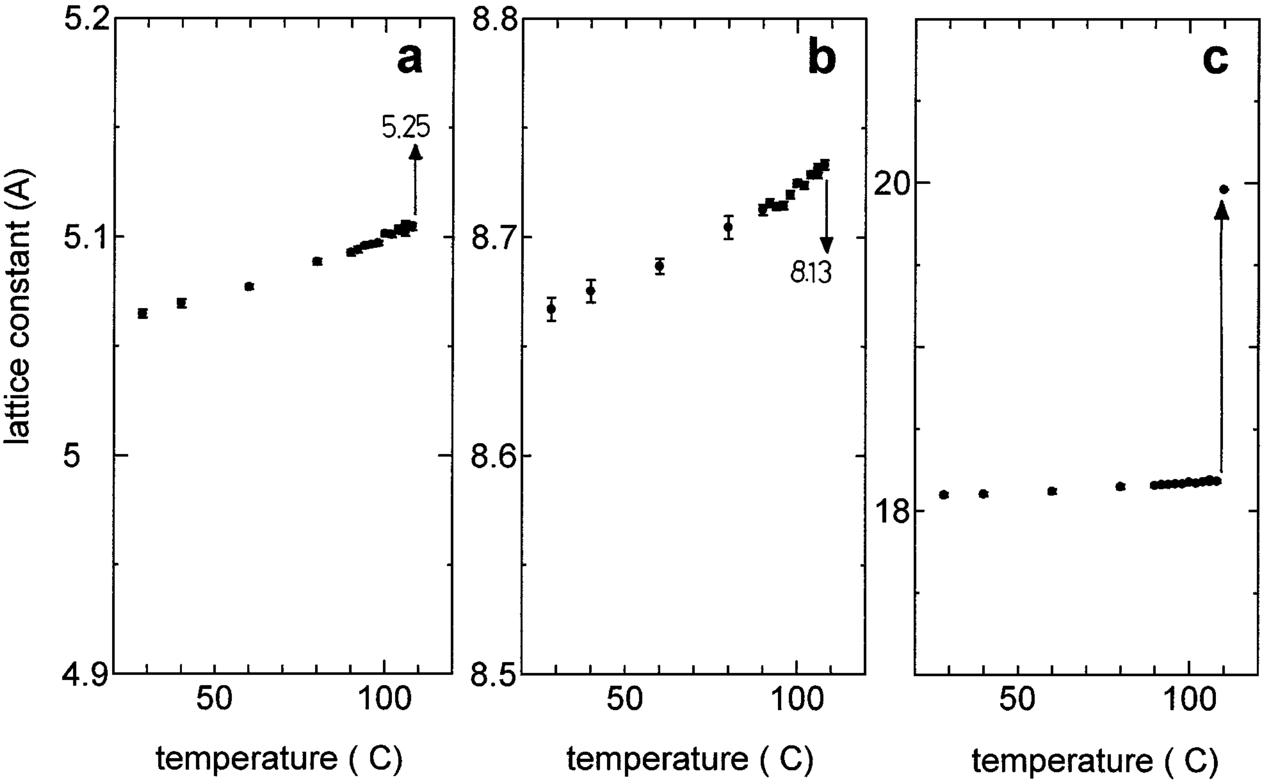

Figure 3 Changes with temperature in the A-phase lattice. The lattice constants *a*, *b*, and *c* increases gradually until T_c. By the transition, the low temperature lattice ($\mathbf{a}_A, \mathbf{b}_A$) is considered to transform to a high temperature lattice ($\mathbf{a}_H, \mathbf{b}_H$) (see Fig. 4). Taking this correspondence, the lattice constants in the high temperature phase C are also plotted.

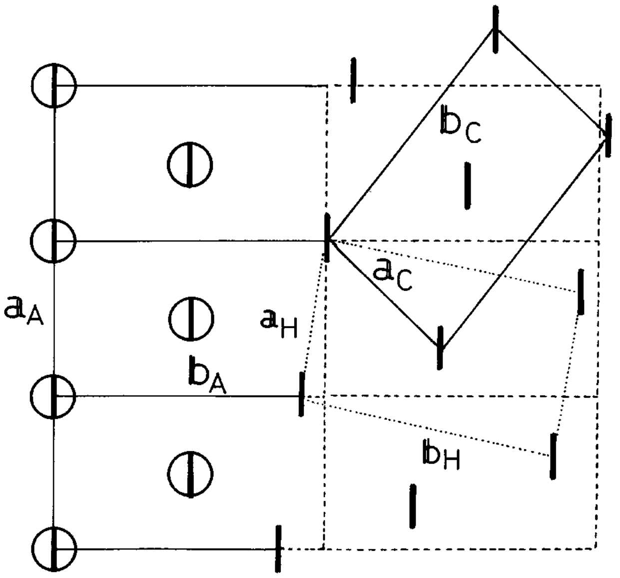

Figure 4 Orientation of the C-phase lattice ($\mathbf{a}_C, \mathbf{b}_C$) relative to the matrix A-phase ($\mathbf{a}_A, \mathbf{b}_A$). Molecules in the A phase are represented by circles with diametrical lines which represent the projected directions of the S-S, while those in the C-phase are depicted as bars along the planar zigzag direction of the molecules. Another choice of the C-phase *lattice* ($\mathbf{a}_H, \mathbf{b}_H$), though not crystallographically sound, closer to the A-phase lattice is also shown.

3.3. Optical observation

Since the two crystal modifications A and C will have distinct optical properties, the nucleation and growth of the C-phase domain in the matrix A-phase will be detected conveniently by polarizing microscope. Fig. 5a shows a flat-on view of the A-phase crystal, where the platelet is surrounded by {010} and {110} surfaces. Around T_c, suddenly appears a C-phase domain which is remarkably elongated along one direction(Fig. 5b). The growth of the C-phase domain in that direction $\langle -1,\ 1,\ 0\rangle$ is very fast and is completed within 1/30 sec of one video-frame; strong intermolecular cooperation along that direction is quite marked. It should be noticed that the long axis of the C-phase domain is slightly canted from the *a*-axis of the matrix A-phase. Comparison with Fig. 4 shows that the boundary of the two phase is very likely to be the {110} planes of the C-phase.

With progress in transformation, the color of the C-phase domain changes very quickly from blue to green (Fig. 5b–d). This increase in the retardation will be a reflection of the phase transition at different depth from the surface. Color shift to longer wave-length suggests that the degree of birefringence Δn is larger in the C-phase. This seems to be somewhat strange, since the high temperature phase should be more disordered and the optical anisotropy is expected to be reduced [9]. However planar zigzag chains in the C-phase, when they are aligned parallel, should lead to an increase in the optical anisotropy.

The 10% increase in the crystal *c*-axis length deduced from the X-ray analysis was directly confirmed by the optical microscope. Fig. 6 shows the edge-on view of a thin crystallite, where upper-left side is below T_c and the lower-right is above T_c. Macroscopic thickening of about 10% is quite evident.

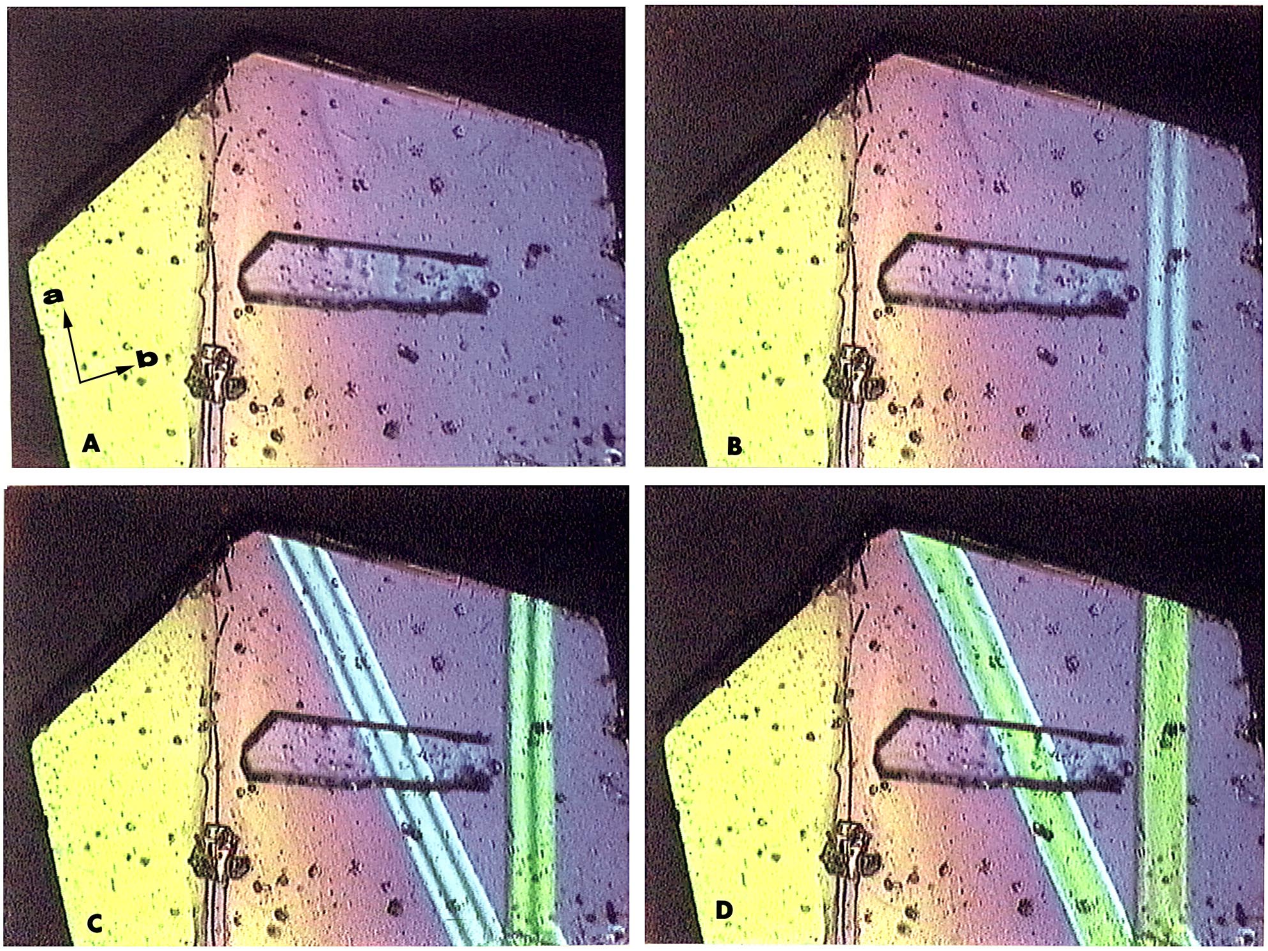

Figure 5 Optical images of the crystal (flat-on view) during the transition A → C obtained by the polarizing microscope. The crystallite is surrounded by the {010} and {110} planes of the orthorhombic lattice. When the A-phase crystal (a) is heated up to T_c, the C-phase domains elongated near the *a*-axis direction suddenly appear (b, c, d). Changes in the color of the domains, from blue to green, are quite remarkable.

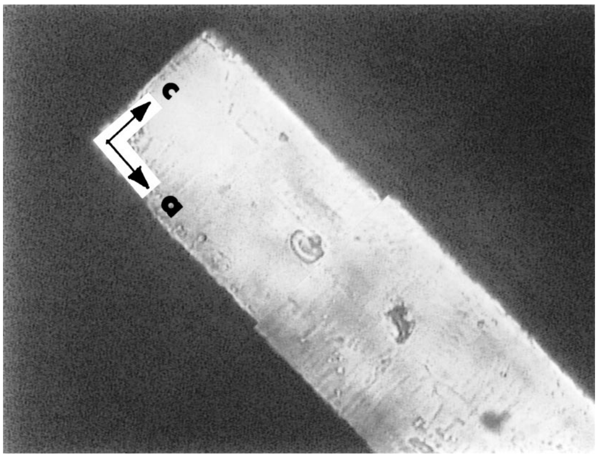

Figure 6 Optical images of the crystal (edge-on view) during the transition. The upper-left and the lower-right parts are from the low temperature A-phase and the high temperature C-phase, respectively.

3.4. Computer modeling

The solid-solid transition in TDPA is accompanied by a 10% elongation in the chain axis direction and a 4% lateral shrink. Though the detailed molecular mechanisms underlying such large structural changes are very interesting, direct experimental information is rather limited. We therefore made a preliminary simulation study of the transition to the high temperature phase.

First we made up the A-phase crystal by use of the atomic positions determined by our X-ray single crystal study. Then we have carried out the molecular dynamics simulation at several elevated temperatures. At lower temperatures below around 300 K, the crystal structure of the A-phase was quite stable. But above around 300 K, the structure spontaneously transformed to another form in which the molecules have fully extended and nearly planar-zigzag conformation (Fig. 2b). Probably due to inaccuracy of the force filed, the temperature of transition deviate considerably. Furthermore the transition seems to depend sensibly on the heating rate; we need sufficient computation time to obtain equilibrium transition temperature. The simulated transition can therefore hardly be said to be realistic. However, the parallel planar zigzag chains and their orientation along the (110) planes correspond nicely to the experimental information.

4. Conclusions

People have long investigated crystalline phase transitions of long chain molecules, such as *n*-alkanes, *n*-alcohols, fatty acids, etc. The molecular conformations are there nearly kept constant with the rotation-translation of the whole molecule being the most relevant degree of freedom. We here investigated somewhat rare crystalline transition where the molecules make large conformational changes.

Thermal analysis by DSC clearly showed that TDPA has a high temperature phase C near the melting point. The structure of the C-phase was revealed to be monoclinic, by X-ray diffraction, with the molecules having nearly extended conformation; this is quite in contrast with the largely zigzagged conformation in the low temperature phase A. We also found a large structural disorder in the phase C which reminded us the rotator phases of *n*-alkanes and *n*-alcohols.

From the optical study of the single crystal by use of polarizing microscope, the nucleation and growth of the C-phase domains were resolved very clearly. The domains were seen to grow very rapidly in the $\langle -1,\ 1,\ 0\rangle$ direction forming the boundaries parallel to the $\{110\}$ planes of the C-phase. We also found a crystallite thickness increase, of about 10%, which corresponds very well to a microscopic change in the unit cell. The crystal structure of the C-phase was also investigated by molecular dynamics simulation. Though the structure simulated was found to be reasonable, detailed crystal structure in the C-phase and the molecular mechanism of the transition need further investigations.

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