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Study of Cholesteryl Formate and Cholesteryl Octanoate by Means of Thermal Analytic Microscopy with a Thermoelement

Kazuko Sasaki Kunihisa and Seiichi Hagiwara*
National Chemical Laboratory for Industry, Honmachi, Shibuya-ku, Tokyo 151
**Tokyo Riko Company, Kitamachi, Hoya-shi, Tokyo 188*

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A simple apparatus using a thermoelement was constructed for thermal analytic microscopy and the phase transitions of cholesteryl formate and cholesteryl octanoate were studied. The isotropic–cholesteric transition of cholesteryl formate and the cholesteric–smectic transition of cholesteryl octanoate were observed microscopically but not thermally. Upon slow cooling cholesteryl octanoate gives large spherulites with a cholesteric focal conic texture. The spherulites are optically negative. They give rise to the vortices which turn to smectic reeled yarns in specimens with appropriate thickness. The solar spectrum which appears at the cholesteric-smectic transition of cholesteryl octanoate was observed repeatedly, namely, blue, yellow, red, blue, *etc*. A melt recrystallized sample of cholesteryl formate forms a block similar to a sphere in the thermal cell. Both solid phases of cholesteryl formate and octanoate grow radially in the microscopic cell plates.

One of the authors (K.S.K.) developed thermal analytic microscopy, simultaneous observation by polarizing microscopy and by DTA.[1] This was applied to cholesteryl myristate using an improved apparatus with a modified sample holder.[2] The present work was carried out in order to systematically study (1) the aliphatic esters of cholesterol and (2) the operation of the apparatus using a thermoelement in place of the thermocouple for DTA. The temperature sensitivity of the thermoelement is 180 μV/°C based on the contact potential difference between copper and the thermoelement,[3] three or four times EMF of thermocouple. Cholesteryl formate (Ch. F.) and cholesteryl octanoate (Ch.O.) were studied. The interior of a hot stage for a microscope was reconstructed.

Apparatus

Only the reconstructed part will be described. Three thermoelements protrude like arms from the copper block wall as shown in Fig. 1. This protrusion is necessary to make the thermoelement sensitive to the temperature gradient between the specimen and the heat wall. The center arm has a copper ring at the terminal to hold a microscopic sample which is sandwiched between two quartz plates (1 mm thick). The sample thickness usually is 10—15 μ. Both side arms have their copper cell holders attached to DTA cells which are also made of copper (inside volume, 130 μl). The leads to the amplifier extend from the bases of the holders for the purpose of detecting the potential proportional to the temperature difference between the sample and the reference substance (Al_2O_3).

The copper block is surrounded by a manganin heater and has no cover. It is assumed that the temperature distribution near the specimen is approximately homogeneous due to nearly equivalent conduction of heat through the thermoelements. The temperature of the sample was measured by setting a copper–constantan thermocouple (0.1 mm ϕ) at the center ring for microscopy. The thermocouple for temperature monitoring, also copper–constantan (0.3 mm ϕ), is placed between the block wall and the manganin wire. The central part of the bottom of the block is made of glass for the sake of light transmission. The light source is an ordinary tungsten lamp of 30 W. The surroundings of the hot stage are covered with moltprene and teflon sheets.

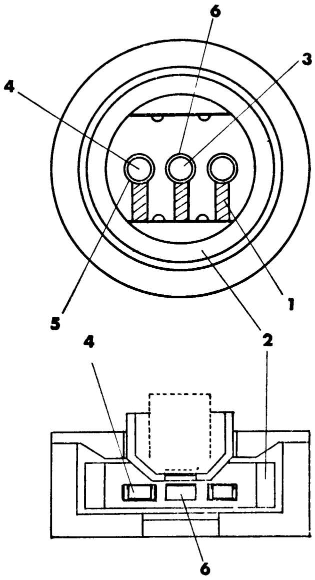

Fig. 1. Hot stage devised for thermal analytic microscopy.
1: Thermoelement, 2: copper block, 3: quartz cell, 4: copper DTA cell, 5: copper cell holder, 6: copper ring.

Sample

Commercial Ch. F. and Ch. O. were successively recrystallized from 1-pentanol[4] and ethanol, washed with acetone and dried at 60 °C for one day, as in the case of cholesteryl myristate (Ch.M.).[2]

Performance of the Apparatus

Stearic acid recrystallized from benzene was used to calibrate the heats of transition. The heats of transition were determined by taking three copies for the respective peaks and weighing the copied peak areas.

Table 1. Transition values for cholesteryl myristate

		Cryst.-Sm.		Sm.-Ch.		Ch.-Iso.	
		T °C	*Q* cal/g	*T* °C	*Q* cal/g	*T* °C	*Q* cal/g
Heating	This work	70.6	18.2	78.4	0.5	83.5	0.3
	Barrall II *et al.*5)	73.6	18.7	79.7	0.41	85.6	0.41
	Davis *et al.*6)	70.5	18.6	77.8	0.56	83.2	0.41
Cooling	This work	52—67	16.3	78.5	0.6	83.5	0.5
	Barrall II *et al.*5)	36.7	16.8	70.0	0.56	76.5	0.44

This was done for the purpose of averaging the fluctuations (about 2%) of the density of the paper and of the mode of trimming the peak area.

Table 1 gives the transition values for Ch.M., which was further purified from the compound previously studied.2) Thermal data are available for Ch.M.9) since it is a typical sample giving rise to both liquid crystalline states, cholesteric and smectic, which are enantiotropic. The result of Davis *et al.*6) is the most recent. The work of Barrall II *et al.*5) refers to the cooling data besides heating ones. Our values of the heat of transition do not exceed the reference ones in accuracy mainly due to the fluctuations in the copy paper density. However, the transition temperatures show a better agreement between heating and cooling than the reference ones regarding every transition. The precision of the transition temperatures on heating is ±1 °C, which is independent of the scanning rate (0.25, 0.5, 1, 2, and 4 °C/min).

Results and Discussion

The transition points of both esters on heating (mp) were reproducible and independent of the heating rate (0.25, 0.5, 1, 2, and 4 °C/min), but not those on cooling. The transition temperatures on cooling change with cooling rate and sample. Both Ch.F. and Ch.O. sometimes crystallize leaping over the mesophases, as pointed out by Friedel.10) Discrepancy was found between the temperature determined by the DTA peak and that determined by the microscopic change. Table 2 gives the results of Ch. F. The mesophase transition was not detectable by DTA curves,** while the cholesteric texture appears microscopically a few degrees above the solidification temperature. In most cases, solidification temperature determined by DTA was higher than that by microscopy.

Table 2. Transition temperatures of cholesteryl formate, depending on DTA or microscopic samples and the cooling rates

Cooling rate	Transition temperatures (°C)		
	DTA	Microscopy	
°C/min	Crystn. point	Ch. focal conic	Crystn.
0.25	61.2	58.5	56.4
1	60.3	58.0	55.0
4a)	57.6	57.7	52.4

a) The practical rate was 1.2 °C/min around 60 °C, due to no water circulation.

In order to clarify the discrepancies, the temperatures of thermal and microscopic samples were measured simultaneously by setting another thermocouple on the DTA cell holder of sample side. The temperature difference between the microscopic sample and the DTA sample diminishes with the decrease in the scanning rate. Both temperatures coincided within ±1 °C below 100 °C. It seems that the difference in shape of the two sample cells causes the discrepancy rather than the inhomogeneity of the temperature distribution in the block, even taking into account the instability of the

Table 3. Transition values for cholesteryl formate and cholesteryl octanoate

		Heating		Cooling			
		Cryst.-Iso.		Cryst.-Ch.		Ch.-Iso.	
		T °C	*Q* cal/g	*T* °C	*Q* cal/g	*T* °C	*Q* cal/g
Ch.F.	This work	96.0	12.4	55.0	9.4	(58.0)	(0.1)
	Berrall II *et al.*5)	97.3	12.8	50	8.6	97.1	0.2
	Davis *et al.*6)	96.6	12.6	—	—	57.1a)	0.08a)
	Gray7)	97.5	—	—	—	60.5	—
Ch.O.	This work	108	13.9	81	11.1	87	0.2
	Barrall II *et al.*8)	112.7	17.5—18.9	81.7	14.2—13.5	92.7	0.45—0.38
	Gray7)	110	—	69.5	—	96.5	—

a) *cf.* Ref. 6.

** The mesophase transition of Ch. F. in DTA appeared only once. The heat evolution was estimated to be 0.1 cal/g (shown in parentheses in Table 3).

mesophase of Ch.F. Translational or rotational motions start easily in the DTA sample in liquid state in the free space inside the cylindrical cell, solidifying directly without taking the mesophase. On the other hand, a microscopic sample in the thin space between the quartz plates is not free since it receives adhesive forces at the boundaries, being forced to take the course to the mesophase.

Multiplicate runs on a microscopic sample give rise to some depression of the transition temperature of Ch.F. It seems that the space in the plates becomes thinner due to flowing out of the sample by repetition of melting. The sample can hardly undergo transformation against the boundary forces. This is supported by the fact that a thick sample of Ch.F. for microscopy shows no cholesteric texture, solidifying at 59.6 °C under 1 °C/min cooling. No quantitative relations between the mesophase appearance and the sample thickness were studied.

The transition temperatures become lower with the increase of the cooling rate also in DTA samples as shown in Table 2. This indicates that the transformation can not follow the cooling rate above a certain rate. The lowest cooling rate 0.25 °C/min gave the highest crystallization temperature 61.2 °C.

Disagreement of the transition temperatures determined by DTA with those by microscopy also occurred in the case of Ch.O. However, the isotropic–cholesteric transition was observed by DTA and microscopy. The cholesteric–smectic transition was observed by microscopy but not by DTA. The transition temperatures of Ch.O. on cooling (Table 3) are the most probable values, their fluctuations being ±5 °C. The reported values of both substances also markedly differ (Table 3).[5–9] The results of Ch.F. and Ch.O. may be due to the unstable properties of the mesophases as well as to the apparatus conditions. Davis *et al.*[6] concluded from their DSC studies that the lowest molecular weight saturated aliphatic ester of cholesterol to show mesophase behavior is the propionate.

Microscopy. Optical studies on aliphatic esters of cholesterol were carried out by Fridel[10] and others.[7] The studies dealt with the characteristic color reflections of the cholesteric phases and the results were restricted to liquid crystalline states. Our results might give some new information on the morphological mechanism of the transformation. The observations for the solid states may be useful to elucidate their liquid crystalline states.

Cholesteryl Formate. Ch.F. shows a mesophase similar to the cholesteric focal conic texture of Ch.M. a few degrees above the solidification temperature. When the cholesteric texture appears slowly, the phase front makes spherulitic balls and then takes them in the texture (Photo. 1). The view field is faintly light (turns faintly orange by taking off analyser) until the texture appears. Indigo blue appears near the boundary of the texture in a specimen of proper thickness. Photograph taken with a color sensitive plate gives an ordered cholesteric phase somewhat like woolen texture (Photo. 2).

The solidification speed is considerably great as compared with that of the cholesteric phase growth. The solid phase develops radially like a film which seems to retain the liquid property. The cholesteric texture is once destroyed and transformed into isotropic (dark in view) before solidification. In a properly thick specimen, the flow caused by the texture destruction appears in dark vermilion and dark green under crossed polars. The two color directions appear to make a right angle.

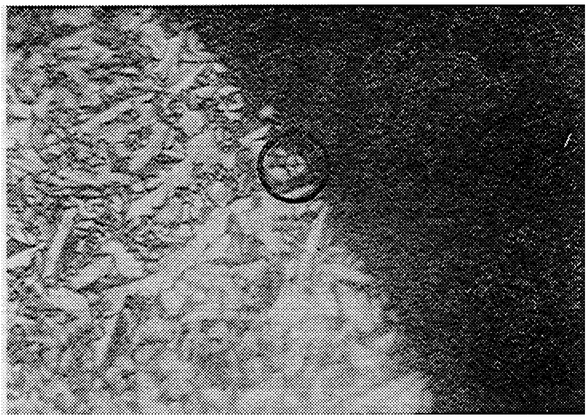

Photo. 1. Cholesteric texture appearance of cholesteryl formate. 0.25 °C/min cooling at 58.5 °C,
The circle in the photograph indicates the spherulitic ball.

Radial cleavages occur after solidification. Photograph 3 shows the center of a radially grown solid phase which indicates a spherulitic growth. A sample recrystallized after melting in the DTA cell forms a block similar to a sphere and to an illustration, drawn by G. W. Gray, for an explanation of a smectic phase.[11]

Cholesteryl Octanoate. In this work, the homeotropic texture gave colors from blue to yellow. The most retainable color was sapgreen. Both the brilliance and hue are dependent on the thickness of sample. The color increases in luminosity and approaches the longer wavelength with the thickness, similar to the case of Ch.M.

Ch.O. lies in the series of aliphatic esters of cholesterol whether the smectic phase appears or not. The focal conic texture is sometimes similar to the cholesteric focal conic of Ch.M. and at others to the smectic focal conic of Ch.M. With a very thin specimen ($<10\,\mu$) the cholesteric focal conic texture disappears and turns isotropic, a smectic texture like the smectic strings of Ch.M. appearing at the transformation into solid phase. The strings turn many small spherulites before a solidification wave front appears discontinuously.

Photographs 4—9 show the course of spherulitic growth of the cholesteric focal conic texture from occurrence to destruction by invasion of the solidification wave front. It is evident by means of a color sensitive plate that the large spherulite is also optically negative.***

The spherulite causes a rapid rotation around the center somewhat like a spinning wheel or a vortex just

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*** The colors, yellow and blue, of the quadrants of the spherulite interchange their positions by photography.

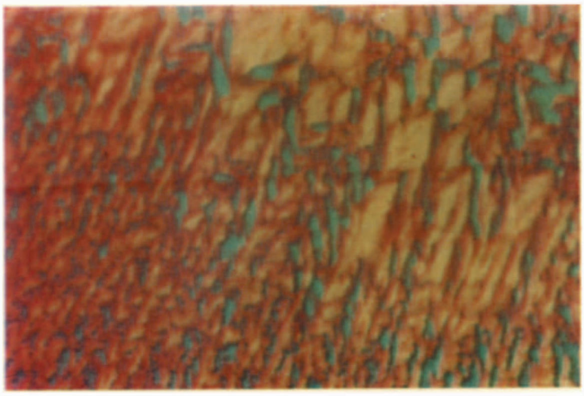

Photo. 2. Ordered texture of the cholesteric phase in cholesteryl formate. 2 °C/min cooling, at 57.5 °C.

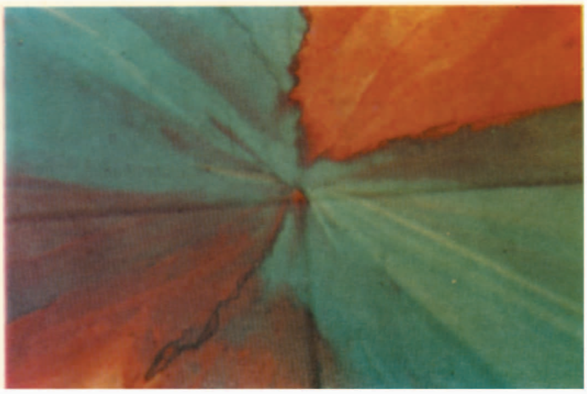

Photo. 3. Center of radial growth of the solid in the same specimen as Photo. 2.

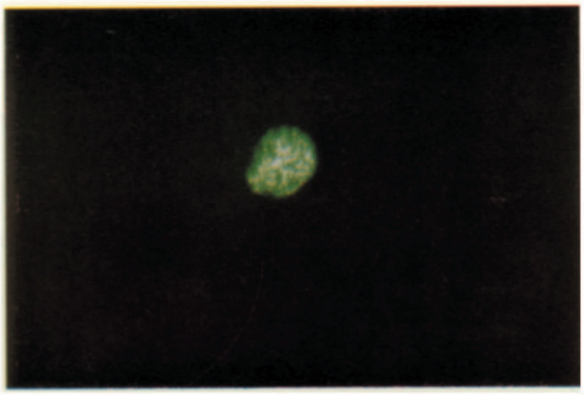

Photo. 4. Initiation of cholesteric focal conic texture. 86.3 °C.

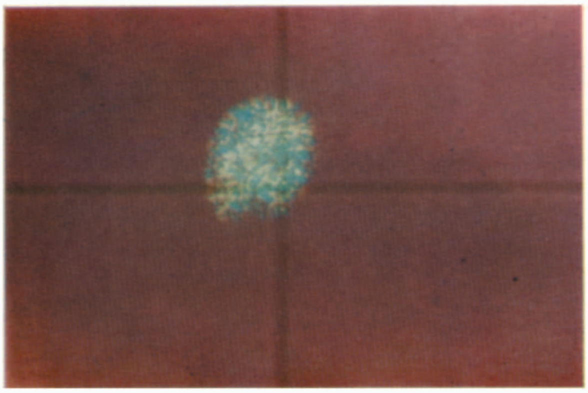

Photo. 5. 86.0 °C.

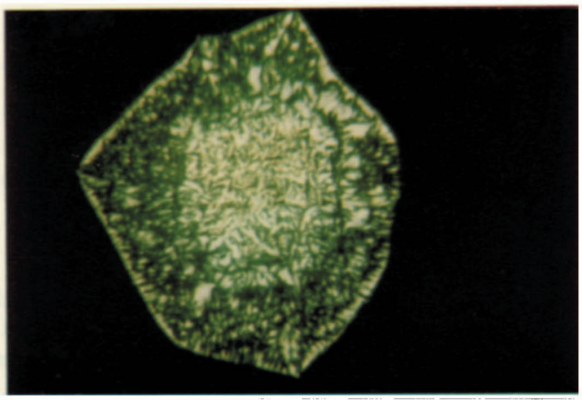

Photo. 6. 83.6 °C.

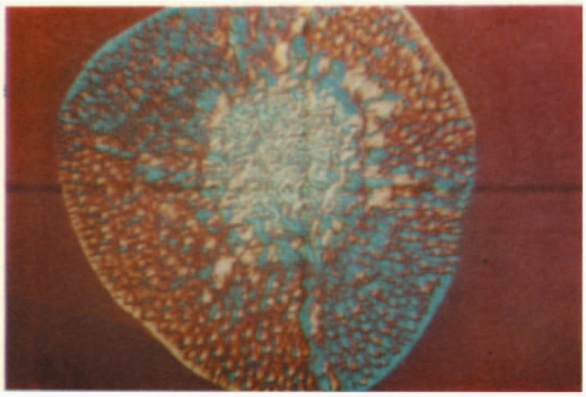

Photo. 7. 83.1 °C.

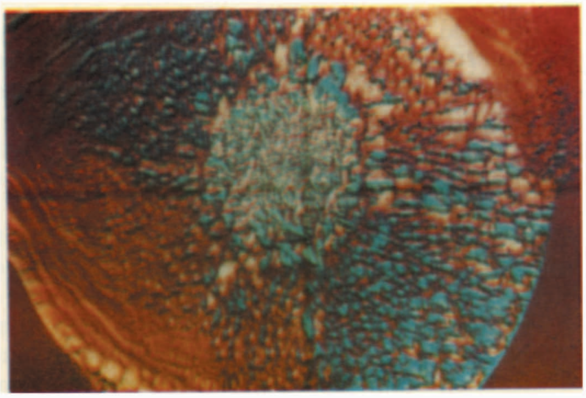

Photo. 8. Beginning of the destruction of the spherulite, 82.7 °C.

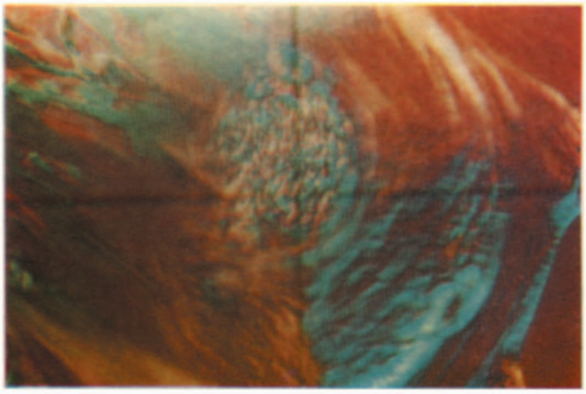

Photo. 9. Beginning of the invasion of the solid wave front, 82.6 °C.

Photos. 4—9. Spherulitic growth of cholesteric focal conic texture in cholesteryl octanoate.

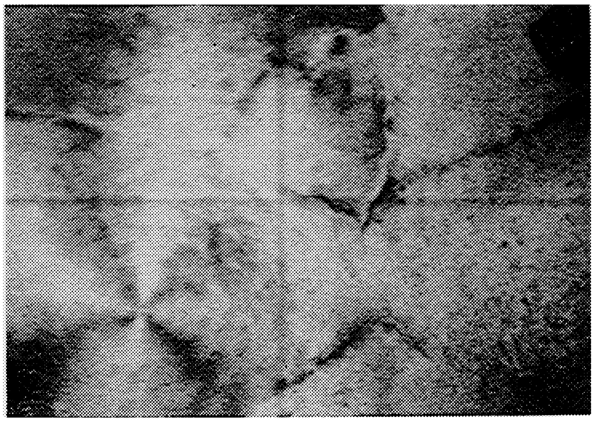

Photo. 10. Generation of the spherulites in the cholesteric phase.

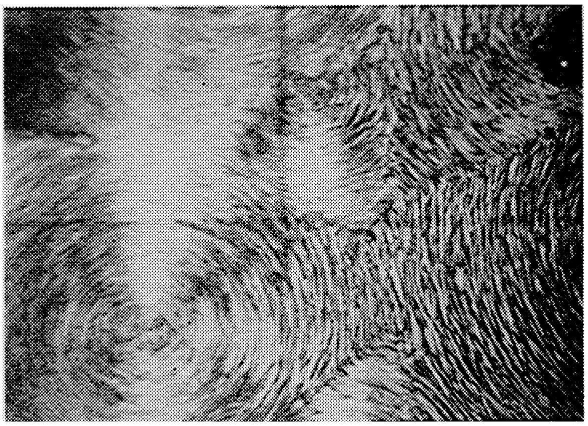

Photo. 11. Vortices around the spherulitic centers, just before the solidification.

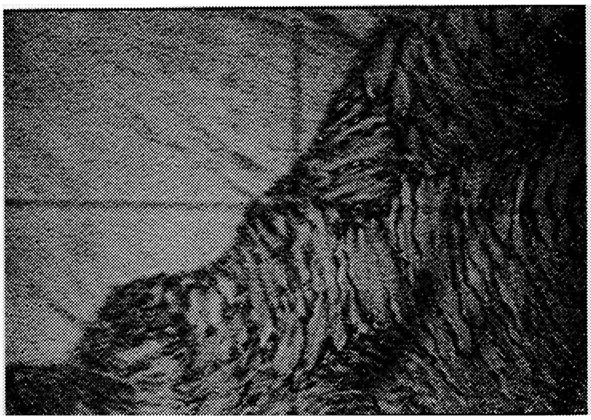

Photo. 12. The solid wave front and the smectic phase as the finish of the vortices.

Photos. 10—12. Vortices caused by the spherulites in cholesteryl octanoate.
All the photographs show observation under crossed nicols. (× 100)
A color sensitive plate was used for Photos. 2, 3, 5, 7, 8, and 9.

before solidification (Photos. 10—12). The vortex is accompanied by iridescent colors, blue, yellow, red, blue and so on. The colors do not end at red but blue appears successively. It seems that the visible spectrum does not reflect the characteristic wavelength at a certain temperature but repeats from short wavelength to long one at the transformation. The color intensity decreases with the lowering of the rotational speed. We cannot observe the repetition of the solar spectrum completely. In many cases, blue does not appear a second time. The vortex turns a state similar to big reels of yarn, which suggest a smectic texture when the speed is lowered. The yarns are suddenly invaded by the solid phase. The domains formed by the growths of the cholesteric spherulites hold their regions when the smectic phase appears. The boundaries are clarified by the formation of the smectic yarns (Photo. 12).

The solid phase of Ch.O. also grows radially but the center of the growth is entirely independent of the center of the mesophase spherulite. Photograph 13 shows a dendritic growth of the solid phase with a free surface. A radially grown solid sample is gradually transformed into regular ordered state similar to Photo. 13.

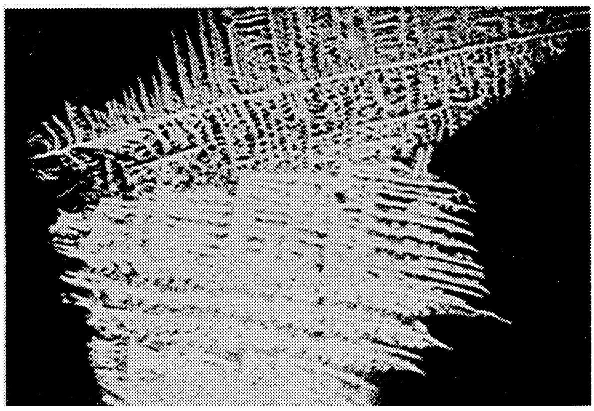

Photo. 13. Dendritic crystal growth of cholesteryl octanoate with the free surface.

The above results can be classified as follows.

Spherulitic Growths at the Phase Transitions. We observed spherulitic growths in both mesophases of Ch.F. and Ch.O. "Focal conic texture" as called by Friedel might be interpreted as the resultant texture of the spherulitic growth. According to Friedel's study, a cholesteric phase is optically negative while the smectic phase is optically positive. The cholesteric spherulites of both Ch.F. and Ch.O. are also optically negative. It is not clear whether the smectic spherulites of Ch.O. are optically positive because they appear only for an instant. Ch.M. makes small but very stable smectic spherulites which show themselves to be optically positive. It seems to be of significance that the optical sense of the spherulites coincides with that of the mesophase.

We also observed the radial growths, that is the spherulitic growths of the solid phases in the large scales. The texture has an almost spherical symmetry even in the large scale (Photo. 3). Many kinds of spherulites seem to have been studied in the field of polymer. Fischer[12] and Kobayashi[13] found that a spherulite in polymer is constructed by the layers which have essentially the same structure as the single crystals deposited from the solutions. Studies of spherulites in polymer field may be useful for elucidating the spherulitic growths of the liquid crystals.

Color Appearance and Phase Transition. Coloration appears twice, in Ch.O., before the appearance of the cholesteric focal conic texture and the smectic phase. The former color covers the range from blue to yellow and the latter from blue to red repeatedly.

Ch.F. which is colorless, still scatters iridescent colors just before solidification, when it is rapidly quenched.

Vortices Caused by the Cholesteric Spherulites. The vortices seem to be of interest. It is not clear whether they are a characteristic of Ch.O. or not. The formation of the smectic reeled yarns was observed with a sample of proper thickness. The aggregation force of the strings may be strong enough for them to reel themselves up in a large quantity, but not in a small amount, due to hindrance by quartz boundaries.

DTA Peaks and Their Textures. Ch.F. shows the mesophase thermally only once but displays the cholesteric texture microscopically. Since the smectic phase of Ch.O. appears microscopically for an instant just before solidification it can not be detected thermally.

Both isotropic–cholesteric transition points of Ch.F. and Ch.O. are a few degrees above their solidification temperatures.

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