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An Attempt at Simultaneous Observation by Polarizing Microscopy and by Differential Thermal Analysis*

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An apparatus for differential thermal analysis using a polarizing microscope has been developed. With this device it is possible to observe the state of a sample under the heating or cooling conditions with a polarizing microscope and to obtain the DTA curve simultaneously. The transformations of several substances—potassium laurate, ammonium nitrate and tripalmitin— were observed. The results are in agreement with those obtained by X-ray diffraction. The relation between the appearance of Phase III of NH_4NO_3 and the water content of the sample was considered on the basis of the microscopic observations. In the case of tripalmitin, two types of transformations were observed under cooling conditions. The relation between the DTA curve of tripalmitin and the heating rate has also been studied. The apparatus may be useful for the study of liquid crystals.

Recently, various kinds of apparatus for thermal analysis have been developed. Particularly, the simultaneous measurement of two parameters, such as X-ray diffraction —differential thermal analysis or thermogravimetry— differential thermal analysis, has been established.

The apparatus has been devised to observe the state of the substance microscopically on heating or cooling and simultaneously to obtain the DTA curve. The device has been constructed by setting the furnace for DTA on the sample stage of a polarizing microscope.

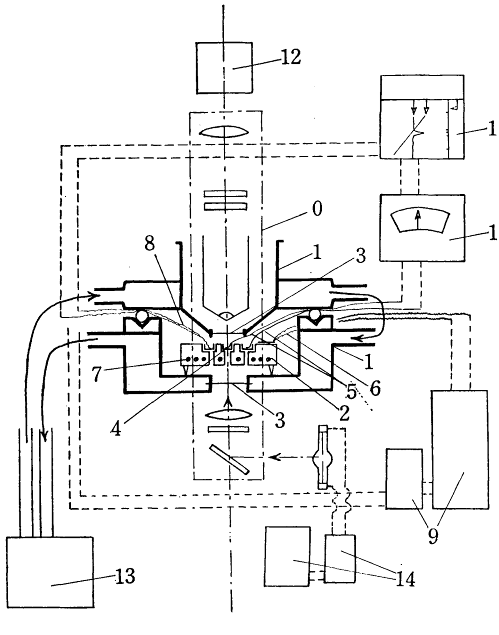

Fig. 1. The structure of DTA furnace and other parts.
0; microscope part 1; furnace body 2; copper block 3; quartz plates 4; quartz sample holders 5; differential thermocouple 6; thermocouple sheet 7; heater 8; thermocouple 9; temperature programmer 10; amplifier 11; recorder 12; photograph system 13; cooling system 14; light source system.

Apparatus

Figure 1 shows a diagram of the apparatus and illustrates the structure of the furnace. Both the lid and the base of the furnace (1) have transparent parts (3) made of quartz at their centers, water can be circurated in them from the cooling system (13). A flat cyrindrical copper block (2) was made with an embedded sheath nichrome wire heater (7) (1 mmϕ, 33 ohm) and three hollows. Each hollow has a slit at the bottom to admit light. Disc-like sample holders (4) made of quartz are inserted into the hollows of the block. The inner size is 3 mm$\phi \times$1 mm. The thickness of the quartz is 0.5 mm. The lid and bottom of the sample holders are polished optically. Both the differential thermocouple (5) and the temperature thermocouple (8) are Al–Cr of the sheath type (0.5 mmϕ). The input of the heater embedded in the block is controlled by a temperature programmer (9) together with a sheet-like thermocouple (6) on the block.

Microscopic observations have been made through crossed nicols and a color-sensitive plate. The multiplicity is 100. The light source (14) is usually a Tungsten lamp (30 W) or Xenon lamp (150 W).

A microswitch was set up at the tip of the release of the camera in order to interlock the camera shutter

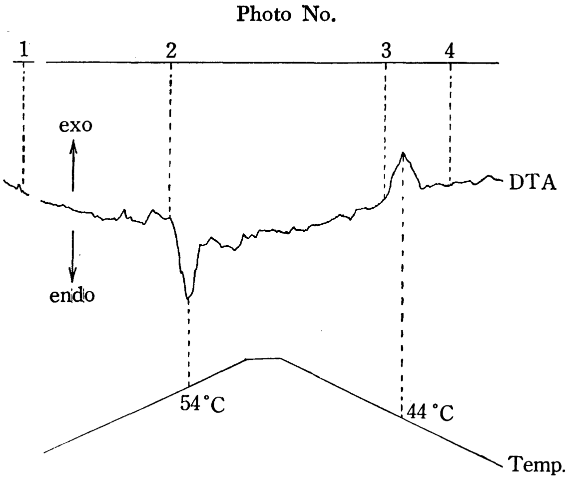

Fig. 2. DTA of potassium laurate at heating and cooling condition. Rate, 1.25 °C/min., Sensitivity, ±50 μV.

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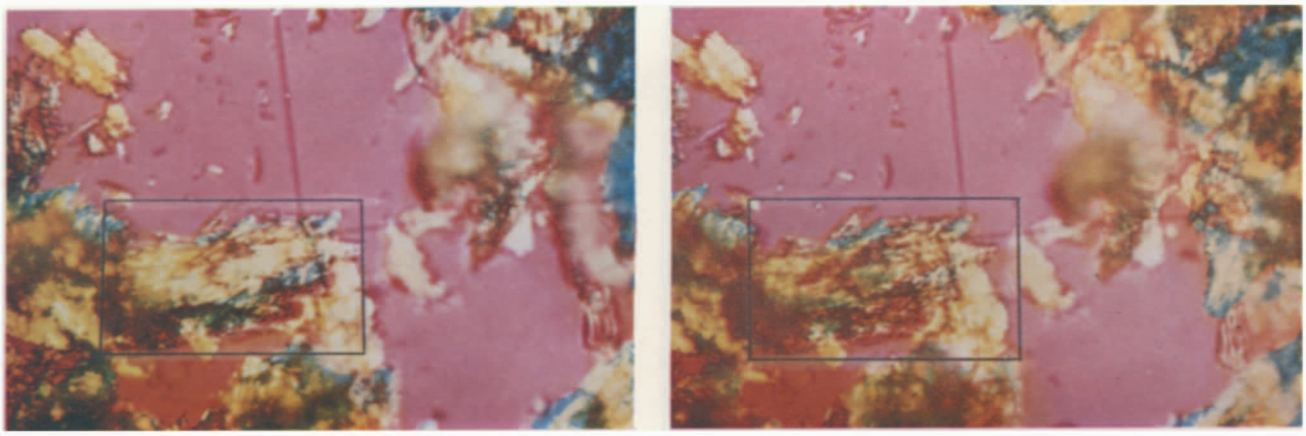
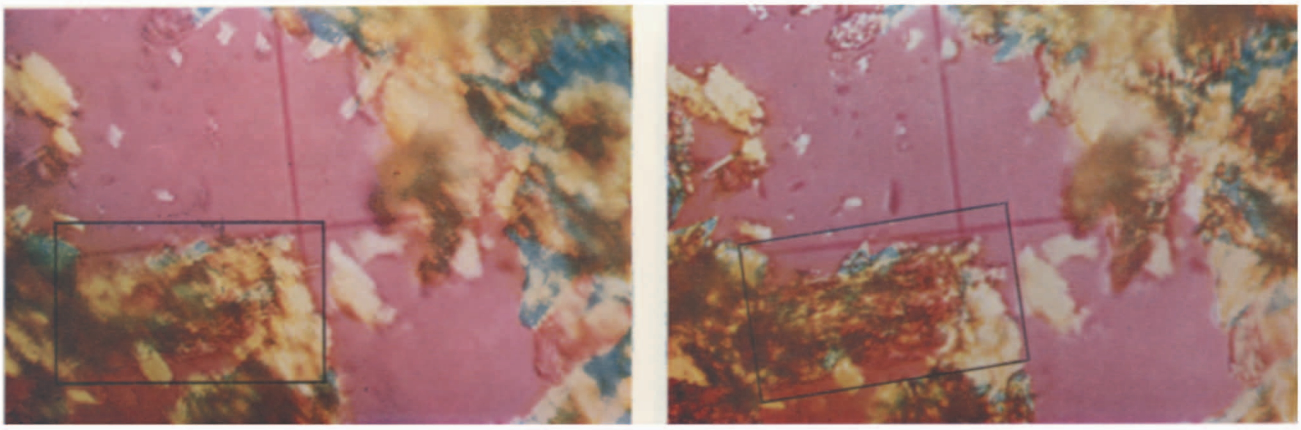
* Presented in part at the 4th Conf. Therm. Anal. Japan (1968) and the 23th Conf. the Chem. Soc. Japan (1970).



3-1. B-type potassium laurate at room temperature.

3-2. Beginning of transformation from B-type to C-type at heating condition.



3-3. Beginning of transformation from C-type to A-type at cooling condition.

3-4. Potassium laurate which transformed into A-type.

Fig. 3. Microscopic photographs of potassium laurate.

and the marker of the recorder for the DTA. It is possible to mark the position of taking a photograph on the recording paper.

Application

Potassium Laurate. Potassium laurate is transformed from the B type to the C type on heating, but it is transformed from the C type to the A type on cooling at 54 °C.[1] Figure 2 shows the DTA curve of the transformation of potassium laurate. Figures 3-1 to -4 are the microscopic photographs corresponding to the points indicated by the photonumbers in Fig. 2.

There is an outstanding difference between Figs. 3-1 and 3-2. That is, the yellow, shining part of a crystallite near the center (surrounded by a line) in Fig. 3-1 clearly turns green and red (Fig. 3-2). Figure 3-3 shows the progress of the transformation upon cooling. The photograph seems to be out of focus because of the movement of the crystallite during the transformation. Figure 3-4 shows the final state, which suggests a structure different from that of the initial state (Fig. 3-1). The movement of the crystals can be explained by the variation in the intersection of the cross wire in

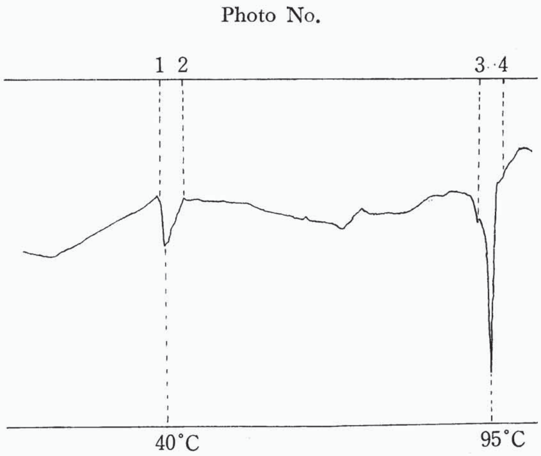


Fig. 4. Transformations of ammonium nitrate from IV to III and III to II. Heating rate, 1.25 °C/min., Sensitivity, ±100 μV.

Fig. 3-4, a variation which does not appear in Fig. 3-1. The circumstances of the movements and the color changes of the crystallites during the transformation may be observed by cinematography.

Ammonium Nitrate. Ammonium nitrate has five stable crystalline modifications. Hendricks, Ponjak,

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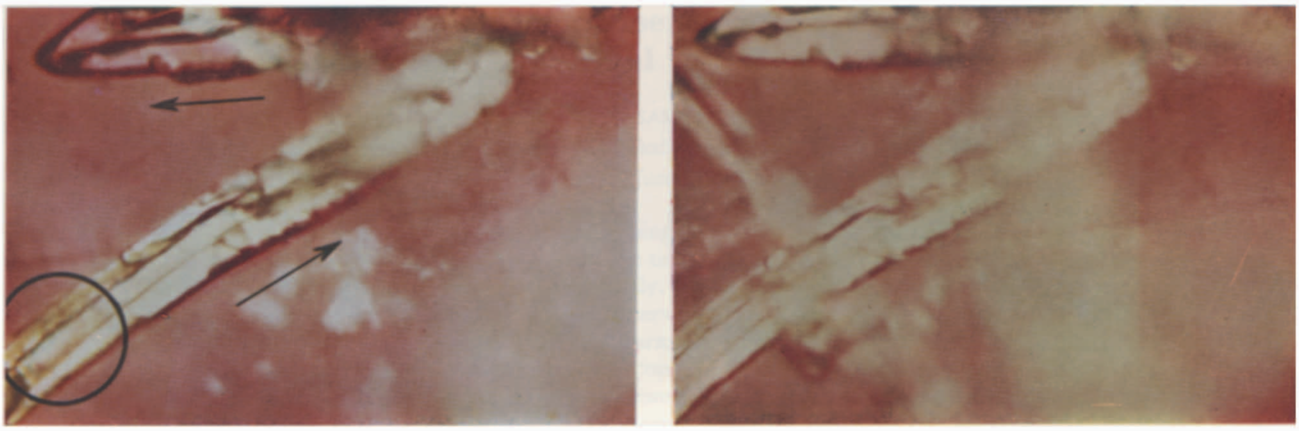
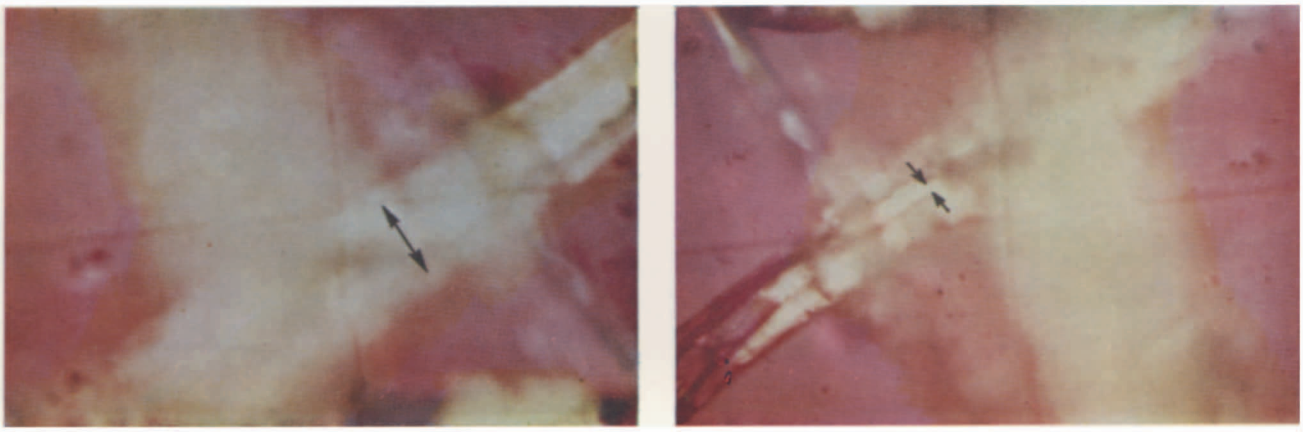
1) T. R. Lomer, *Acta Crystallogr.* **5**, 11 (1952).



5-1. Beginning of transformation from IV to III.
The arrow indicates the direction of shining in the crystal.

5-2. Final state of transformation from IV to III.



5-3. Beginning of transformation from III to II.
The arrow indicates the direction of expansion.

5-4. Final state of transformation from III to II.
The arrow indicates the direction of contraction.

Fig. 5. Microscopic photographs of ammonium nitrate.

and Kracek (1932) gave the transition temperatures as:

$$\mathrm{V}\overset{-18\,^{\circ}\mathrm{C}}{\text{——}}\mathrm{IV}\overset{32.3\,^{\circ}\mathrm{C}}{\text{——}}\mathrm{III}\overset{84.2\,^{\circ}\mathrm{C}}{\text{——}}\mathrm{II}\overset{125.2\,^{\circ}\mathrm{C}}{\text{——}}\mathrm{I}.$$

It has been found by Brown and McLaren²⁾ (1962) that the IV—III and III—II transformations depend on the extent of moisture in the sample. Nagatani and Seiyama³⁾ studied the relation in samples between the temperatures of the transformations and the extent of moisture in the region of less than 1%. Their conclusion was that the transition points rise as the water content in a sample decreases and that the temperature of IV—III rises to 51.5 °C and that of III—II rises to 89 °C. They also found that Phase III disappeared in a water content of less than 0.04 wt%.

In this experiment, the analytical-grade reagent was recrystallized by ethanol in a usual atmosphere. The recrystallized sample was kept in a desiccator, using silica gel. The DTA curve in Fig. 4 indicates 40 and 95 °C as the temperatures of the transformation of IV—III and that of III—II respectively.

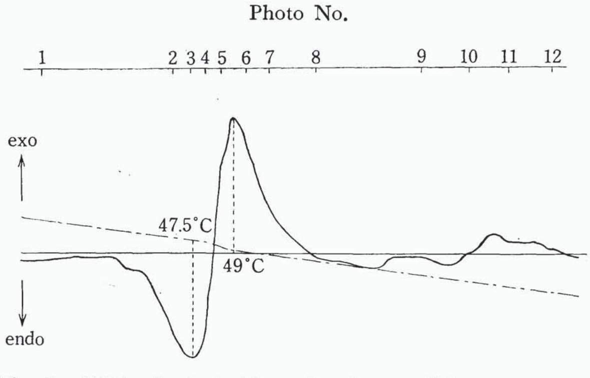


Fig. 6. DTA of tripalmitin at heating condition.
Rate, 2.5 °C/min. Sensitivity, ±50 μV.

The appearance of the transformation of IV—III and that of III—II are extremely different. In the case of IV—III, a yellow, shining part extends in a sword shape from end to end of each crystal. The shining part is similar to the tip of the crystal in Fig. 5-1, indicated by the circle. Figure 5-2 shows the results of the transformation. Upon the transformation of III to II, a marked expansion occurs in the crystal breadthwise (indicated by the arrows in Fig. 5-3), and

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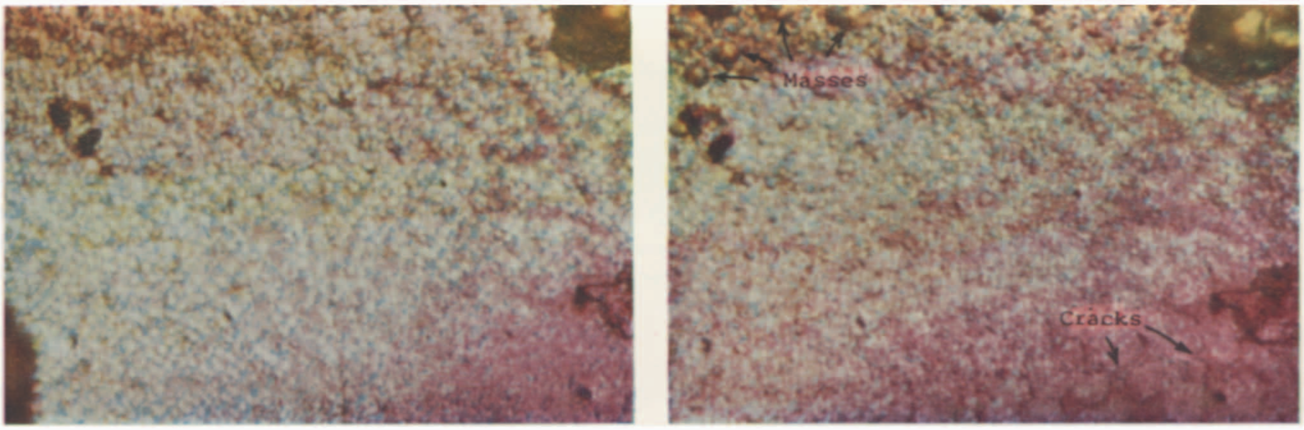
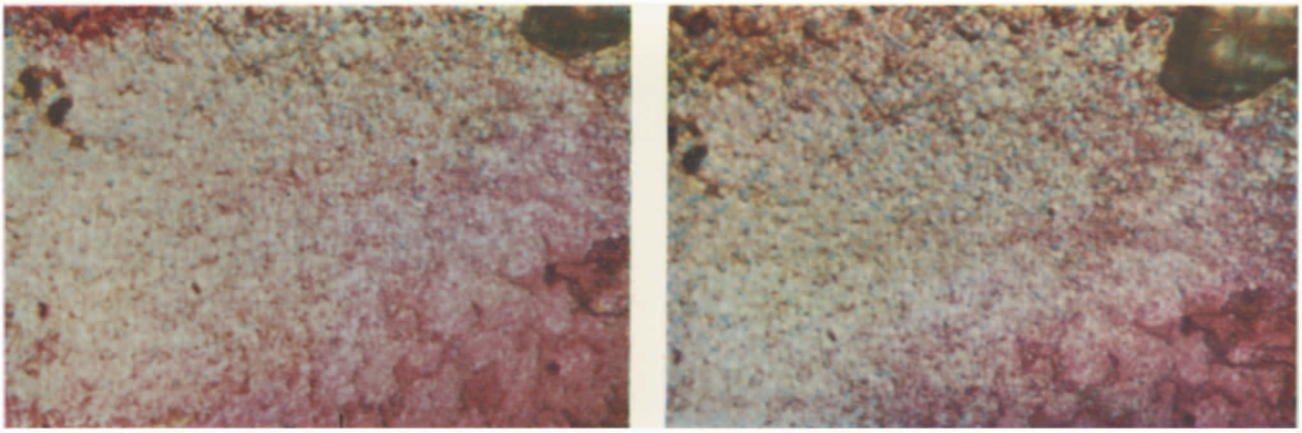
2) R. N. Brown and A. C. McLaren, *Proc. Roy. Soc., Ser. A*, **266**, 329 (1962).

3) M. Nagatani and T. Seiyama, *Kogyo Kagaku Zasshi*, **67**, 2010 (1964).



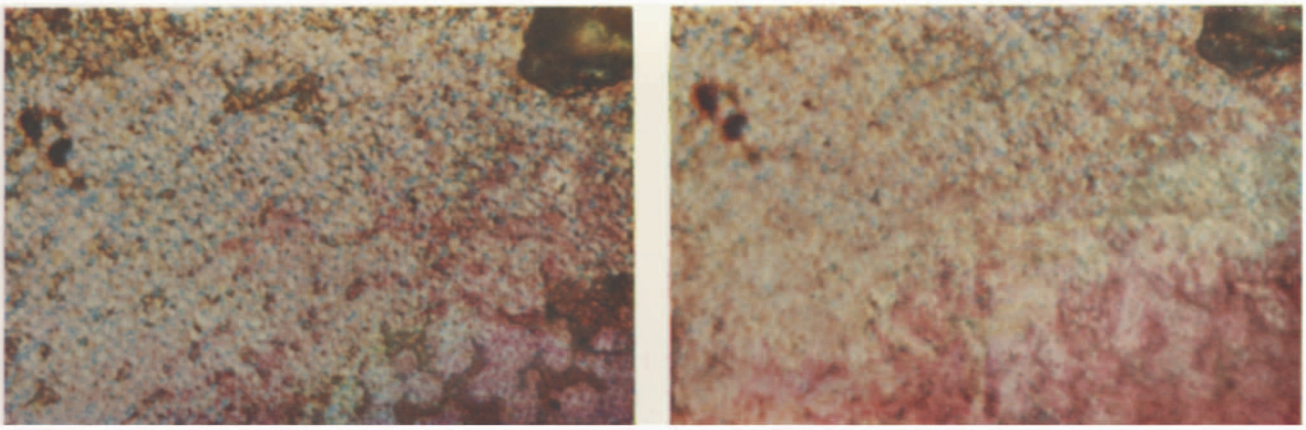
7-1. α-Tripalmitin at room temperature, (photo No. 1 in Fig. 6)

7-2. Beginning of transformation from α to β. (Photo No. 2 in Fig. 6)



7-3. At the peak of endothermic state. (Photo No. 4 in Fig. 6)

7-4. Near the peak of exothermic state. (Photo No. 6 in Fig. 6)



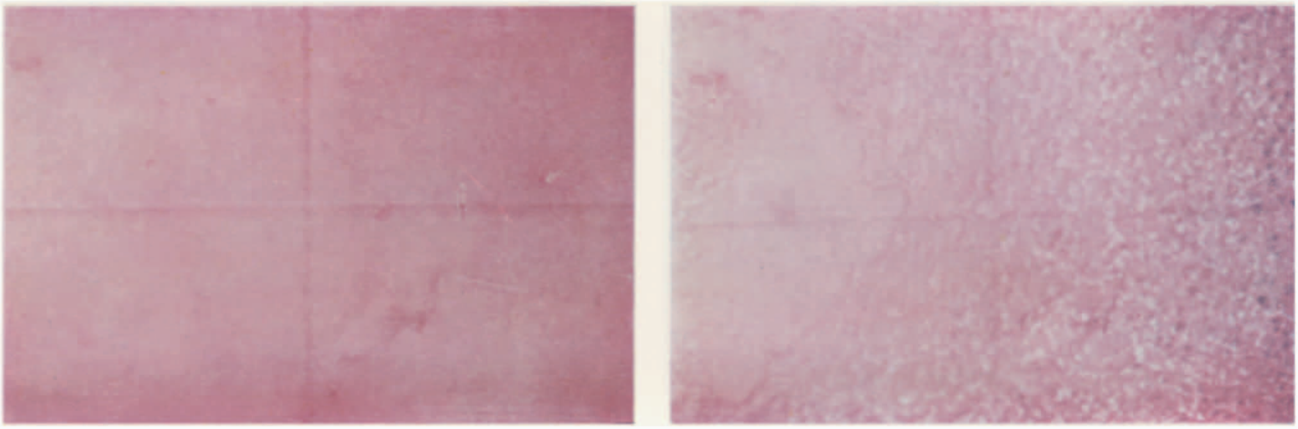
7-5. β-Tripalmitin near 58 °C. (Photo No. 12 in Fig. 6)

7-6. Beginning of melting near 66 °C.

Fig. 7. Microscopic photographs of tripalmitin at heating condition.

there is a strong brightness. Figure 5-3 looks very much out of focus because of the drastic expansion. After the expansion, there is a contraction as the sample returns to its original size and to the state of no brightness. The tip of the crystal, which was shining at room temperature (Fig. 5-1), becomes transparent, which indicates that it is isotropic at the final state of the III—II transformation (Fig. 5-4); "transparent" means that there is the same reddish color as the back of the sample when using a color-sensitive plate and crossed nicols.

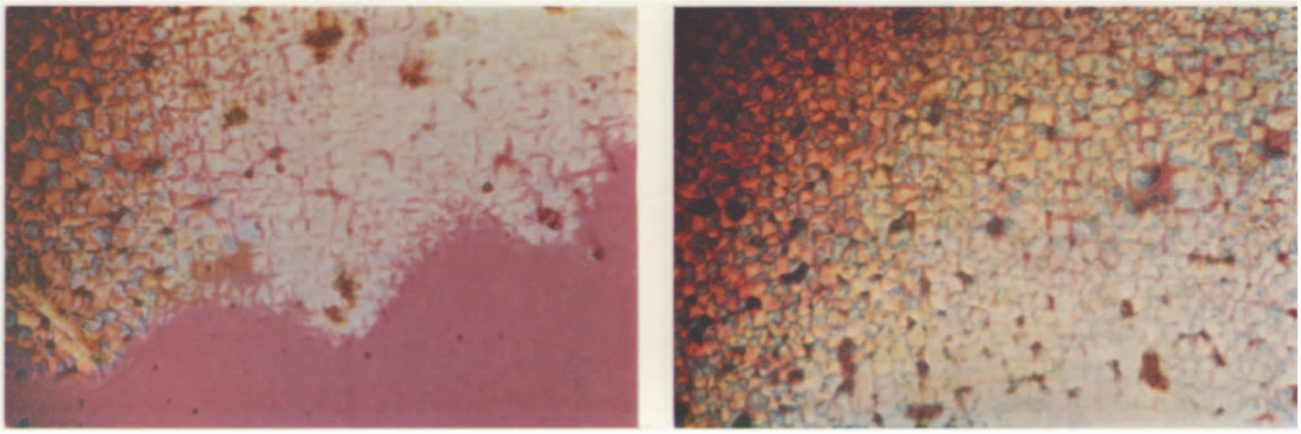
Tripalmitin. Triglycerides such as tripalmitin usually have three polymorphic forms, which are designated α, β′, and β in the increasing order of their melting point. The β′ forms are relatively fleeting compared to the α and β forms. The α forms melt



9-1. Supercooled state of tripalmitin.

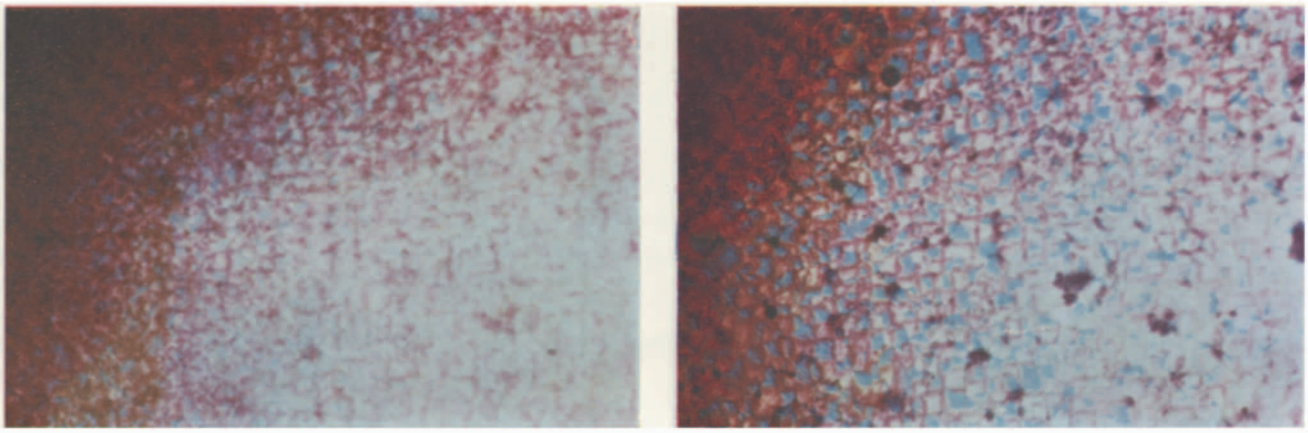
9-2. Beginning of crystallization of tripalmitin.

Fig. 9. Microscopic photographs of tripalmitin at natural cooling. (1 st case)



11-1. Beginning of crystallization of **tripalmitin** near the melting point.

11-2. Crystallized triplamitin at 60 °C.



11-3. Occurrence of transparency near the transition point.

11-4. Restoration to anisotropic state of crystal layer near room temperature.

Fig. 11. Microscopic photographs of tripalmitin at cooling. (2 nd case)

when rapidly heated, but are transformed to the β form when relatively slowly heated about the melting point of the α form. The α form of the triglyceride results from a rapid or moderately rapid cooling of the melt.[5]

Figure 6 shows the DTA curve of the α form of tripalmitin changing to the β form upon heating. The appearance of both heat absorption and evolution is usual in triglycerides when the proper heating rate is used.

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4) M. Gotoh, E. Asada, H. Uchida, and K. Ono, *Yukagaku*, **18**, 299 (1969).

5) G. H. Charbonnet and W. S. Singleton, *J. Amer. Oil Chemists' Soc.*, **24**, 140 (1947).

Figure 7-1 shows the thin layer of the α form made by the rapid cooling of the melt at 0 °C. Figure 7-2 shows the beginning of the transformation. The color of Fig. 7-2 is more similar to the back of the sample than that of Fig. 7-1. This means that the crystal layers are becoming transparent. At the same time, contraction occurs, as can be proved by the cracks in at the lower right in Fig. 7-2 and the several masses produced at the upper left in Fig. 7-2. Both the cracks and the masses are indicated by arrows.

At the peak of the endothermic state (Fig. 7-3), the sample becomes more transparent than at the beginning (Fig. 7-2). This means that the sample has turned more isotropic, like liquid.

Near the exothermic state, the crystalline state of the sample begins to recover. This can be deduced from the fact that Fig. 7-4 is less transparent than Fig. 7-3.

Figure 7-5 shows the sample at 58 °C. This photograph looks almost the same as Fig. 7-1 except for the cracks. Since the heating rate of this experiment is 2.5 °C/min, about 4 min elapse from Figs. 7-4 to 7-5. This means that the sample recovers a complete crystalline state after 4 min.

Figure 7-6 shows the beginning of the melting of the β form (66 °C). The photograph looks out of focus because of the movement of the crystal layer.

Upon cooling, two types of phase changes were observed. In this case, no temperature programming was carried out, as is shown in Fig. 8.

In the first case, the supercooled state was maintained from the melting point of the β form to the transition point, at which point crystallization suddenly began, accompanied by both heat absorption and evolution (Figs. 9-1 and 9-2). In the second case, crystallization took place as soon as the temperature arrived near the melting point of the β form (Figs. 11-1 and -2): afterwards, the crystal layer became transparent near the transition point (Fig. 11-3). In this case, no heat absorption was observed, but heat evolution was (Fig. 10).

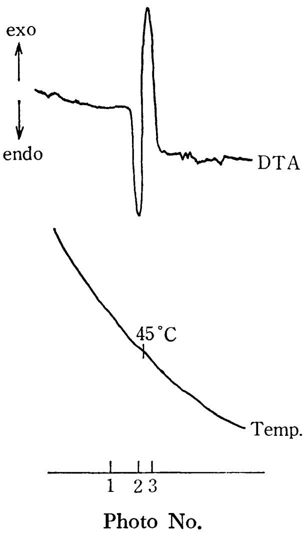

Fig. 8. DTA of tripalmitin at natural cooling. (1st case)

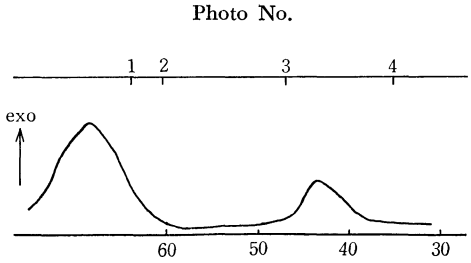

Fig. 10. DTA of tripalmitin at natural cooling. (2nd case)

Discussion

The results of the above experiments suggest that the apparatus is quite useful, even though the photographs are not very good. These results are in agreement with those obtained by X-ray diffraction.

Two transformations of ammonium nitrate made a particularly good contrast with each other. Brown and McLaren suggested that the IV—III transformation requires the presence of some moisture because of the severe structural change involved. They theorized that the transition took place by means of the dissolution and recrystallization of the solid. As proof, they cited the large increase in electrical conductance on the IV—III change. However, a large increase in electrical conductance is also observed upon the III—II change.

The transformations among IV, III, and II seem to take place with some regularities, according to the author's microscopic observations. That is, in the case of IV—III, a brightness appears longitudinally in the needle (a-axis) single crystal, but in the case of III—II, the brightness appears laterally in the crystal with expansion and contraction. If the IV—III modification takes place by means of dissolution and recrystallization, the sample should be more at random.

The III—II transition is far more drastic than that of IV—III as a phenomenon. Considering the similarities among I, II, IV, and V,[2] the presence of moisture seems to disturb the transformation of Phase IV to Phase II, on the other hand, it seems to make Phase IV turn into Phase III. Therefore, once the sample changes into Phase III, it may be forced to undergo the drastic III—II transformation (*cf.* Fig. 12).

In the case of tripalmitin, the heat absorption upon heating suggests the latent heat of melting of the α form. The successive heat evolution indicates the transformation from the α to β form, because the β form is more stable than the α form. The melting of the α form could not be observed microscopically. However, a transparency could be observed. On the other hand, at the beginning of the melting of the β form (Fig. 7-5), no transparency could be observed, even though the crystal layer started to move. Therefore, the transparency at the transformation may not indicate the melting state of the α form, but only an isotropic state during change to another form, β.

The heat absorption disappears with a decrease in the heating rate. In the case of a low heating rate it seems that the α form changes to the β form directly without actually passing through the melting state.

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6) E. S. Lutton, *J. Amer. Chem. Soc.*, **67**, 524 (1945).

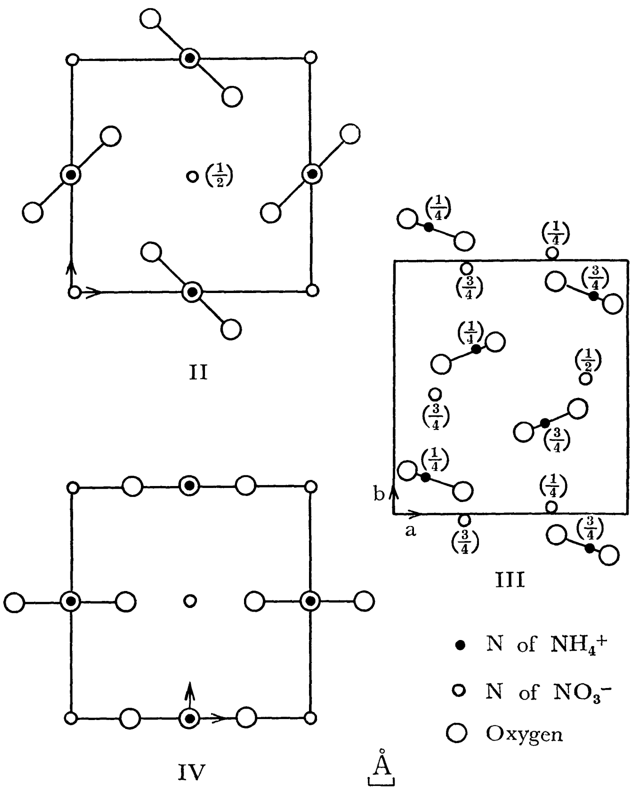

Fig. 12. Projections onto (001) of the structures of forms II, IV and III of ammonium nitrate.[2]

Figure 13 shows the relation between the heating rate and the DTA curve. The peak of the heat absorption becomes higher with increase in the heating rate, but that of the heat evolution becomes lower. These results support the theory that the α form melts directly when rapidly heated.[5] The peak of the heat absorption becomes lower with a lowering of the heating rate, but that of the heat evolution becomes higher. These results support the microscopic observation that the α form changes to the β form directly, with no melting, when slowly heated.

Upon cooling, it is reasonable to consider that the endothermic peak of the first case (Fig. 8) indicates the heat of the transformation of the β form to the α form and that the exothermic peak indicates the solidification of the α form. The second case (Fig. 10) can be interpreted as meaning that the melted sample does not cause a supercooled state; instead, the β form is deposited directly and is then transformed into the α form at the transition temperature. However, the β form does not usually change into the α form, because the β form is more stable than the α form. Considering the inhibition rule, it does not seem reasonable to assume that the first deposited phase corresponds to the β form. Since the solid state appeared over 60 °C, it did not seem to be the β′ form (mp 55.5 °C). It must be studied further in the future.

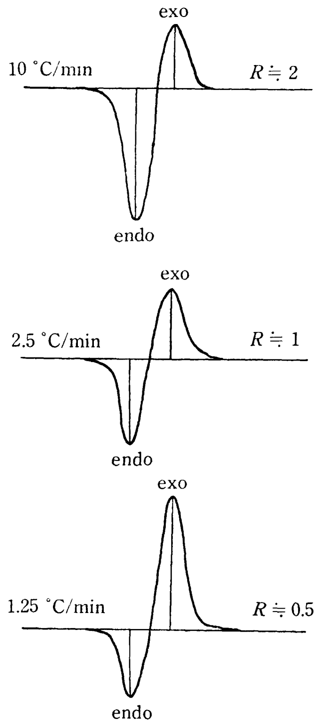

Fig. 13. The influence of heating rate on DTA curve of tripalmitin. R; ratio of endothermic peak to exothermic peak.

Conclusion

The above attempt at simultaneous microscopic and DTA observation has been achieved qualitatively, but not yet quantitatively. However, several useful results have been obtained by the use of this apparatus. They may contribute to the study of liquid crystals.

The present apparatus is limited to use from room temperature up to 350 °C because of the limits of the heat-resistivity of the sheet-like thermocouple and the other materials. Practically, all the experiments were done below 200 °C. Photography was restricted by the illumination of the light source.

The author wishes to thank Mrs. Midori Gotoh of this laboratory for offering the potassium laurate and tripalmitin, materials of her own study. She also kindly presented many references concerning them. The author also wishes to thank Mr. Satohiro Tanaka of this laboratory for his advice and encouragement.