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Lateral habits of *n*-alkane single crystals

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The lateral crystal habits of *n*-alkanes ($n\text{-}C_nH_{2n+2}$) have been observed just below the melting points by optical microscopy for $n = 18$, 19, 20, 22, 24, 34, 44, 50 and 65. The shape of the crystals depends on the crystal phase: circular in the rotator phase, lenticular in phase C, and diamond in the low-temperature phase. The rounding of the lateral shape can be explained in terms of thermal roughening of the lateral faces in the disordered phases at high temperature.

1. Introduction

When *n*-alkane crystallizes from the solution under the usual conditions, the single crystals are well faceted and the lateral shape is diamond (Fig. 1a) [1, 2]. The single crystals of polyethylene, a homologue of *n*-alkane, also show well faceted habits (Fig. 1b) under the usual conditions [3]. On the other hand, the lateral shape is curved (Fig. 1c) when polyethylene crystallizes from the solution at relatively high temperatures or from the melt [4–8]. The rounding of the lateral shape was proposed by Sadler [9] to be produced by the mechanism of thermal roughening which is a roughening of the crystal face due to the decrease in the free energy of steps at high temperatures [10]. Sadler estimated the roughening temperature to be about 100 °C assuming that the unit of a straight step is not a stem crossing the lateral face, but is a segment of five or six CH_2 units (Fig. 2). If his estimation is correct, the lateral faces of *n*-alkane single crystals will be thermally roughened in the high-temperature range because each unit of a straight step must be one *n*-alkane molecule or even smaller, and the size will be similar to that assumed by Sadler.

In previous studies, *n*-alkane crystals with well faceted habits were obtained from solutions at relatively low temperatures. Although experimental studies on the lateral habits of melt-crystallized *n*-alkane have not been reported, the habits are expected to be rounded near the melting point. Further, in melt crystallization, we can also expect different morphologies in the high-temperature phases, e.g. rotator phase, near the melting point. In the present work, the lateral habits of *n*-alkane single crystals grown from the melt or from solution at higher temperatures were observed.

2. Experimental procedure

The following *n*-alkanes (C_nH_{2n+2}: C*n*) were used: $n = 18$, 19, 20, 22, 24, 34, 44, 50 (industrially produced) and 65 (synthesized and purified by Takamizawa *et al.* [11]). In order to adjust the thickness of the sample to be suitable for optical microscopy, pure *n*-alkane was melted on a hot glass slide with a spacer several tens of micrometres thick and pressed by a cover glass. The sample of a mixture of *n*-alkane was prepared from the solution in octane at 130 °C; the solution was poured on to a hot glass slide in order to evaporate the octane. These samples were melted on a Mettler hot stage and crystallized. After crystals in the field of the microscope grew to several tens of micrometres wide, the temperature, T_c, was held as close as possible to the melting point, T_m ($|T_m - T_c| \ll 0.1$ °C) using a hand set, manual temperature setting apparatus, of the Mettler hot stage, so that the crystals did not grow further nor melt. Thus the crystals were under very near equilibirum conditions.

3. Results

Fig. 3 shows the plots of the results of the variation of phase transition temperatures with the number of carbon atoms of *n*-alkanes [11, 12]. The following results were obtained (Figs 4 and 5).

1. Crystals of C19, 22, 24 and 34 showed circular lateral habits; the anisotropy of the crystal structure was lost. They were in the rotator phase (phase D) just below the melting points.
2. The lateral habits of C44, 50 and 65 crystals were also curved; the shape was lenticular. These crystals were in a high-temperature phase, phase C, just below the melting points.
3. The habits of C18 and 20 crystals were well faceted lozenge-shaped. Because both the two *n*-alkanes do not have a rotator phase, they were in the ordered low-temperature phase even just below the melting points.
4. In contrast to C34 crystals in the melt (Result 1), the crystals of C34 in the mixture of C19 and 34 showed well faceted habits in the low-temperature

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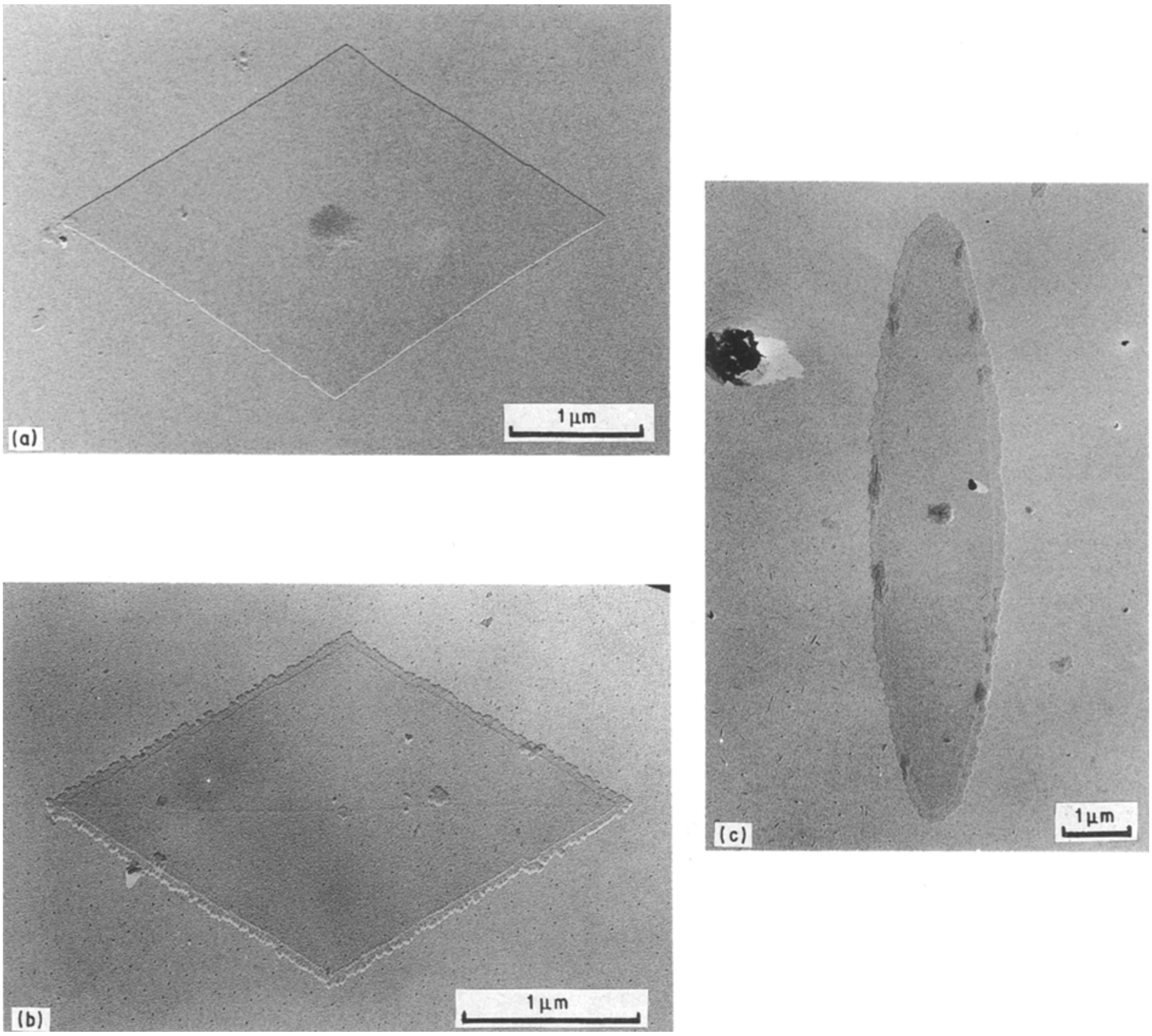


Figure 1 Electron micrographs of lateral habits of (a) *n*-hexacontane, $C_{60}H_{122}$, and (b, c) polyethylene ($M_w = 1.1 \times 10^4$ and $M_w/M_n = 1.16$) single crystals; (a) crystallized from octane solution by the evaporation method, (b) crystallized from xylene solution of 2.5×10^{-5} wt % at 73 °C, and (c) crystallized from dotriacontane solution of 0.1 wt % at 110 °C. The *b*-axis of the crystals is vertical. All are shadowed with Pt–Pd.

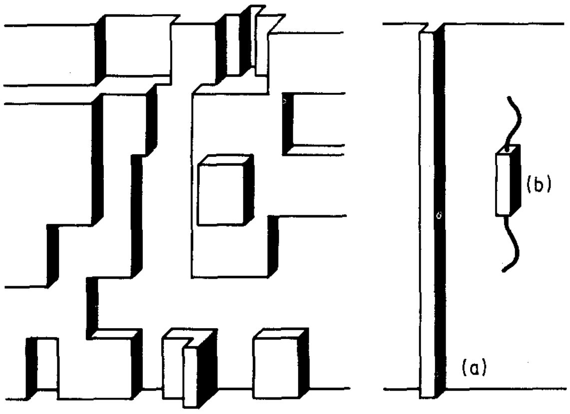


Figure 2 Schematic representation of the rough lateral face of polyethylene crystals (from [9]). The surface is roughened with the unit of a straight step of not (a) but (b).

phase below the transition temperatures to the high-temperature phases. Because the mixture was eutectic, the melting point of C34 could be adjusted by changing the composition of the mixture.

5. While the lateral habits of pure C18 and C20 crystals were well faceted (Result 3), the crystals of the solid solution of C18 and 20 showed circular lateral habits when the composition was in a definite range: C18/C20 = 10/90–90/10 wt/wt. It is known that the solid solution has the rotator phase within this composition range.

These habits, circular, lenticular and diamond shaped, in each phase did not change with temperature, provided that no phase transition occurred.

In the present experiments, the growth rate of crystals could not be measured because the supercooling could not be precisely controlled. Although we can set the temperature with an interval of 0.1 °C, growth at the supercooling of 0.1 °C was still too fast to measure the growth rate by optical microscopy.

4. Discussion

From Results 1–3, it is seen that there is a distinct correspondence between lateral habits and crystal phases; Results 4 and 5 support this hypothesis. The

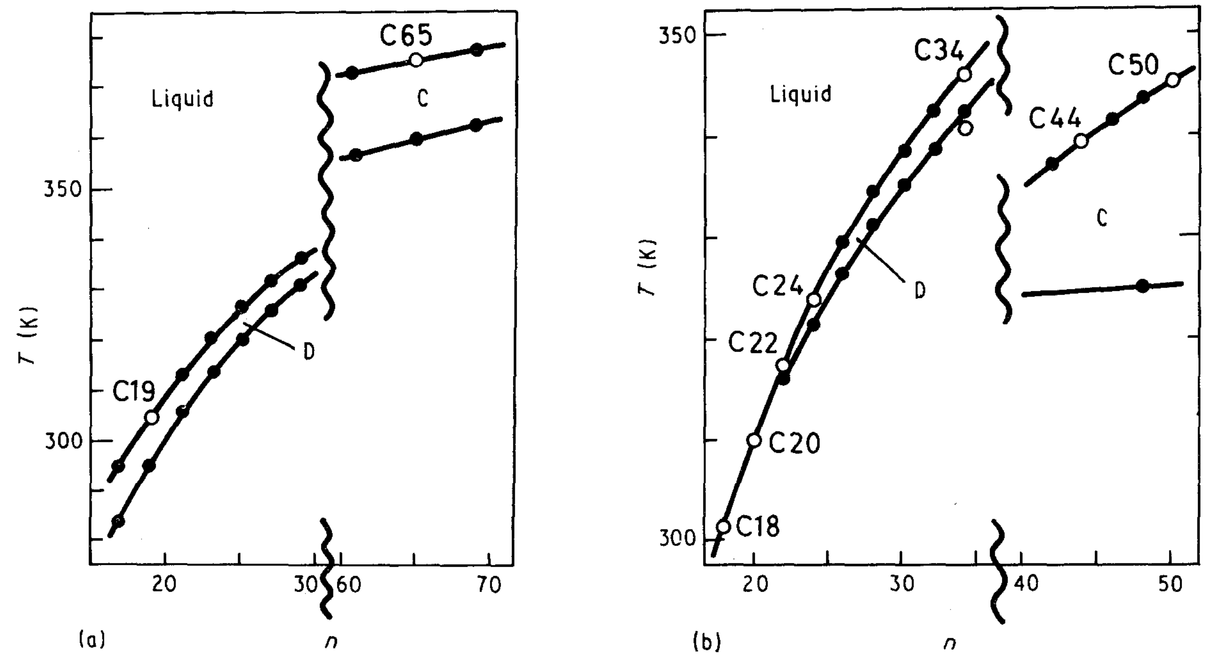
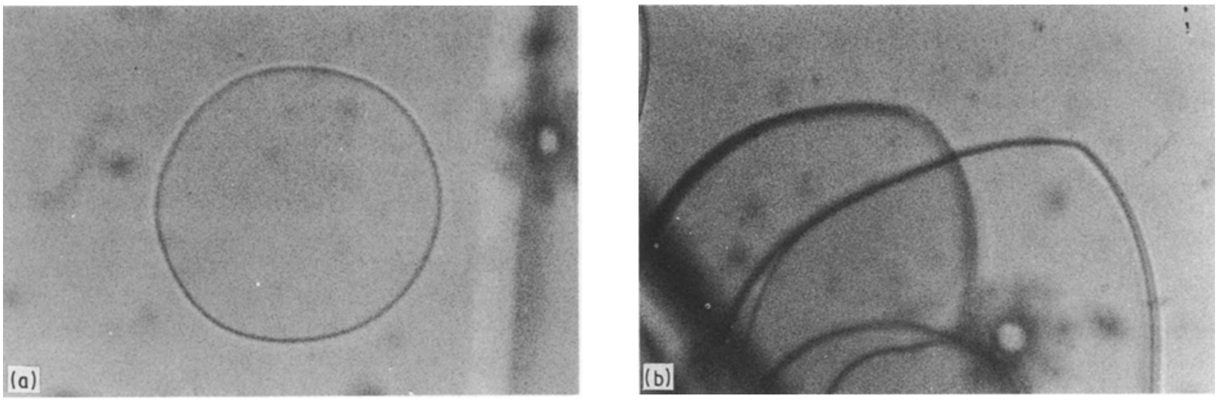


Figure 3 Plots of experimental results (○) on a diagram of phase transition temperatures (●) against the number of carbon atoms of *n*-alkane: (a) odd numbers, (b) even numbers. C and D denote phase C and rotator phase, respectively.



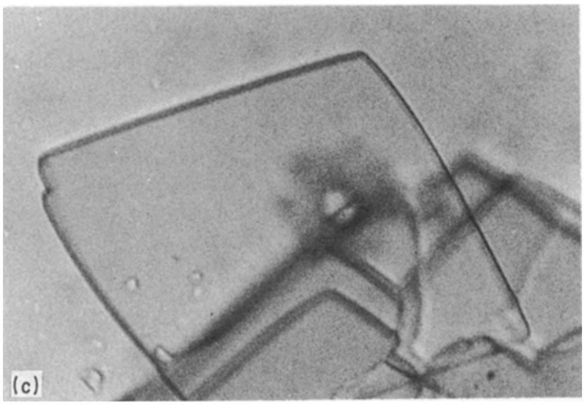


Figure 4 Optical micrographs of lateral habits of *n*-alkane crystals observed just below the melting point: (a) C34 in the rotator phase, (b) C50 in phase C, and (c) C20 in the low-temperature phase.

ordered low-temperature phases transform to the disordered ones with increasing temperature, in the order of phase C and rotator phase [13]. Therefore, it can be concluded that the lateral habit changes from a well faceted habit to curved ones as the crystal phase transforms to disordered ones.

The rounding of the lateral habits can be ascribed to the thermal roughening caused by the phase transitions of the crystals. Thermal roughening occurs when the free energy of steps on the surface of a crystal face vanishes. Under the condition of thermal roughening, it has been shown that the crystal surface becomes microscopically roughened and the external shape loses anisotropy and becomes curved [10]. For *n*-alkane crystals, the following change in the free energy of steps at the phase transition of crystals is expected. Firstly, the energy required for the formation of steps will decrease as the crystal phase transforms to the disordered phase, because the heat of fusion of the crystal decreases with the release of heat at the crystal phase transition of first order. Secondly, the entropy of steps will increase with increasing disorder of the crystals, because the number of configurations of steps will increase as a result of the decrease in the formation energy of kinks on the step. Therefore, the free energy of steps is expected to decrease as the crystal becomes disordered, and the free energy will eventually vanish in the rotator phase. It should be noted that the rounding of the crystal face of *n*-alkane accompanies the phase transition of the

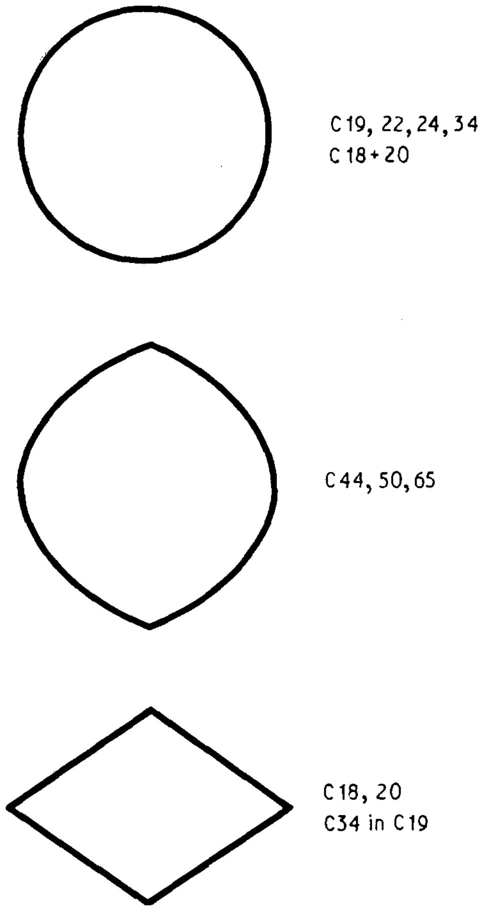


Figure 5 Schematic representation of observed habits.

crystals rather than the rise in temperature, as is the usual case.

If the lateral face of the crystals is really thermally roughened in the high-temperature phases, the growth rate of the crystals should be proportional to the driving force of crystallization, supercooling, because nucleation on a flat surface is not required. Although the growth rate was not measured in the present experiments, Hoffman [14] reported a linear supercooling dependence of the growth rate of C94 crystals in melt crystallization. Because the crystals of C94 must be in a high-temperature phase near the melting point, this dependence also suggests the thermal roughening of the growth face in the high-temperature phases.

When considering the possibility that the rounding of the lateral shape is caused by the impurity effect of inclusions such as homologues of different chain length, we can discount that the rounding is solely due to the impurity effect, because C18 and C20 crystals have well faceted habits while the lateral shape of C19 crystals is circular; there is no particular difference in the purity of these samples. However, we cannot discount the possibility that the effect of impurities becomes stronger as the crystal phase transforms to the disordered phases. While the hypothesis of thermal roughening is supported by the evidence of a linear supercooling dependence of growth rate, as discussed above, detailed study on the kinetics of crystallization from the melt with differing purities will be required in order to determine whether or not impurities influence the lateral shape and growth kinetics of *n*-alkane crystals.

Compared to the *n*-alkane crystals with curved habits, those of polyethylene show strong anisotropy of growth; the axial ratio of the lateral habits is very high as is shown in Fig. 1c. The rounding and anisotropy for the curved habits of polyethylene should be explained. Because the growth of a thermally roughened face should be enhanced compared to that of a flat face with the barrier of step-free energy, the reduced growth of the curved face cannot be explained by thermal roughening. Alternative approaches have been suggested for the curved habits; the rounding may be caused by reduced propagation of steps on the growth face and the resultant accumulation of these steps on the surface [15–18].

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