Studies of Phase Transitions in Cholesteryl Myristate by Means of Simultaneous Measurements of Polarizing Microscopy and Thermal Analyses*

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(Received June 7, 1975)

An improved DTA furnace and sample cell have been used for accurate DTA measurements and clear polarizing microscopic photographs. The photographs, DTA and TTA curves were obtained simultaneously at different heating or cooling rates for solid-smectic, smectic-cholesteric and cholesteric-isotropic liquid phase transitions in cholesteryl myristate.

Polarizing microscopy has been used for observing the static state of the substance microscopically, and differential thermal analysis (DTA) and total thermal analysis (TTA) for studying the thermal behavior of a substance dynamically. With simultaneous use of the two methods, it is possible to observe the process of transition more in detail.

We have studied the solid-smectic, the smectic-cholesteric and the cholesteric-isotropic liquid phase transitions in cholesteryl $CH_3(CH_2)_{12}COOC_{27}H_{45}$.

Experimental

Apparatus. A DTA furnace and a cell were constructed for increasing the accuracy of DTA measurements and for obtaining clear polarizing microscopic photographs. The furnace is illustrated in Fig. 1. A heater (ϕ=0.3 mm, manganin) and all the electrical lead wires are wound around A. A sectional view of the sample or reference cell, made of pyrex glass (0.6 mm thick) and a quartz plate, with an internal volume *ca.* 0.07 ml, is shown in Fig. 2. The thermocouple, a chromel *p*-constantan type, is used for the absolute or difference temperature measurements. Measurements for the calibration of the absolute temperature scale were reported previously.[1] For increasing the accuracy of DTA measurements, two differential thermocouples were connected in series. Operations for polarizing microscopy and DTA were the same as those described previously.[2]

Material. Cholesteryl myristate (Tokyo Kasei Kogyo Co., Ltd.) was recrystallized from *n*-pentanol twice, pumping being carried out for 22.5 h with a rotary pump in order to remove any trace of solvent. Cholesteryl benzoate (Tokyo Kasei Kogyo Co., Ltd.) was used as a refernce substance.

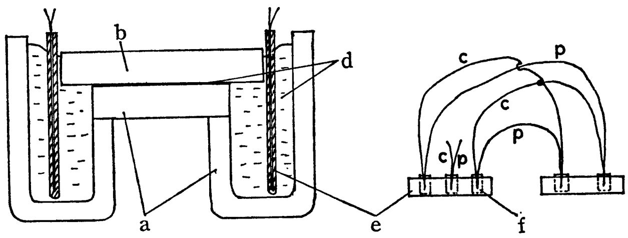

Fig. 2. Cross-section diagram of sample or reference cell and the devised thermocouple junctions.
a: pyrex glass, b: quartz plate, c: constantan wires, d: sample, e: copper plate, f: insulated paper, p: chromel-*p* wires.

Microscopic observations were carried out through crossed nicols and a color-sensitive plate, magnification being 200. A tungsten lamp (30 W) was used as a light source. The position for taking a photograph is marked on the recording paper for the DTA and TTA.

Results and Discussion

Annealing Effects. Polymorphic behavior of solid phases of substances forming liquid crystals has been reported for PAA,[3] MBBA[4] and OH-MBBA.[5] In the course of annealing the solid specimen, polymorphic behavior for cholesteryl myristate has also been observed. The results are shown in Figs. 3 and 4. The solid state established by cooling the specimen of isotropic liquid state with an average cooling rate of

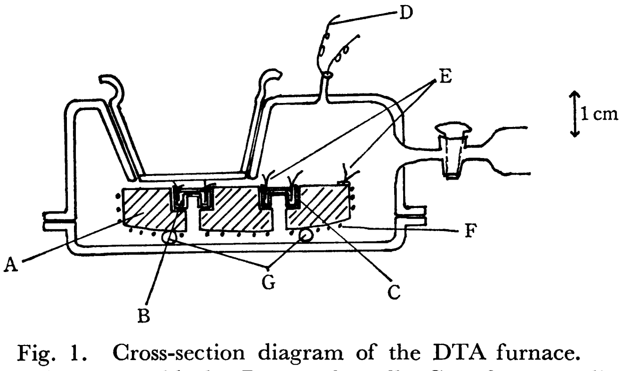

Fig. 1. Cross-section diagram of the DTA furnace.
A: copper block, B: sample cell, C: reference cell, D: lead wires, E: thermocouples, F: heater, G: O-ring.

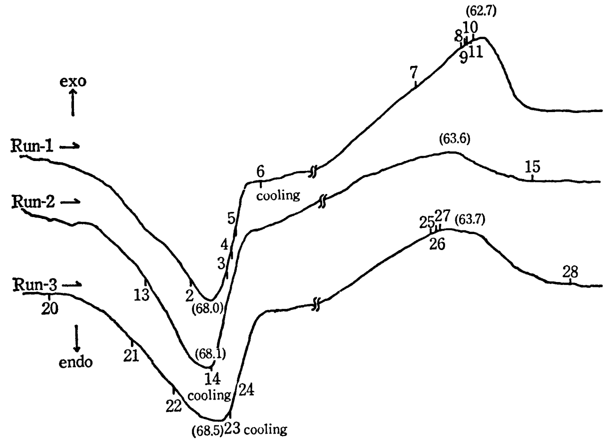

Fig. 3. DTA curves of annealing effects for solid cholesteryl myristate. Numerals in parentheses indicate T_{max} (°C).

* Presented at the 32nd Annual Meeting of the Chemical Society of Japan, Tokyo, April 1, 1975.

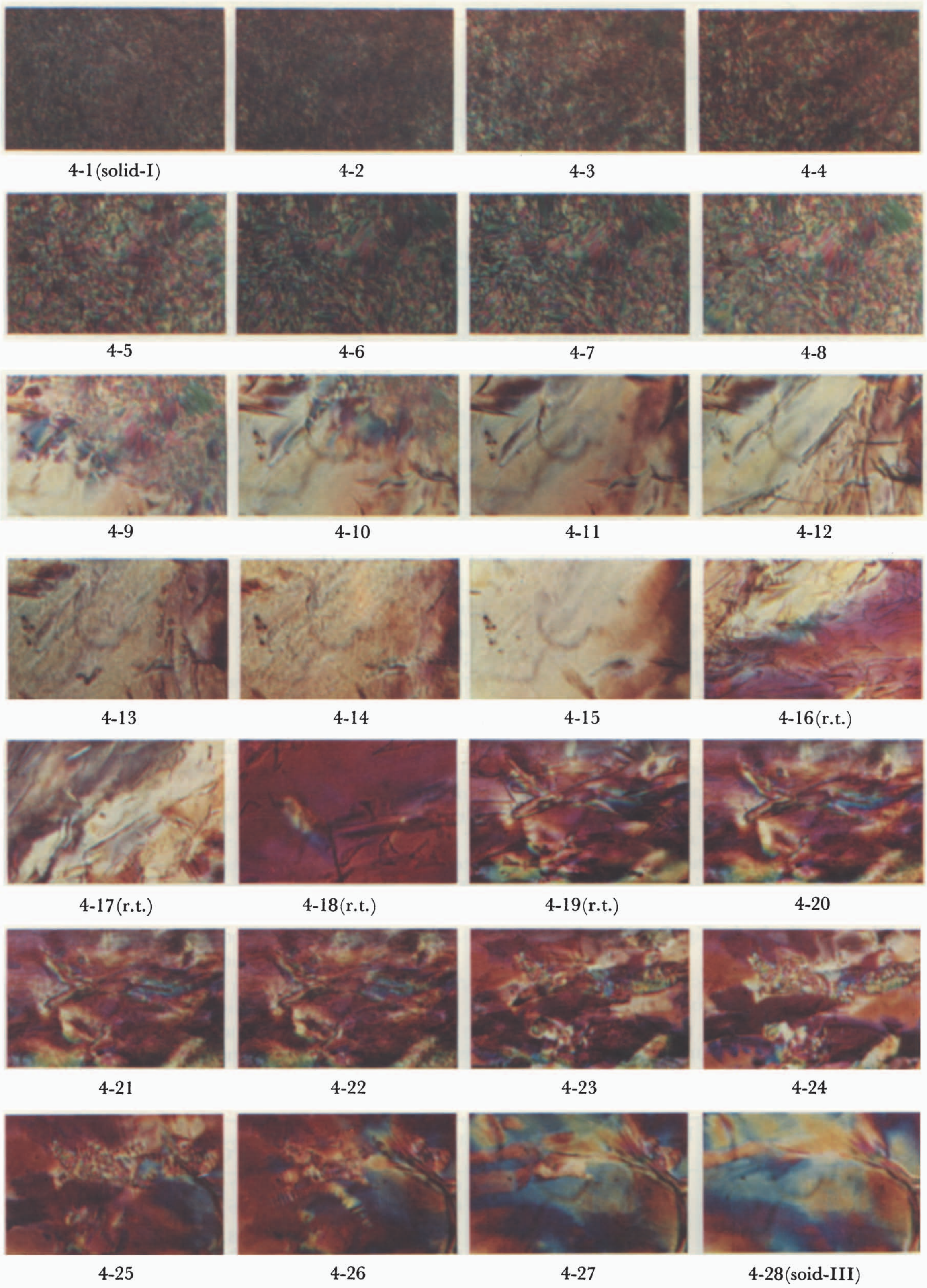

Fig. 4. Microscopic photographs of annealing effects for solid cholesteryl myristate.

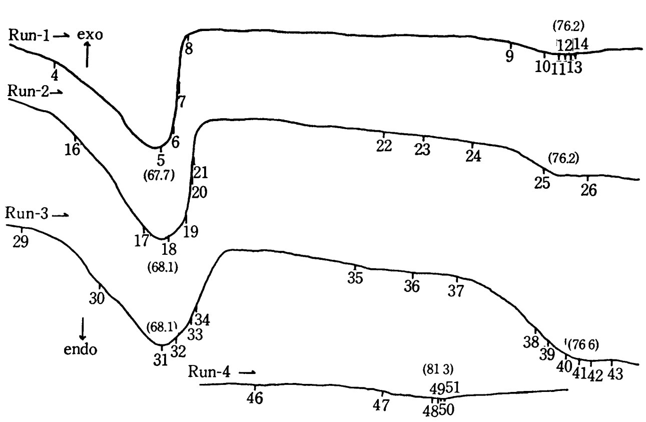

Fig. 5. DTA curves of cholesteryl myristate at heating condition. Numerals in parentheses indicate T_{max} (°C).

ca. 1.79 °C min^{-1} to room temperature, is denoted by solid-I. In Fig. 3, Run-1 represents a DTA curve obtained by heating solid-I at the rate 0.22°C min^{-1} from room temperature to point 6, and then by cooling at the rate 0.23 °C min^{-1} to room temperature. Figure 4-12 gives a photograph of the solid obtained at 32 °C after 18.5 hr. The annealing effects for this solid are shown by the DTA curve at the heating rate 0.23 °C min^{-1} and the cooling rate 0.22 °C min^{-1} for Run-2. Figs. 4-16, 4-17, 4-18 and 4-19 show the annealed solid states at room temperature after 19 hr. Run-3 gives a DTA curve obtained by annealing the specimen (Fig. 4-19) at the heating rate 0.24 °C min^{-1} and the cooling rate 0.22 °C min^{-1}. The last established solid is denoted by solid-III.

Heating Process. Another solid state denoted by solid-II (Fig. 6-15) was obtained by cooling the specimen of isotropic liquid state to 49.4 °C at the cooling rate *ca.* 0.22 °C min^{-1}. We found that the situation of the transitions from solid to smectic and then to cholesteric depends upon the starting solid-state. The DTA curves for solids-I, II and III are shown by Runs-1, 2, and 3, respectively, in Fig. 5, at heating rates of 0.21, 0.21 and 0.23 °C min^{-1}, respectively. Figs. 6-1 to 6-43 show the microscopic photographs taken during the course of transformation.

Figure 6-1 shows the microscopic photograph of solid-I at room temperature, Figs. 6-2 and 6-3 being those of partial solid-I states. Figs. 6-4 to 6-14 show photographs corresponding to the points indicated by the numbers in the DTA curve for Run-1 in Fig. 5, Fig. 6-8 giving the smectic-state obtained from solid-I state. The smectic-to-cholesteric transition takes place directly from the openings of the rod (or bunch) shaped smectic-liquid crystals, as shown in Figs. 6-12 and 6-13. Figure 6-14 shows the established cholesteric state.

Figures 6-15 to 6-26 show microscopic photographs of solid-II corresponding to the DTA curve of Run-2 in Fig. 5. Figure 6-22 shows the smectic-state obtained by heating the specimen of solid-II. The upper part on the left is similar to the smectic-state obtained from solid-III. The lower part on the right shows the rod shaped smectic-state found in solid-I. Figure 6-26 gives the cholesteric-state obtained and resembles Fig. 6-14.

We found locally the state of solid-III at room temperature as shown in Fig. 6-28. It might be a glassy solid-state. Figures 6-29 to 6-43 show the microscopic photographs for solid-III (Fig. 6-27) corresponding to the DTA curve of Run-3 in Fig. 5. The established smectic-state(Fig. 6-35) was transformed into the cholesteric-state by way of establishing the spherical-state (Figs. 6-36 to 6-40). The thermal behavior was also observed on the DTA curve in Fig. 5 (compare with Runs-1 and 3). The obtained cholesteric-state (Fig. 6-43) is much the same as shown in Figs. 6-14 and 6-26.

We see from Figs. 5 and 6 that there is some difference between the thermal behavior of solids-I, II and III not only in the solid-to-smectic transition but also in the smectic-to-cholesteric one. However, no difference was observed in the cholesteric-to-isotropic liquid transition between solids-I, II and III. The transition for solid-II is shown by the DTA curve for Run-4 in Fig. 5 and by the microscopic photographs (Figs. 6-46 to 6-51). The cholesteric-state of cholesteryl myristate (Fig. 6-46) is a state in which spherical-liqud crystals (Figs. 6-37 to 6-39) stick to each other. It might be assumed that the difference in color between the yellow part and the blue part corresponds to the molecular orientation of the block, the red part being similar to the isotropic liquid state. The red part spreads with the progress of cholesteric-to-isotropic liquid transition.

Figures 6-44 and 6-45 give microscopic photographs

TABLE 1. TRANSITION TEMPERATURES AND ENTHALPY RATIOS OF TRANSITION FOR CHOLESTERYL MYRISTATE

	Heating rate (°C min^{-1})	$t_{solid-to-smectic}$ (°C)	$t_{smectic-to-cholesteric}$ (°C)	$t_{cholesteric-to-isotropic}$ (°C)
Solid-I	1.73	68.8	77.3	82.8
	0.89	68.4	76.8	82.1
Annealed solid	1.79	70.3	78.5	83.7
	0.90	68.7	77.0	82.0
	Heating rate (°C min^{-1})	ΔH-ratio (solid-to-smectic)	ΔH-ratio (smectic-to-cholesteric)	ΔH-ratio (cholesteric-to-isotropic)
Solid-I	1.73	47.0 (95.6%)	1.2 (2.4%)	1.0 (2.0%)
	0.89	43.5 (95.1%)	1.2 (2.7%)	1.0 (2.2%)
Annealed solid	1.79	39.4 (93.7%)	1.7 (3.9%)	1.0 (2.4%)
	0.90	34.2 (91.2%)	2.3 (6.1%)	1.0 (2.7%)
Griffen and Porter[7]	—	45.4 (95.0%)	1.4 (2.9%)	1.0 (2.1%)

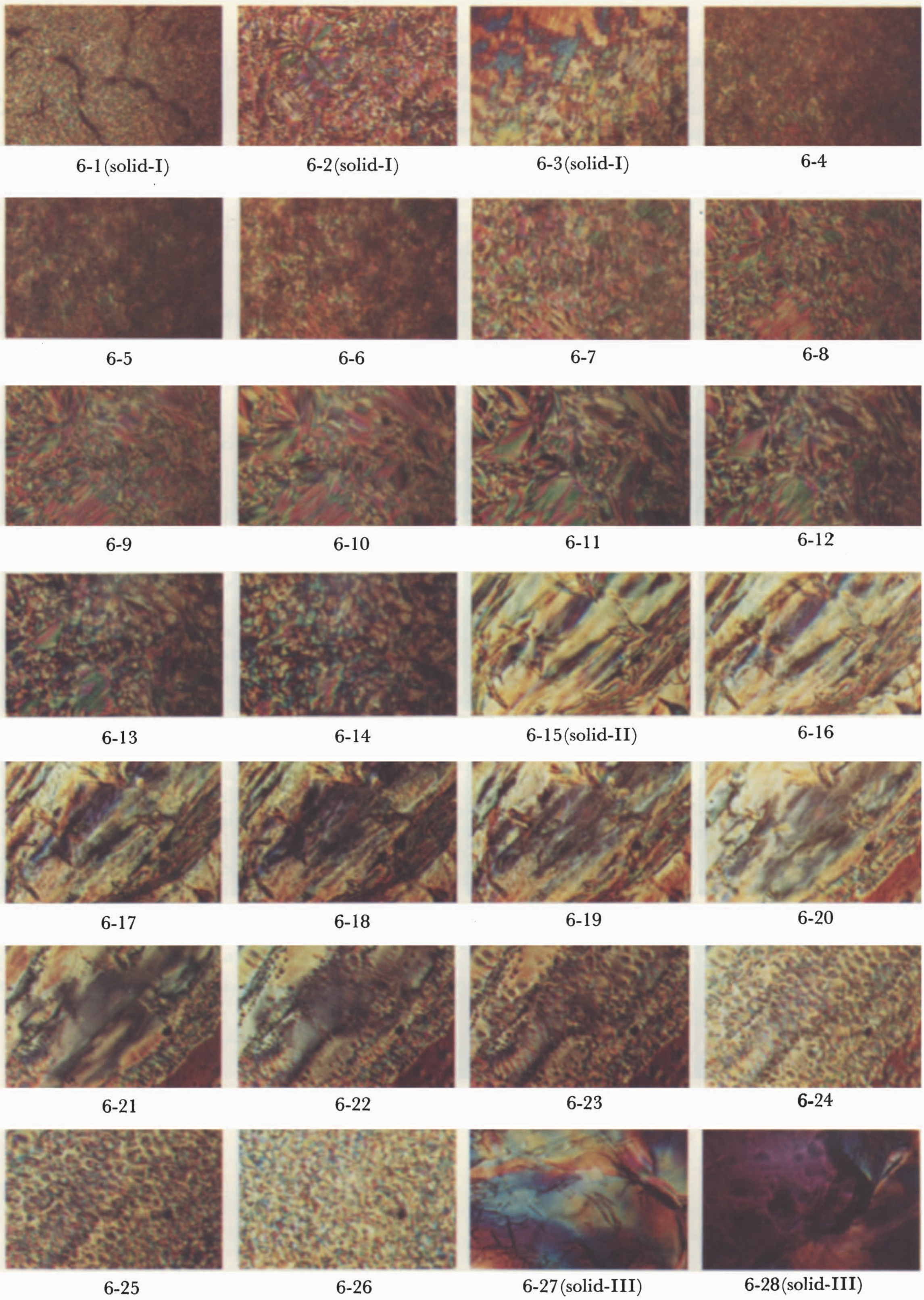

Fig. 6. Microscopic photographs of cholesteryl myristate on heating and cooling processes.

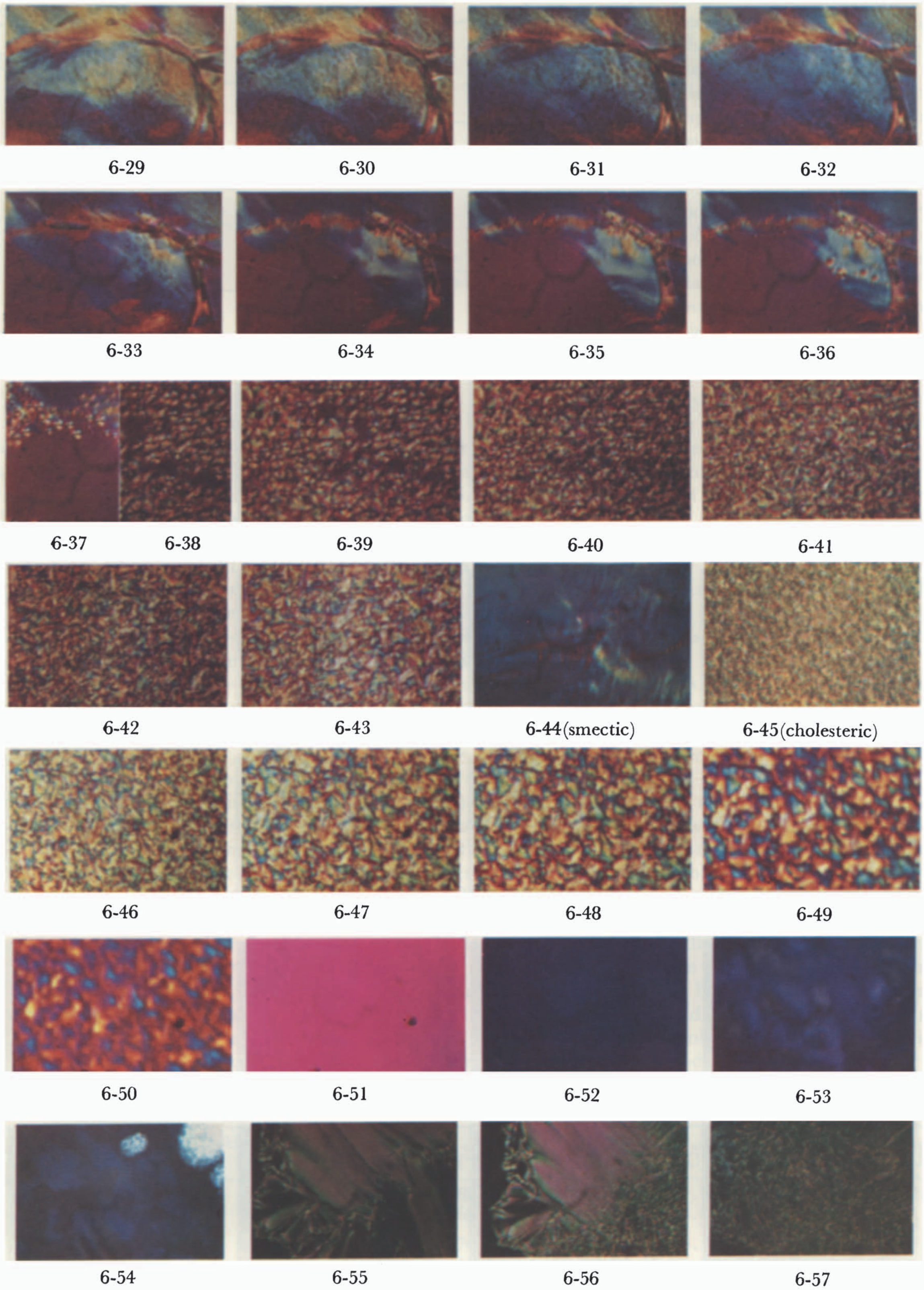

Fig. 6. (Continued)

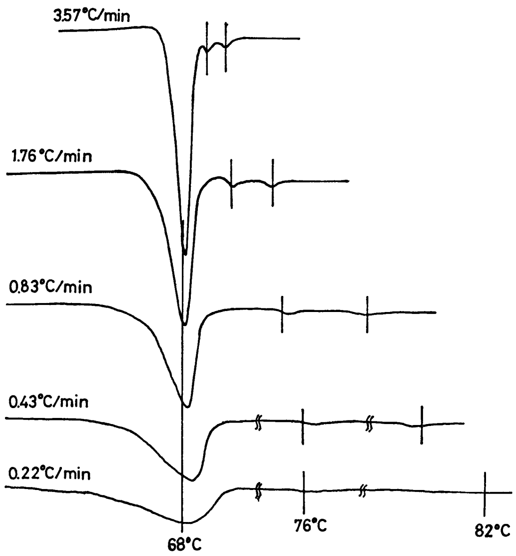

Fig. 7. DTA curves obtained at various heating rate of solid-I.

of the smectic and cholesteric states established by heating the specimen of the solid-state obtained by heating solid-I from room temperature to the maximum point of the solid-to-smectic transition and by cooling to 42.5 °C at a rate of *ca.* 0.22 °C min^{-1}. It is suggested that on the basis of molecular configuration solid-I is a frozen-in solid state of cholesteric-state(compare Figs. 4-1 and 6-45), the annealed solid (Fig. 4-12) is a frozen-in solid state of smectic-state (Fig. 6-44), and solid-II is a mixed state of these solids (compare Figs. 6-8, 6-22 and 6-44).

Cooling Process. All states obtained during the course of heating were also observed in the course of cooling the specimen from isotropic liquid-state to solid-state.

Figures 6-52 to 6-54 show the process of isotropic-to-cholesteric transition at such a slow cooling rate that no DTA curve can be observed. The blue color turns light with the thickness of the specimen, probably because of high optical-rotatory power[6] of the cholesteric state. Figures 6-52 to 6-57 were taken without color sensitive plate but with crossed nicols. Figures 6-55 to 6-57 show the microscopic photographs during the course of smectic-to-solid transition. The solid-state became wrinkled horizontally with the width of the rod shaped smectic-block.

Differential Thermal Analysis (DTA). DTA measurements at several heating rates were made for the specimen of solid-I. Figure 7 shows the DTA curves obtained. The changes in the transition temperature due to the discrepancy of heating rate were found to be considerably small. Two measurements of solid-I and annealed-solid were also made at different heating rates. The transition temperature and the enthalpy ratio* of transition are summarized in Table 1.

The transition temperatures from solid to smectic and to cholesteric for the annealed-solid are higher than those for solid-I. The transition temperature from cholesteric to isotropic liquid for the annealed-solid is much the same as that for solid-I. The enthalpy of the solid-to-smectic transition for the annealed-solid is smaller than that for solid-I, the enthalpy of the smectic-to-cholesteric transition for the annealed-solid being larger than that for solid-I.

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* Since we cannot obtain the enthalpy of transition directly from DTA curves, the ratio of the enthalpy of each transition to that of cholesteric-to-isotropic liquid transition is given.