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Pattern Formation by Rhythmic Crystallization of Methyl Mesitylcarbamate

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Rhythmic crystallization behavior of methyl mesitylcarbamate from chloroform solutions under appropriate conditions was found. Effects of temperature, evaporation rate of solvent, and sample weight per area on this behavior are studied in detail, and the qualitative explanation based on the autocatalytic branching process is proposed.

It has been demonstrated that some chemical systems far from equilibrium occasionally show regular changes of the concentrations of intermediate species in space or time during the reactions.[1] The well-known example is the Belousov-Zhabotinskii reaction,[2,3] where malonic acid is oxidized by bromate in the presence of cerium (or iron, manganese) ions. When the reaction is carried out in a well-stirred homogeneous medium, sustained oscillations in concentrations of intermediate chemicals appear spontaneously. On the other hand, when the same reaction is carried out in a thin layer, pattern of developing spiral bands appears.[4]

As a similar example of the periodic spatial structures,[5] the Liesegang rings are well-known since long ago. When crystalline $AgNO_3$ is placed in a thin layer of swollen gelatin gel containing K_2CrO_4, after several days concentric rings of Ag_2CrO_4 crystals are formed around the original $AgNO_3$ crystal. Recently, Feinn *et al.* proposed a model of coupled autocatalytic coagulation and diffusion for explanation of this ring formation.[6,7]

We found occurrence of the rhythmic crystallization on a glass wall of an eggplant type flask, when methyl mesitylcarbamate was crystallized from its chloroform solution in a rotary evaporator equipped with a water-jet pump. A typical example is shown in Fig. 1.

The similar crystallization phenomena of the other substances in the thin films of concentrated solutions or molten substances were sometimes noticed. Miers reported rhythmic crystallization of potassium dichromate from its aqueous solution.[8] The explanation for rhythmic crystallization given by Miers is as follows: the first precipitation ring is formed by inoculation in a labile, supersaturated solution. The precipitates grows so rapidly that the concentration of the solution in an immediate neighborhood decreases within its solubility limit and then the crystallization ceases: in the meantime the next ring of solution becomes labile by vaporization or cooling and induces the next rapid crystallization. Such an explanation seems to meet one aspect of the rhythmic crystallization but more detailed explanation is needed to make clear total mechanism of the rhythmic crystallization. For instances, it should be clarified what switching mechanism is working to produce such periodic patterns.[9] Moreover, it is important to reveal the autocatalytic process involved, if it exists, because an autocatalytic process is always necessary for the appearance of some peculiar behaviors like chemical oscillations or other periodic phenomena according to the recent knowledge on the dissipative structure formation.[10]

In this paper, we wish to report a result of detailed observation of the rhythmic crystallization behavior of methyl mesitylcarbamate following after evaporation of its chloroform solution and to propose a tentative mechanism of the pattern formation involving the autocatalytic process. These investigations serve to systematic understanding of rhythmic crystallization as a typical example of pattern formation in nature.

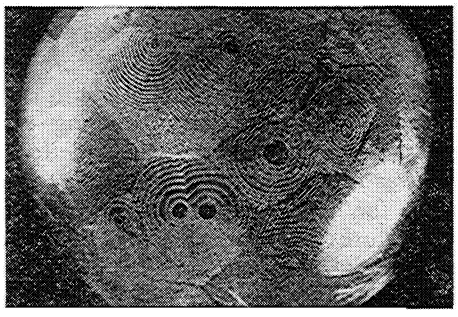

Fig. 1. Typical crystal pattern of methyl mesitylcarbamate from chloroform solution in a 50 cm^3 eggplant type flask.
A rotary evaporator equipped with a water-jet pump was used. Sample weight and bath temperature are about 100 mg and 40 °C, respectively.

Experimental

Materials. Methyl mesitylcarbamate was prepared by the reaction between methanol and mesityl isocyanate, which was produced by thermal rearrangement of mesitonitrile oxide,[11] in xylene at its reflux temperature. Recrystallization of the precipitates from methanol–water solutions yields colorless needle-like crystals. This compound was purified twice by recrystallization. Chloroform was purified with a standard procedure[12] before use.

Procedures. Schematic feature of the apparatus used for observation of crystallization behaviors is shown in Fig. 2. A 0.5 cm^3 portion of a chloroform solution of methyl mesitylcarbamate was put into a watch glass (6 cm in inner diameter and 1 cm in height) settled in a temperature-controlled bath of ethylene glycol. The watch glass was surrounded by a cylindrical polyethylene wall, of which the diameter is fixed to be 7.5 cm and the height is varied from 3 cm to 50 cm in order to control evaporation rate of chloroform. The watch glasses were specially ordered to polish smoothly their inside walls. The temperature of the meas-

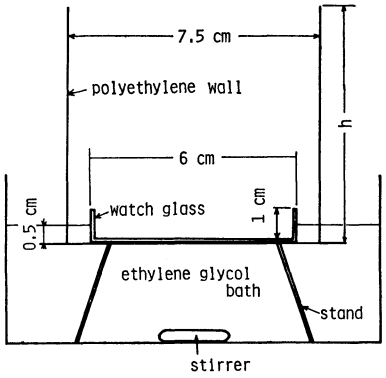

Fig. 2. Schematic feature of measuring apparatus.

uring room was kept constant at about 24±1 °C. Measurements were carried out under the conditions changing the following items: (a) the height of polyethylene wall (the vaporization rate of solvent), (b) the sample weight per area (weight density), and (c) the temperature of bath. All the results were recorded by photographs.

Results

Effect of Wall Height (Vaporization Rate). Each of 0.5 cm^3 chloroform solution containing 60.5 mg (2.14 mg/cm^2) of methyl mesitylcarbamate was put into a watch glass in the temperature-controlled ethylene glycol bath at 39.5 °C, and the rhythmic crystallization behaviors were investigated for various heights of the polyethylene wall. The results are shown in Fig. 3. The evaporation rate of chloroform from the solution decreases with an increase of polyethylene wall height. When the wall height h is 3 cm, the rhythmic crystallization does not appear, and when h is 5 cm, large and small rhythmic patterns appear simultaneously. In the range of h from 6 to 9 cm, we can see clear rhythmic crystallizations and, as h increases higher than 10 cm, the rhythmic patterns become obscure, although the local faint patterns can be observed even at h=50 cm.

Effect of Sample Weight Density. The bath temperature and the wall height are fixed to be 39.5 °C and 7 cm, respectively. Various amounts of methyl mesitylcarbamate were dissolved into 0.5 cm^3 of chloroform and these solutions were put into respective watch glasses. The results are shown in Fig. 4. The rhythmic crystallizations do not appear, when the sample weight density is 0.71 mg/cm^2 or less, but when the weight density is larger than 0.71 mg/cm^2, the rhythmic crystallizations appear in rather wide range of weight density; the clearest pattern is observed at the weight density of 2.14 mg/cm^2.

Effect of Bath Temperature. A 0.5 cm^3 chloroform solution containing 60.5 mg (2.14 mg/cm^2) of methyl mesitylcarbamate was put into a watch glass surrounded by a polyethylene wall of 7 cm in height and the rhythmic crystallization behaviors were investigated at various bath temperatures. The results are shown in Fig. 5. When the bath temperatures are 29.5 and 39.5 °C, the rhythmic crystallizations are clearly observed, but when the bath temperature is 21.0 °C, they disappear completely. When the temperature is 49.5 °C or higher, the rhythmic crystallizations become obscure and only vague periodicity is observed.

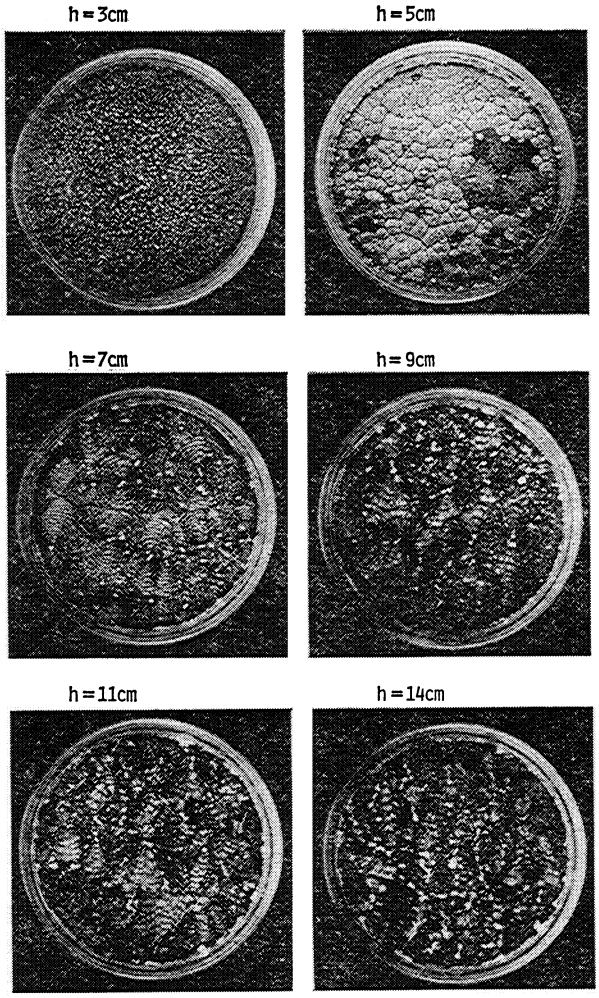

Fig. 3. Effect of polyethylene wall height on the rhythmic crystallization.
Sample weight density and bath temperature are 2.14 mg/cm^2 and 39.5 °C, respectively.

Discussion

The studies of effects of the bath temperature, the sample weight density, and the wall height on the rhythmic pattern formation imply that coupling of the solvent evaporation process with the crystallization process plays an essential role for the phenomena. In order to confirm the steady coupling effect, the following experiment was done: while methyl mesitylcarbamate was rhythmically crystallizing, the atmosphere inside the wall was exchanged by fresh air; by this procedure the evaporation of chloroform increased suddenly. The experimental result is shown in Fig. 6, which shows sudden stop of pattern formation. That is, the increase of evaporation rate of solvent extinguishes the rhythmic crystallization. This result supports our idea.

According to the Mier's explanation,[8] the solvent evaporation leads to formation of a supersaturated solution. As it is labile state, once nucleation occurs

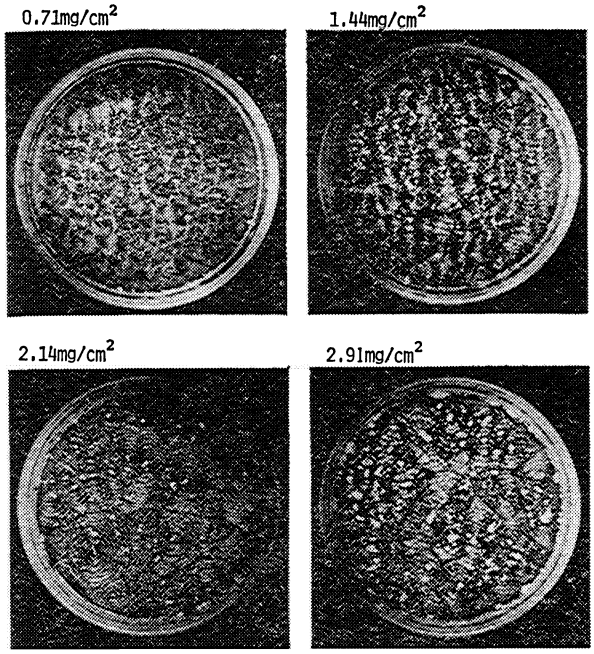

Fig. 4. Effect of sample weight density on the rhythmic crystallization.
Wall height and bath temperature are 7 cm and 39.5 °C, respectively.

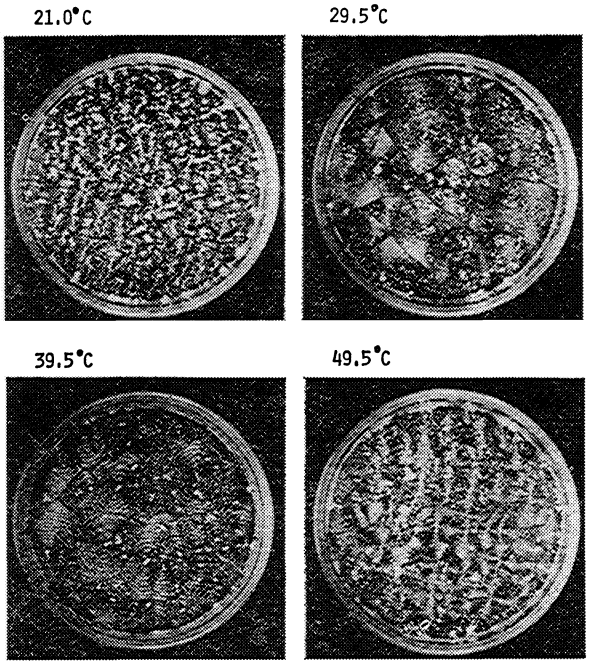

Fig. 5. Effect of temperature on the rhythmic crystallization.
Sample weight density and wall height are 2.14 mg/cm² and 7 cm, respectively.

somewhere, it is followed by a rapid crystal growth. The crystallization process reduces the solute concentration in front of crystals, and slows down until the evaporation process of solvent produces again a new supersaturated state. Repetition of these processes produces the rhythmic crystallization.

Detailed observation of periodic precipitate zones of methyl mesitylcarbamate clarified that two neighboring zones are clearly distinguishable and they are formed alternately. In order to explain completely the precipitate pattern formation, the mechanism of alternating from one zone to another zone should be made clear.

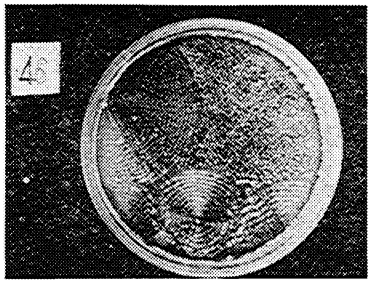

Fig. 6. Effect of sudden change in evaporation rate of chloroform on the rhythmic crystallization.
Sample weight density and wall height are 2.14 mg/cm² and 7 cm, respectively. When the atmosphere inside the wall was exchanged by fresh air, the rhythmic crystallization ceases.

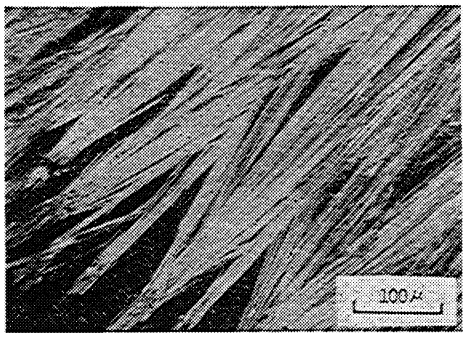

Fig. 7. Feature of crystals near the roots of crystal zone.
Branching and growing of needle-like crystals are clearly observed.

In Fig. 7, the detailed microscopic feature of crystals formed during the rhythmic crystallization is shown. The crossed polaroids were used for the observation with a microscope. The black parts indicate no existence of crystals. The crystals begin to grow from several roots, being followed by repetition of branching to form bundles of needle-like crystals. The branching process is an autocatalytic process, because branching continues to produce new sites for branching. On this account, the number of branches increases nonlinearly as crystallization proceeds. Such an autocatalytic irreversible process may produce a periodic change of crystallization rate, which is recognized as a periodic pattern.

We presume that the number of branches N in every zone is given by

$$\frac{dN}{dx} = f(C, T)N, \tag{1}$$

where $f(C, T)$ represents the number of branches produced per unit length from one branch at the concentration C in the front of crystals and the temperature T, and x is the distance measured from the root of each crystal zone.

The advancing rate of the front at crystal zone

is about a few millimeters per second and it is large compared to the diffusion rate of solute in a liquid phase. Therefore, the front boundary contacts always with a fresh liquid; the concentration of solution at the front of crystals is not practically affected by the crystallization process. This supposition is different from the Mier's view. According to this view, the function $f(C, T)$ is independent of x, and the solution of Eq. 1 is given by

$$N = N_0 e^{fx} \tag{2}$$

at a given temperature, where N_0 is the initial number at $x=0$.

As mentioned already, the crystallization rate is large compared to the diffusion rate and, therefore, we could presume that the total amount w of the substance in a unit volume of crystal zone is constant and expressed by

$$w = \rho N \pi r^2, \tag{3}$$

where N is the number of branches per unit area, r is the radius of each branch, and ρ is the density of crystal. As w is independent of x, the radius r decreases with an increase in N. When N becomes indefinitely large and r becomes indefinitely small, the crystallization rate increases drastically and the solute concentration in the front of the crystal zone reduces remarkably and the diffusion is too slow to compensate this reduction. At this point, the crystallization process ceases. After then, the solution in the vicinity of crystal zone is concentrated by vaporization and the crystallization starts again at some points.

We investigated some specific behaviors of the rhythmic crystallization of methyl mesitylcarbamate and proposed a tentative explanation for it. The explanation is somewhat awkward and a detailed and mathematically elegant treatment is needed. For this purpose, the treatment of Haase *et al.*[9] for the oscillatory zoning in plagioclase feldspar is very suggestive.

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