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Kinetics of Crystallization of Anthracene from the Vapor

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Abstract—Anthracene was purified by zone melting, chromatography and sublimation. It was again zone melted in a closed system within which it was transferred to a crystal-growth tube.

A sublimation apparatus was constructed allowing direct, automatic control of temperature-difference ΔT between sublimand and crystallization site as well as photography of the growing crystal.

In evacuated tubes and in the presence of propane at 1 torr, it was not possible to control nucleation at 120°C. In the presence of N_2 at 1 torr, single nuclei were formed at $\Delta T = 9.5° \pm 0.5°$ and these were grown to 1 cm diameter crystals of good optical quality. The basal plane of the crystals was the *ab* plane.

Cinematographic observation of growth and evaporation at undersaturations and supersaturations up to 6% showed that growth rate R varies linearly with supersaturation σ. According to the Frank theory, R should be proportional to σ^2 for small σ when growth takes place by a single dislocation. Evidently this very unlikely condition is not fulfilled.

Introduction

Since the classic work of Volmer and Schultze,[1] relatively few papers have appeared dealing with the controlled growth of organic crystals from the vapor. Honigmann has described techniques for observing crystals during growth at known supersaturation,[2,3] but the nucleation process was uncertain and required prolonged manipulation. Bradley and Drury compared the kinetics of crystallization of iodine and carbon tetrabromide[4] with the requirements of the Frank theory, with an apparatus limited to low-temperature operation.

We have been interested in the preparation of relatively large crystals of anthracene and other aromatic hydrocarbons for studies of their electro-optical properties.[5–7] In this connection we have constructed an instrument in which a controlled heat leak is used first to establish a nucleus, and then to allow it to grow at constant, known supersaturation. While nucleation and growth are taking place, a motion picture camera records the process for later analysis. Using these techniques, we have studied the rate of growth of anthracene as a function of supersaturation, and have begun to study effects of purity and growth atmosphere on the nucleation and growth.

Experimental

Purification of Anthracene

Anthracene (Matheson, Coleman and Bell, AX1590) was subjected to fifty zone-melting passes in the usual way.[8] The zone length was about 1/20 of the ingot length. A central fraction amounting to half the ingot was sublimed through a layer of felt (Armalon, made of "Teflon"† tetrafluoroethylene resin) for removal of inorganic contaminants.[8] Because carbazole is not very effectively removed by zone melting, the sublimate was chromatographed on alumina in a recycling apparatus, with hot hexane as the eluant.[8] The product recovered from the hexane was zone melted as before and a central fraction was sublimed through Armalon. All operations were carried out in darkness or in red light.

Preparation of Crystal Tubes

In order to eliminate any impurities resulting from oxidation or fortuitous contamination, the anthracene used for growth of crystals was again zone melted in a closed system within which it could be transferred to the crystal tube without exposure to air. A combination zone-melting/crystal-growing tube (Fig. 1) was cleaned[9] and baked in vacuum at 350° in a box made of thin asbestos sheeting covered with aluminum foil.[10] Purified anthracene (1 g) was placed in section A of the tube. The assembly was

† Du Pont trademark.

evacuated, then filled to 4×10^2 torr with purified nitrogen.[8] The solid was melted and allowed to flow into section B and solidify. The system was evacuated, and the thin film of solid adhering to the constriction between A and B was removed by heating it cautiously at about 150°. Nitrogen was readmitted, and the lower part of the assembly was removed by flame fusion of the constriction. The contents of B were subjected to ten zone-melting passes. The upper quarter of the ingot was melted and decanted into the crystal tube C. The breakseal sidearm D of the combination tube was connected to a vacuum manifold and heated briefly. Nitrogen was admitted to the sidearm to equalize the pressures on the

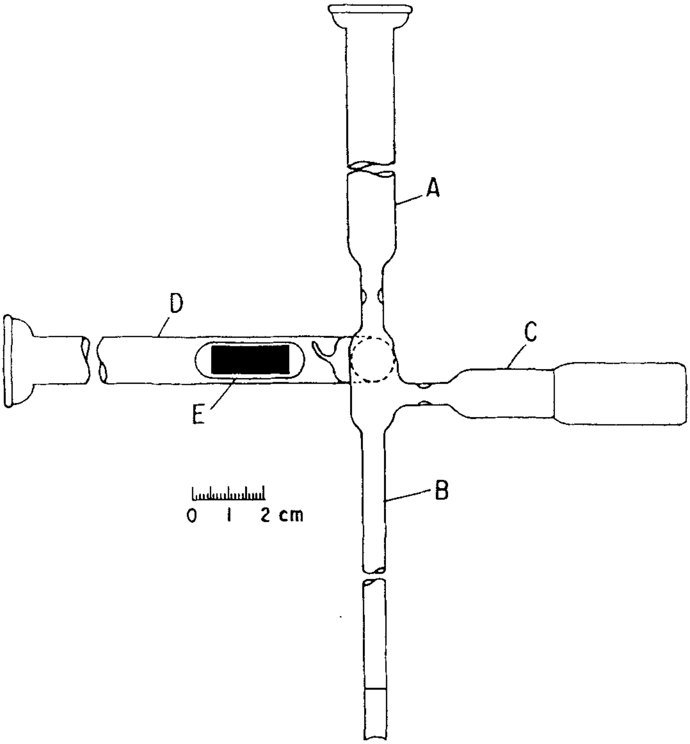

Figure 1. Combination zone-melting and crystal-growing tube.

breakseal. The glass-covered magnet E was raised by an outer magnet and then allowed to fall. The system was evacuated, and the contents of the crystal tube were sublimed at about 125° to remove entrapped nitrogen; the sublimate condensed in the tube, below the constriction. The constriction was cleared, nitrogen was readmitted to a pressure of 1.0 torr, and the tube was removed by flame fusion of the constriction.

SUBLIMATION BLOCK

Figure 2 shows a diagram of a block for sublimation at controlled supersaturation, similar in principle to the apparatus of Honigmann.[2,3] It was machined from a rod of aluminum, 15.25 cm in diameter by 23.5 cm long. The central well receives the crystal tube and is 25.4 mm in diameter; adapter sleeves of stainless steel are inserted in the well to allow use of smaller crystal tubes. The viewing window A consists of a slab of glass (Vycor, 25 × 50

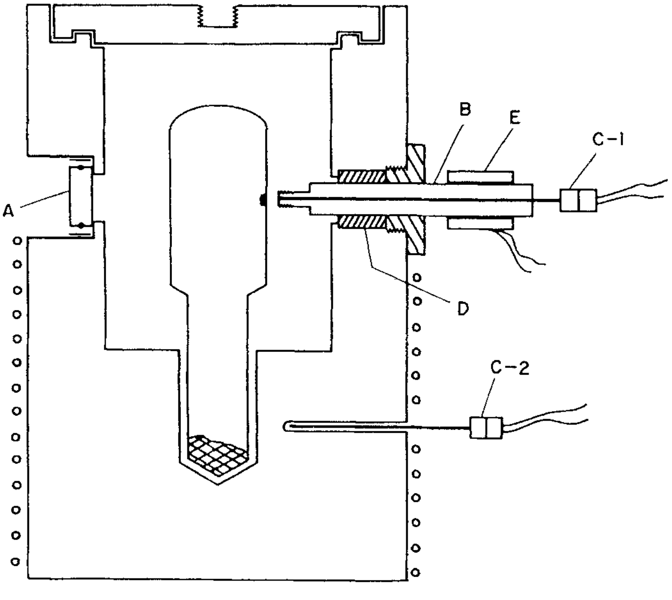

Figure 2. Sublimation block.

mm × 12.7 mm thick). A groove about 3 mm wide and 2 mm deep was ground in the edge of the window to contain a single-loop, 60 W heater to compensate for heat loss. The window-heater was insulated from the block by a thin wrapping of asbestos tape, completely surrounding the window edge. Heat-leak B consists of a stainless steel rod, 2.54 cm in diam. and 15.25 cm long, with a central, axial hole for introduction of thermocouple C-1. B is thermally insulated from the block by several rings of Transite, D; these are held in place by a compression nut. A sleeve heater E (75 W, 2.54 cm long) is clamped tightly on B. An 850 W heater is wrapped on the block, whose temperature is measured by thermocouple C-2. The block is insulated by a jacket of Marinite, 5 cm thick (not shown). The crystal tube is illuminated by a projection lamp (Type DFA, 150 W) via a length of glass rod (Pyrex, 3 mm diam.) passing through the block at the elevation of the leak thermocouple and perpendicular to it.

PHOTOGRAPHIC PROCEDURE

A Cine-Kodak Special II camera with a 102 mm, f2.7 lens mounted on a 38 mm extension tube was positioned about 25 cm from the viewing window of the sublimation block. The camera was supported on a platform bearing a solenoid for tripping its shutter; the solenoid was operated by an automatic controller (Sample Engineering Co., Danville, Ill., Model MC-6). Tri-X reversal film was used.

Figure 3 shows the optical arrangement. A reduced image of stopwatch A is projected by lens B onto front-surface mirror C placed near viewing window D. The intensity of the light from lamp E is adjusted so that the illumination of the crystal is comparable with the room-light illumination of the stopwatch. Thus, each frame bears its own time record. The films were examined in a film editor, and the size of each crystal image was measured.

Temperature Control

The temperature of the block was controlled by a thermocouple-actuated regulator to a constancy of about ± 0.1° C.

The sleeve heater on the heat leak was powered by the arrangement shown in Fig. 4, which afforded constancy of ± 0.02° C in the temperature-difference between block and leak. The differential thermocouple assembly was calibrated by immersion in liquid baths whose temperatures were measured with calibrated thermometers and with a differential thermometer graduated in 0.01° C intervals.

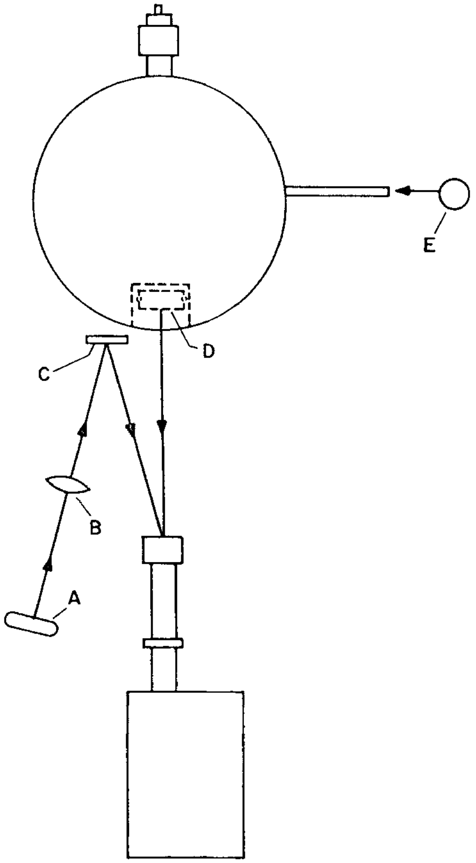

Figure 3. Schematic view of photographic set-up.

Nucleation and Growth of Crystals

A sealed tube was inserted in the growth block, which was then heated to 120°. Power was applied to the heat leak by the controller, which was at first set at $\Delta T = T_B - T_L = 0$, then at progressively larger ΔT's. It was found that a nucleus formed very reproducibly in a few minutes at $\Delta T = 9.5° \pm 0.2°$. As soon as a nucleus appeared, the controller was reset to the value desired during growth. In a few seconds the ΔT was out of the nucleation range, and in 2 or 3 minutes ΔT attained the desired value, although small fluctuations in ΔT persisted for a few minutes longer. Growth and evaporation were carried out at various ΔT's, corresponding to supersaturations between $+5.9$ and -6.7%. The supersaturations were calculated from the vapor pressure equation.[11]

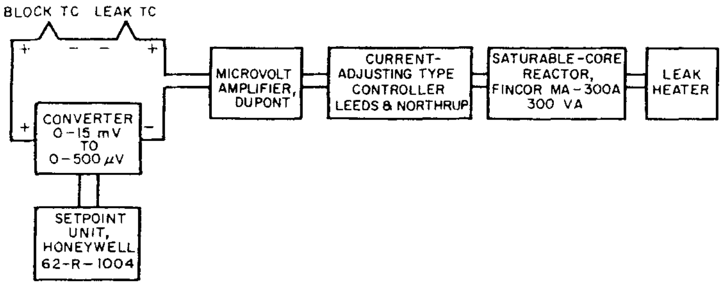

Figure 4. Block-diagram of ΔT controller.

$$\log_{10} P\,(\text{torr}) = -\frac{5102.0}{T} + 12.002$$

The camera was in operation at one frame every 2 seconds throughout the prenucleation increase in ΔT, and then at somewhat lower frequency after formation of the nucleus. The basal plane of the crystal was always the *ab* plane.

In one growth tube, nitrogen was replaced by propane at 1 torr as the "inert" diluent. It was found to be impossible to control the nucleation. All attempts to cool the condensing surface only enough to form one nucleus resulted in a scattering of many nuclei on the condensing surface.

Results and Discussion

Plots of crystal size *vs* time showed that the linear growth rate became constant within a few minutes after nucleation, i.e. as soon as the desired ΔT was established.

A plot of the growth rate R against supersaturation σ is shown in Fig. 5. Within experimental error, it is a straight line for all supersaturations and undersaturations (corresponding to evaporation).

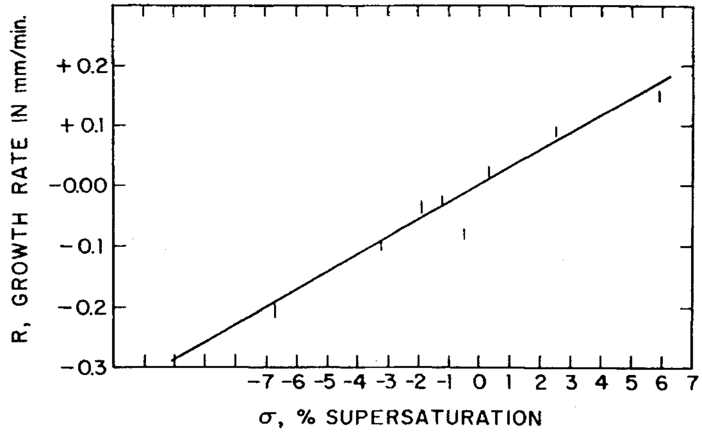

Figure 5. Growth rate *vs* supersaturation.

According to the Frank Theory,[12] the rate of growth on a single dislocation should vary as σ at large supersaturations and as σ^2 at small supersaturations. While the appearance of *many* dislocations has relatively little effect on growth rate at high σ, it changes the situation markedly at low σ.[4] The wide-range linearity of the R–σ plot thus seems to be, in a sense, fortuitous.

Continuation of growth at constant ΔT resulted in conversion of the entire content of the tube to a single crystal, which was usually of good optical quality. The striations often observed in melt-grown anthracene crystals were not present.

The undesirable effect of propane on the nucleation of anthracene probably indicates that propane is more strongly adsorbed on the new nuclei than on the glass tube. In this way, existing nuclei would be rendered unavailable for growth and further nucleation would be expected.

It should be noted that after the crystals had grown to thicknesses greater than about 1 mm, the growth rate fell off, apparently as a result of increased thermal lag between the growing face and the heat leak.

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