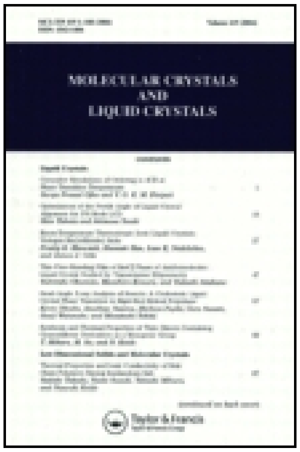

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# Phase Transition of Cholesteryl Acetylferulate

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# Phase Transition of Cholesteryl Acetylferulate†

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Cholesteryl acetylferulate (99.61%) shows complicated thermal aspects of behavior with DSC: a double peak of cholesteric-isotropic liquid transition on first heating, a cholesteric-smectic A transition on cooling, and two types of cold crystallization through a glass transition on second heating. The stability of the solid polymorphs generated from the cold crystallization is discussed from the thermodynamic point of view.

Cholesteryl cinnamate examined for comparison showed no double peak in the cholesteric-isotropic liquid transition. It also showed neither glass transition nor cold crystallization phenomenon. The characteristics were independent of whether the purity was 99 or 100%. From the above results, it can be concluded that the presence of extra functional substituents on the phenyl radical of cholesteryl cinnamate is causative of the complicated thermal properties of cholesteryl acetylferulate.

*Keywords: phase transition, cholesteryl acetylferulate, cholesteryl cinnamate, glass transition, DSC, microscopy*

## INTRODUCTION

The molecular structure of so-called cholesteryl acetylferulate (cholesteryl 4-acetyloxy-3-methoxycinnamate) is shown in Figure 1.

The substance (abbr. CAF) was early synthesized and identified to show a cholesteric phase.[1] It has recently been studied that CAF shows considerably complicated thermal aspects of behavior with differential scanning calorimetry.

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†abbr. title: DSC of Cholesteryl Cinnamates.

Cholesteryl 4-acetyloxy-3-methoxy cinnamate

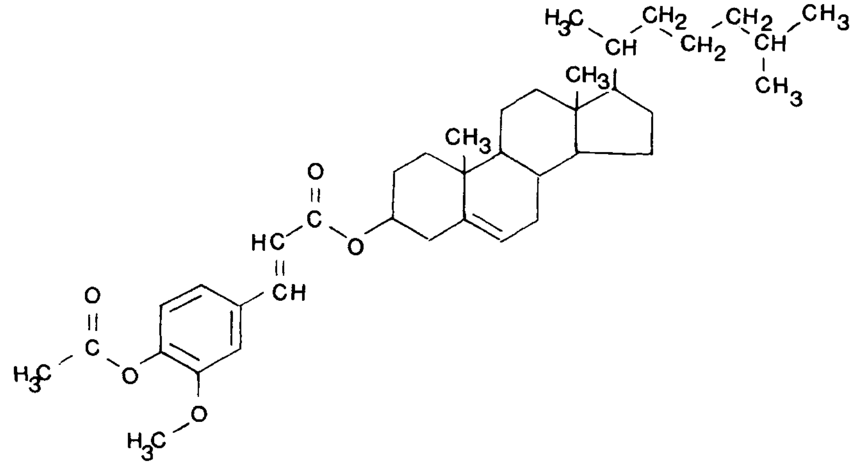

FIGURE 1 The molecular structure of cholesteryl acetylferulate.

# EXPERIMENTAL

## Sample

The synthesis of CAF is reported elsewhere.[1] The sample showed a purity of 99.61% through a high-speed liquid chromatograph.

## Apparatus

Perkin-Elmer DSC-C2 and Mettler FP84 were employed. Scannings were carried out with 20, 10, 5, 2.5, and 1.25 K/min.

# RESULTS

## DSC

On first heating, the crystalline CAF shows a sharp peak of fusion at 443K and then a small peak, indicating mesophase-isotropic liquid transition at approximately 50 degrees over the melting point. The small peak consists of two peaks as shown in the scale-up figure in Figure 2. On cooling, the double peak again appears and another small peak is revealed at a greatly lower level than the melting point without displaying crystallization; besides, an irregular curvature occurs in the neighborhood of room temperature. A cooling curve is

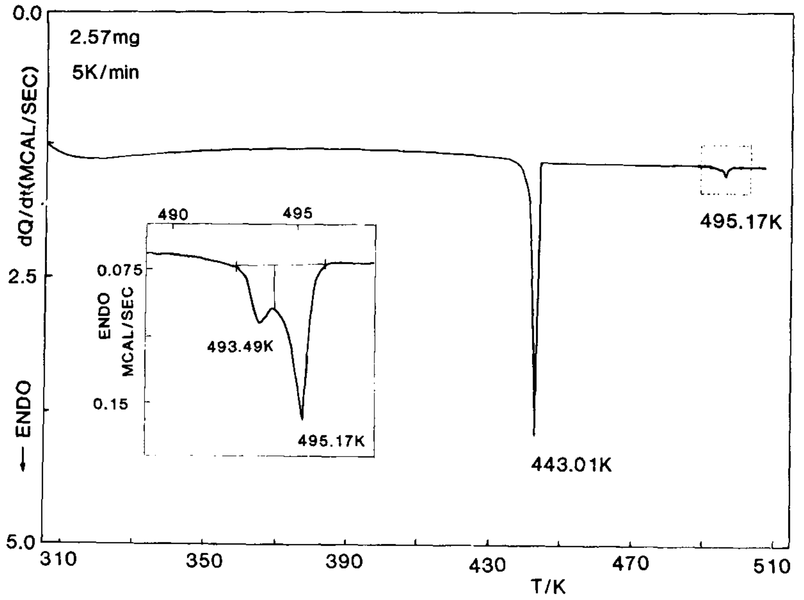

FIGURE 2 DSC trace of cholesteryl acetylferulate on first heating. The inside scale-up figure expresses the dotted area in the main figure.

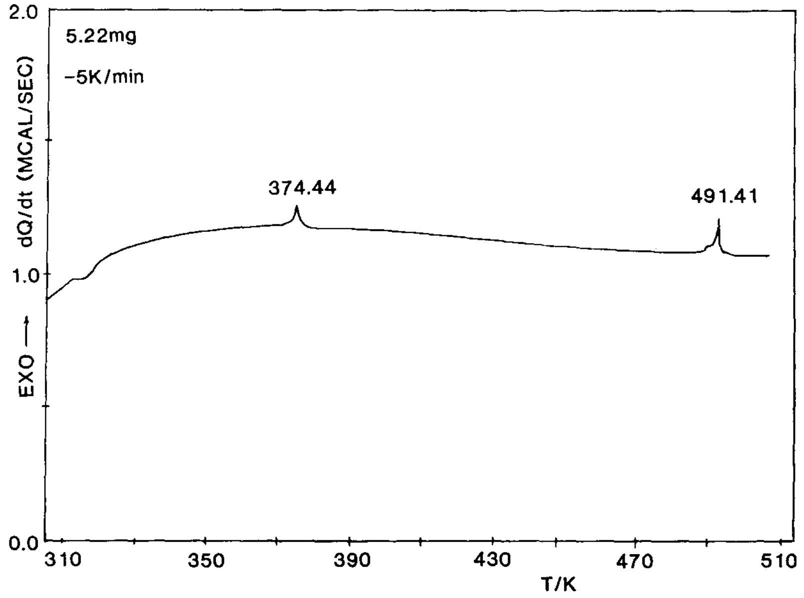

FIGURE 3 DSC trace of cholesteryl acetylferulate on cooling.

shown in Figure 3. The enanthiotropic double peak can be tentatively interpreted to be a cholesteric-blue and blue-isotropic liquid transition. The monotropic peak around 374K, similar to that of cholesteryl nonanoate,[2] implies the cholesteric-smectic A transition. The irregularity at around room temperature suggests a glass transition because of no appearances of exothermic crystallization peaks.

Table I gives the transition temperatures of CAF and the enthalpy changes, which were obtained by extrapolation from the data of scannings at 5.0, 2.5, 1.25 K/min for the isothermal condition.

On reheating CAF which was once melted, two typical curves are obtained as shown in Figure 4. Namely, one kind shows a so-called cold crystallization peak and a fusion peak, while another gives an additional small exothermic peak before melting. The dotted line in the figure is the curve of the crystal from the solution. We denote the crystal as KI, and once melted crystals as KII and KIII in order of higher melting point, respectively. Figure 5 shows the thermal history of CAF. Run 1 and run 2 indicate the first heating and cooling. Run 3 is the reheating curve which shows the crystallization of KII. Run 4 shows that the sample quenched from the cholesteric state was changed into KIII. After run 4, the sample was quenched to 355K

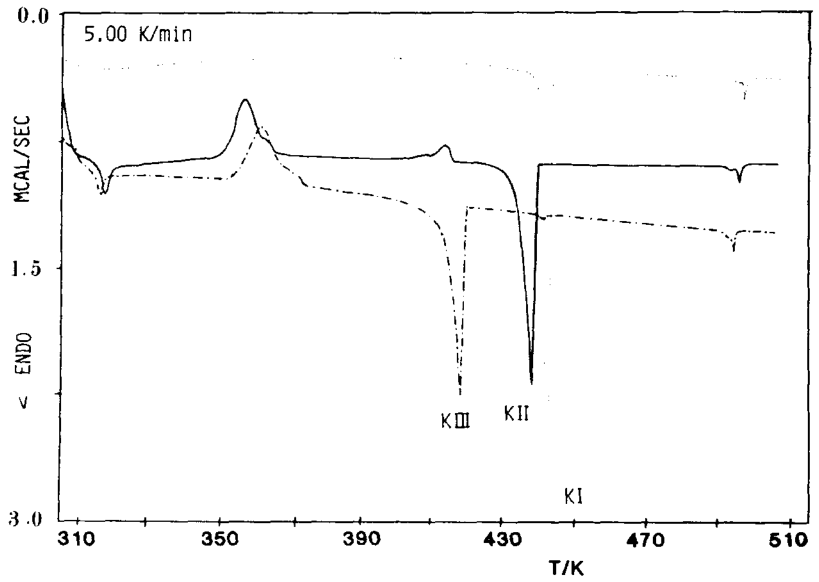

FIGURE 4 Two kinds of DSC curve of cholesteryl acetylferulate on reheating . . . . .; first heating.

TABLE I

Transition temperatures and enthalpy changes of CAF

| | K – Ch | | SM – Ch | | Ch – Bl | | Bl – Iso | |
|---|---|---|---|---|---|---|---|---|
| | $T_p(T_{onset})$ $K(K)$ | $\Delta H$ kJ.mol$^{-1}$ | $T_p$ $K$ | $\Delta H$ kJ.mol$^{-1}$ | $T_p$ $K$ | $\Delta H$ kJ.mol$^{-1}$ | $T_p$ $K$ | $\Delta H$ kJ.mol$^{-1}$ |
| heating | 442.74 (441.54) | 42.44 | – | – | 492.58 | 0.393 | 494.54 | 0.72 |
| cooling | – (–) | – | 372.67 | –0.469 | 491.91 | –0.377 | 493.65 | –0.828 |

TABLE II

Transition values of CAF (reheating)

| Sm(g) – Sm | | Sm – KIII* | | KIII – KII (Ch) | | KII – Ch | |
|---|---|---|---|---|---|---|---|
| $T_g$ $K$ | $\Delta C_p$ J.K.$^{-1}$mol$^{-1}$ | $T_{onset}$ $K$ | $\Delta H$ kJ.mol$^{-1}$ | $T_{onset}$ $K$ | $\Delta H$ kJ.mol$^{-1}$ | $T_{onset}$ $K$ | $\Delta H$ kJ.mol$^{-1}$ |
| 308.4 | 183 | 353 | –18.4 | 413 (414)* | – 3.8 (25.5)* | 433.5 | 32.8 |

*The values in the parentheses are those in the case of the transition of KIII into the cholesteric phase directly, not passing through KII.

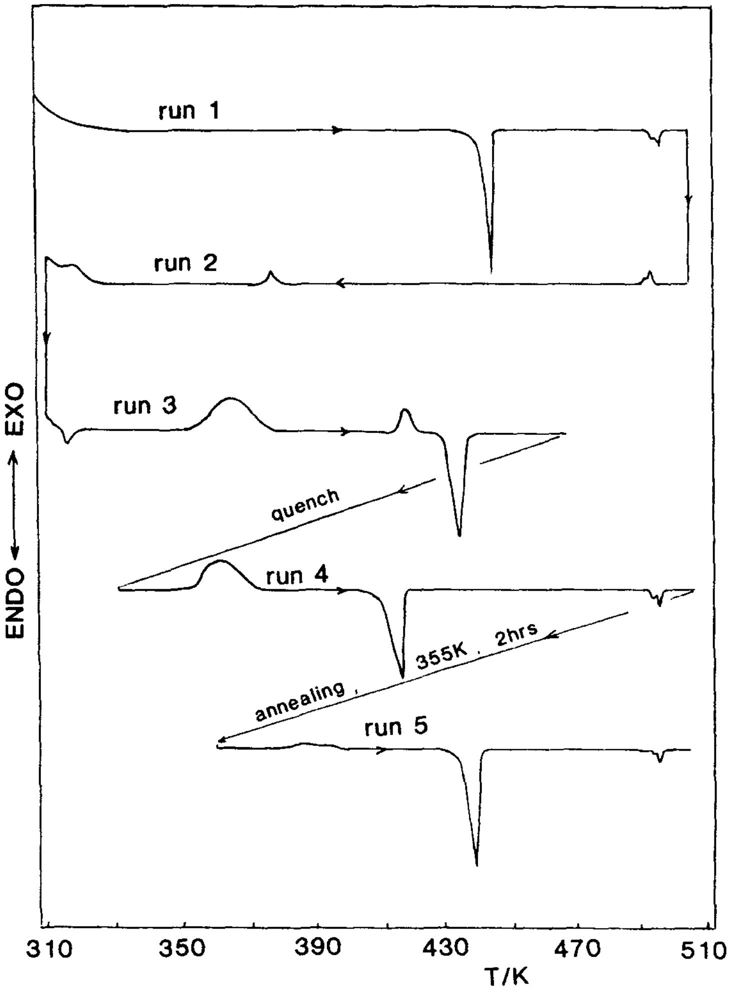

FIGURE 5 Thermal history of cholesteryl acetylferulate.

from the isotropic liquid state and annealed for 2 hrs. at the above temperature. Run 5 shows the result of further reheating the sample. It shows no detectable exothermic peaks of cold crystallization but the melting point is that of KII. It has been clearly shown that KIII can be transformed into KII. This means that KIII is not a further decomposed KII but another polymorph of more unstable form which has a lower crystallinity than KII.

## Glass transition

The glass transition was identified by the clear change of the base line at scanning rates of 20, 10, 5, and 2.5 K/min in the range of 250-350K after quenching the sample from 500K. The glass transition point was determined by the way shown in Figure 6. Figure 7 shows the temperature of the glass transition, depending on the scan rate. We obtain 308.4 K as the temperature of the glass transition by the extrapolation to equilibrium and the difference of specific heat, 183 J.deg.$^{-1}$mol$^{-1}$, which is the average value of all the cases of scannings.

Table II gives the transition values of CAF on second heating. The transition temperatures gives the onset point instead of the peak point.

## Microscopy

Figure 8 shows an example of the result of microscopy on first run at 5 K/min. No visual changes occur up to the melting of crystals (KI) except a mesophase appearance in the rod-like crystal (Photos. 4–

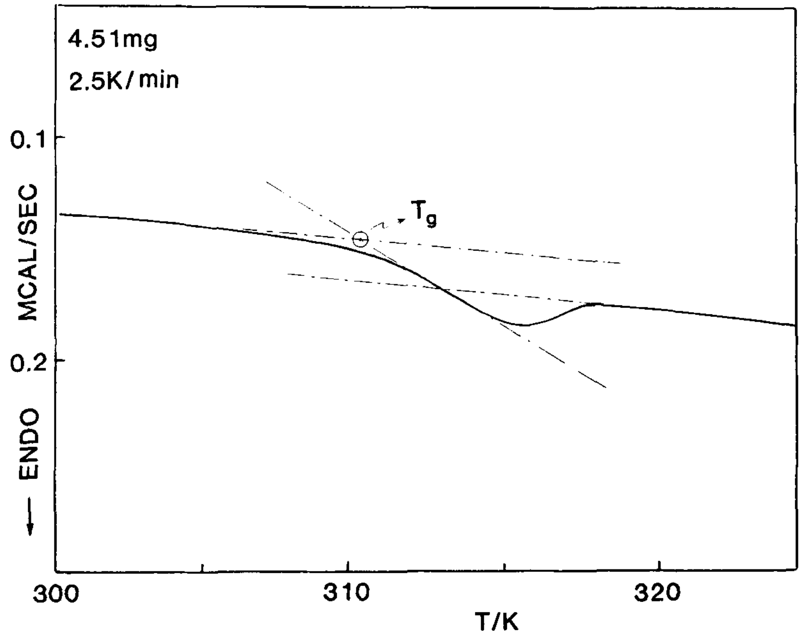

FIGURE 6 The determination of the glass transition point by the change of the base line on heating from 250K after quenching the sample from 500K.

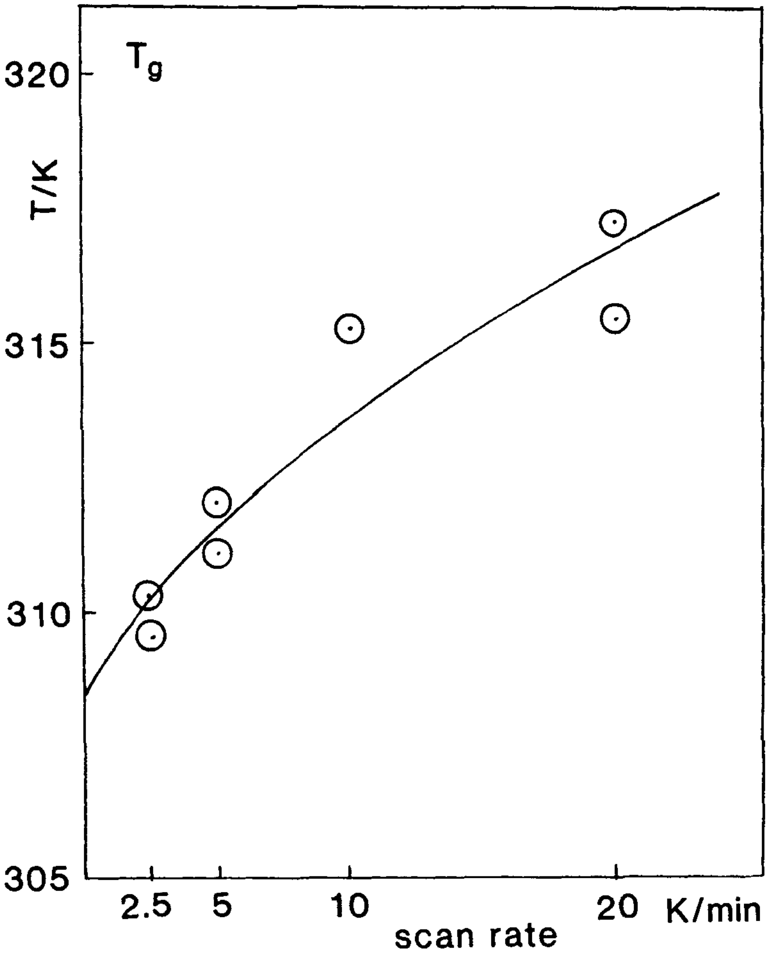

FIGURE 7 The dependence of the temperature of the glass transition upon the scan rate.

5). Photo 7 shows a cholesteric bluish plane texture including oily streaks, which gradually generates the spherulitic polygonal texture (Photo. 8). The iridescent colors change from blue to red as the temperature is elevated, as shown in Figure 9. This photo was taken in the range of 476–492K. The direction of the color shift is the opposite to that of typical cholesteric substances such as normal aliphatic esters of cholesterol, red to blue, with the rising up of the temperature.[3] The plane texture, which includes more or less oily streaks and spherulites, occurs spontaneously on heating, but does not happen on cooling, which inevitably gives the polygonal choles-

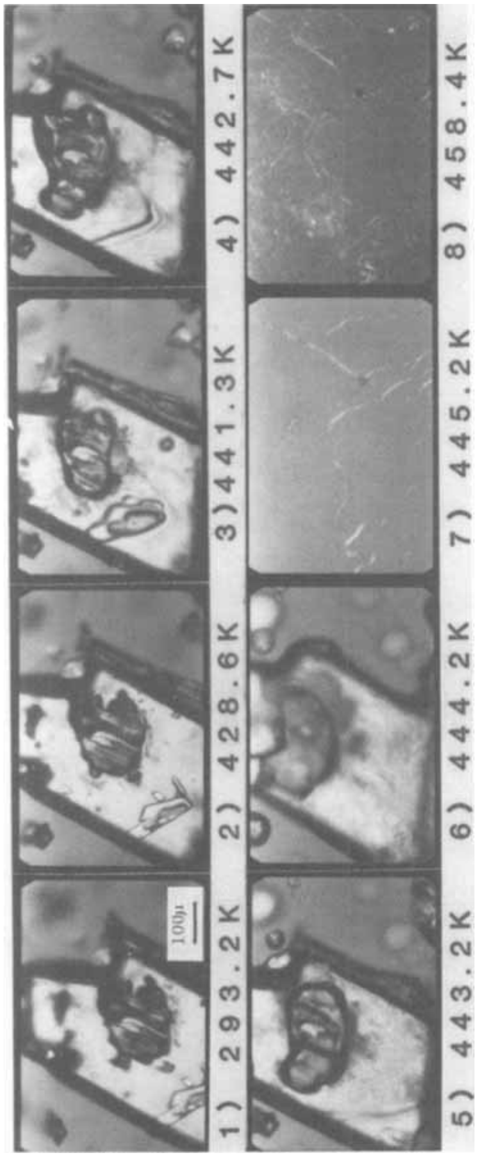

FIGURE 8 An example of the result of microscopy on first run at 5 K/min.

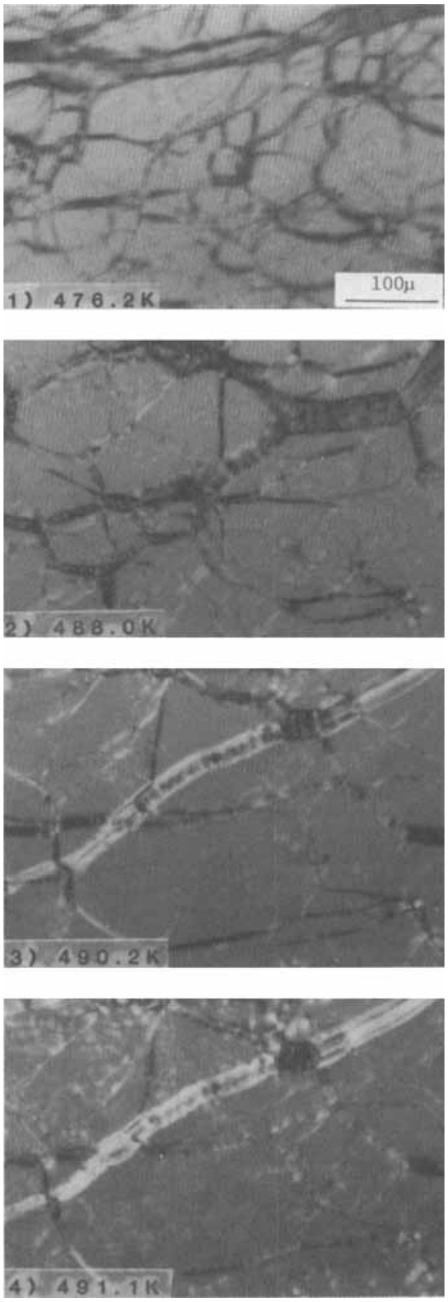

FIGURE 9 The spontaneous iridescent colors of cholesterylacetyl ferulate. See Color Plate I

teric texture. The inclination is also the opposite to that of cholesteryl nonanoate, which usually gives the spontaneous plane texture on cooling towards the cholesteric-smectic transition, unless heating the smectic phase.[4]

Figure 10 shows the cooling run and the successive reheating which results in KIII, corresponding to run 4 in Figure 5. Photos. 1–2 show the generation of a focal conic texture of the cholesteric phase and Photo. 3, its establishment. Photo. 5 shows the transitional state from the cholesteric phase to the smectic A phase and Photo. 7, the final state of smectic A, most parts of which turn into a homeotropic texture. Photos. 8–12 show the steps of the spherulitic growth of KIII at a heating rate of 5K/min from the smectic A at room temperature (Photo. 8) and the establishment of this growth (Photo. 13). Photos. 14–18 indicate the melting steps to the cholesteric phase.

Figure 11 shows another type of reheating run which results in KII through KIII, corresponding to run 3 in Figure 5. Photo. 1 shows the glassy smectic phase. The glass transition at around 300 K shows no visible difference. Photos. 2–4 show the growth of KIII and Photos. 5–8, the transformation from KIII to KII, which is identified by the disappearance of the spherulitic structure and the appearance of another solid phase. Photo. 9 indicates that KII is stable up to over 430 K. Photos. 10–12 show the melting of KII and the generation of the cholesteric phase.

## DISCUSSIONS

The above results of DSC and microscopy lead to the following discussions.

### 1) Double peak at the cholesteric-isotropic liquid transition

As given Table I, the enthalpy change of the cholesteric-blue transition amounts to half of that of the blue-isotropic liquid transition. The ratio is remarkably greater than that of cholesteryl myristate or nonanate,[5] which is approximately 3% of the enthalpy change of the blue-isotropic liquid transition. The temperature difference between both transitions is a few degrees of Kelvin, which is also much more than that in the case of cholesteryl myristate or nonanoate, 0.5 K. Therefore, the speculation that the couple of peaks can be separated into the cholesteric-blue and the blue-isotropic liquid transitions might not be reasonable. It is difficult, however, to attribute the cause of

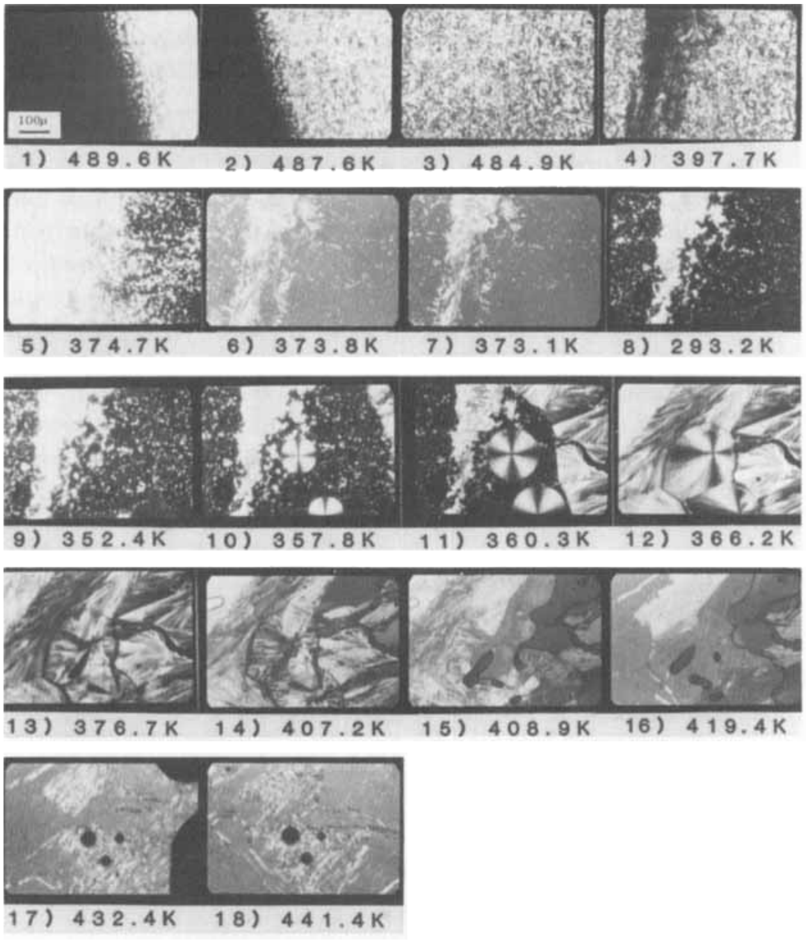

FIGURE 10 The result of the cooling run of the same sample in Figure 8 and the successive reheating which results in KIII.

the double peak to the impurities of 0.4%. We have observed a similar phenomenon—that is, the peak of the cholesteric-smectic A transition of cholesteryl nonanoate was separated into two peaks on a very slow scanning, 0.3 K/min.[4] The common property between the two substances is that the wave length of the iridescent colors becomes longer as the temperature is closer to the double peak. After all, the double peak may be related to the mechanism of the transformation from the cholesteric to another phase.

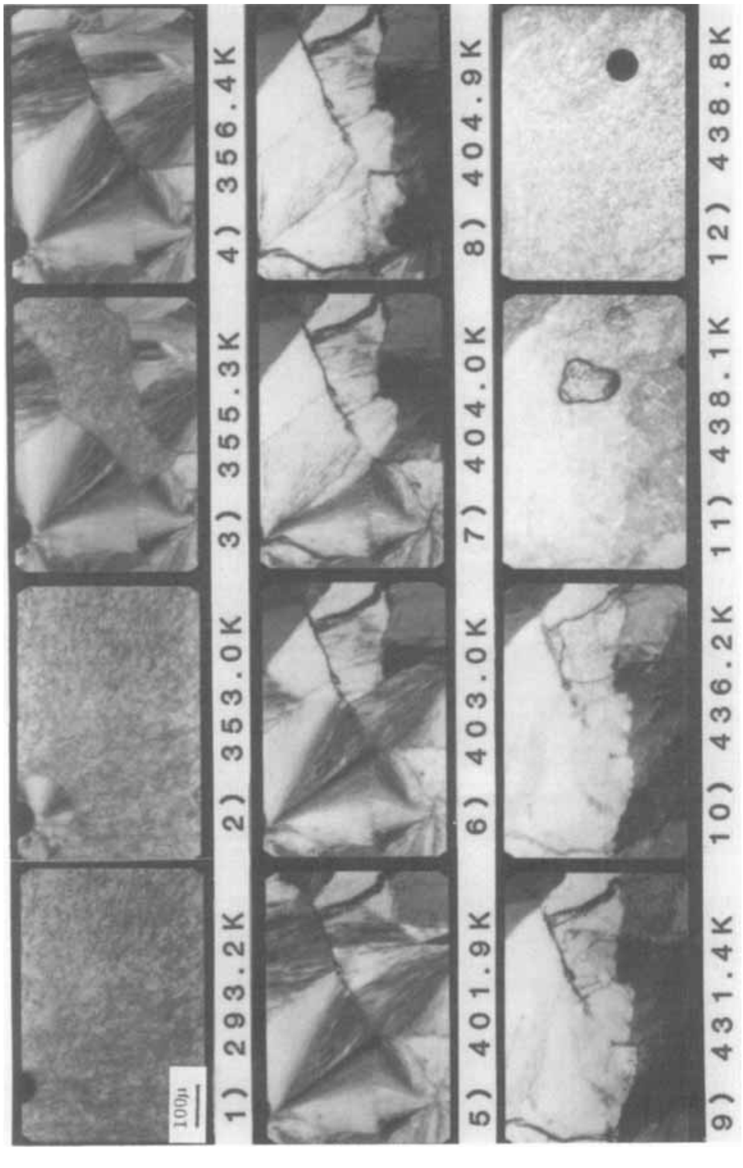

FIGURE 11 Another type of reheating run resulting in KII through KIII.

### 2) Solid polymorph of CAF

Once melted crystals produce two kinds of polymorphs, KII and KIII, excluding KI, the crystal from the solution. The annealing effect which causes the transformation of KIII into KII suggests that both polymorphs are quasi-stable solid states.

Figure 12 illustrates the enthalpy and the Gibbs' free energy of all

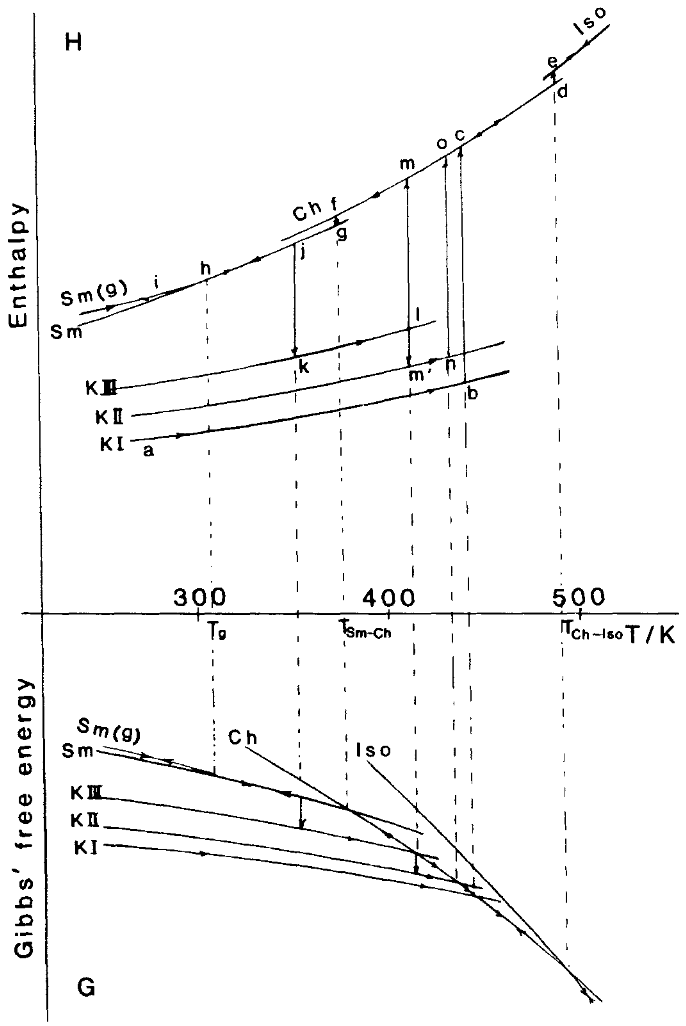

FIGURE 12 The schematic illustrations of enthalpy and Gibbs' free energy of all the phases of cholesteryl acetylferulate.

the phases of CAF schematically. In the plane of H-T, the enthalpy of KI must be laid in the lowest level (curve $a - b$). On first heating, it jumps to the curve of the cholesteric phase ($c - d$) by obtaining the enthalpy change of fusion ($b - c$), and then similarly reaches the enthalpy curve of the isotropic liquid state ($e$). On cooling, the enthalpy curve traces the following order:

*e*, $H$ of the isotropic liquid state
*ed*, $\Delta H$ of the isotropic liquid-cholesteric transition
*df*, $H$ of the cholesteric state
*fg*, $\Delta H$ of the cholesteric-smectic A transition
*gh*, $H$ of the smectic A state
*h*, the glass transition point
*i*, $H$ of the glassy smectic A state.

The enthalpy of the glassy smectic phase should be drawn in a higher level than that of the ordinary smectic phase, because the dH/dT, namely the specific heat $c_p$ of the glassy smectic is smaller than that of the ordinary smectic.

On second heating, the enthalpy of CAF traces the following curves successively:

*ih*, $H$ of the glassy smectic A state
*hj*, $H$ of the ordinary smectic A state
*jk*, $\Delta H$ of cold crystallization stabilized by dropping to the level of KIII
*kl*, $H$ of KIII.

At point, $l$, two cases occur, namely, one reaches point $m$ by obtaining the enthalpy change of fusion of KIII, and another must be further stabilized by dropping to the level of KII.

Corresponding to the H-T plane, Gibbs' free energy can be drawn in the G-T plane, taking account of the relation,

$$G = H - TS, \text{ where, } S \text{ denotes the entropy.}$$

At both temperatures of cold crystallization, the Gibbs' free energy curves of the smectic and KIII, or those of KIII and KII do not intersect by reason of the unequilibrium condition.

### 3) Peculiarity of CAF

Two samples of different purities (100% and 99%) of cholesteryl cinnamate showed no double peaks in the cholesteric-isotropic liquid transition and easily crystallized on cooling. On reheating, neither glass transition nor successive cold crystallization occured, as shown in Figure 13. The difference of the chemical structure of CAF from that of cholesteryl cinnamate is that the former has just a few additional functional groups in the phenyl radical whereas the latter has none. Therefore, it is hardly possible that the impurities of the samples lead to the above different characteristics between them, because the purity of CAF, 99.61%, is included in the region between those of the cholesteryl cinnamate, 99% and 100%. It would rather be possible that only the additional functional groups give rise to the above complicated thermal properties, which are often observed in the polymer field.

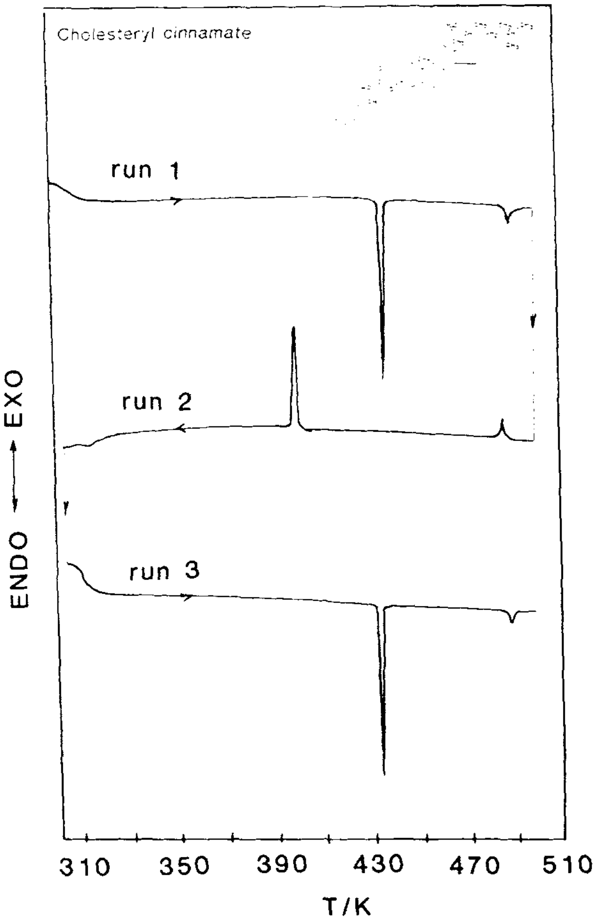

FIGURE 13 Thermal history of cholesteryl cinnamate.

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