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Melts

Melt-Crystallization of n-Alkanes and Polyethylene in a Temperature Gradient

2. Melt-Orientation of Hexatriacontane ($C_{36}H_{74}$)

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Summary

When $C_{36}H_{74}$ was crystallized from a melt-state in a temperature gradient, crystallization proceeded at a crystal-melt boundary plane which is perpendicular to the temperature gradient. The melt-state was studied by striking the incident X-ray near the crystallizing plane.

The intensity profile from the melt-state shows weak anisotropy. This fact suggests that the melt-molecules are slightly oriented perpendicular to the crystallizing plane.

Introduction

Melt-states of long chain molecules have been widely observed and various models including random to ordered structures have been proposed. In the previous papers, we have measured crystalline orientations (ASANO 1983), and structural changes during melt-crystalline transitions (ASANO & ABE 1984) of n-alkanes. In these papers, the crystalline orientation of hexatriacontane ($C_{36}H_{74}$) has been determined as the c*-orientation, where the crystalline c*-axis is perpendicular to the crystallizing plane.

Our main interest is whether the molecular orientation appears only in the crystalline state or there is a similar orientation in the melt-state. In the present paper, the melt-structure near the crystallizing plane is investigated by X-ray diffraction measurement.

Experimental

The sample was normal hexatriacontane prepared by Japan Chromato Industries Co. Ltd., which is more than 99 % in purity. The sample was sealed in a glass capillary which was 1.8 mm in diameter and glass thickness of 0.1 mm. The experimental setup is shown in Fig. 1, which is nearly the same one as described in the previous papers. As the sample capillary was moved by 2mm/hr through a heater and a cooler, melt-crystallization occurred at a narrow gap (about 2 mm) between them. The heater was controlled to 120 °C and the cooler was cooled by water to 15 °C. In this case, the temperature gradient was about 35 °C/mm at the center of the gap.

The X-ray generator was operated at 40 kV and 30 mA, and exposing time was 1000 sec. The Ni-filtered CuKα radiation was used with a pinhole collimator of 400 µm. Diffraction intensity was measured by the Position Sensitive Proportional Countor (PSPC) System of Rigaku Co.Ltd. As shown in

Fig. 1, we define z-axis parallel to the sample capillary, and the direction of the meridian parallel to it. Both equatorial and meridional profiles were measured by rotating the PSPC by 90°.

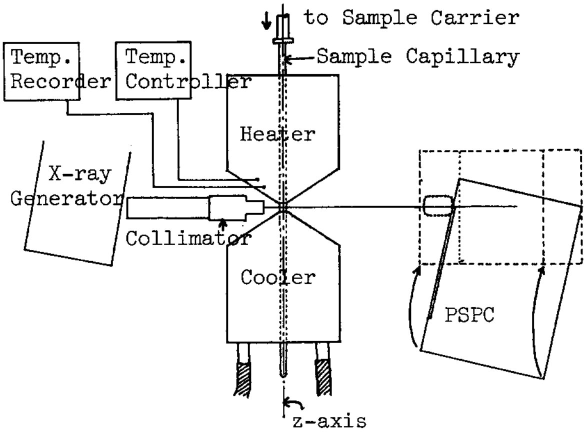

Fig. 1 Schematic view of the experimental apparatus. The broken line shows the setting of the PSPC for measuring equatorial profiles. For counting the intensity from $2\theta=5°$ to $30°$, the PSPC was inclined by 15° from the perpendicular position.

Crystallization starts by moving the sample capillary from the heater to the cooler along z-axis. As described in the previous paper(ASANO 1983), the crystallizing plane descends to lower temperature position for initial 5 min. Then it ascends to higher temperature position and after 30 min it lies about 200 μm from the position before the crystallization. This high temperature crystallizing plane was stable and successive crystallization steadily proceeded at this plane. The position of the crystallizing plane was measured using a polarizing microscope.

Results and Discussion

In order to investigate the melt-state, the primary diffuse peak is carefully observed. The incident X-ray beam was irradiated near the stationary crystallizing plane. Figure 2 shows the meridional and equatorial intensity profiles. The centers of the incident beam were (a) 50 μm,(b) 150 μm,(c) 200 μm,(d) 300 μm,(e) 400 μm and (f) 700 μm apart from the crystallizing plane. The irradiating regions are shown at the top of the Fig 2. The intensity is corrected for the absorption of the specimen and the glass capillary.

In Fig. 2(a) and 2(b), the crystalline reflections are superposed on the melt scattering. After elimination of the crystalline reflection (shadowed areas in the Fig.2), the meridional and equatorial intensities are compared. Intensity profiles from the melt state shows anisotropy ; the equatorial intensity is stronger than the meridional one. The discrepancy decreases in Fig. 2(c) to 2(e), but weak anisotropy is still observed. There are hardly any differences in Fig.2(f).

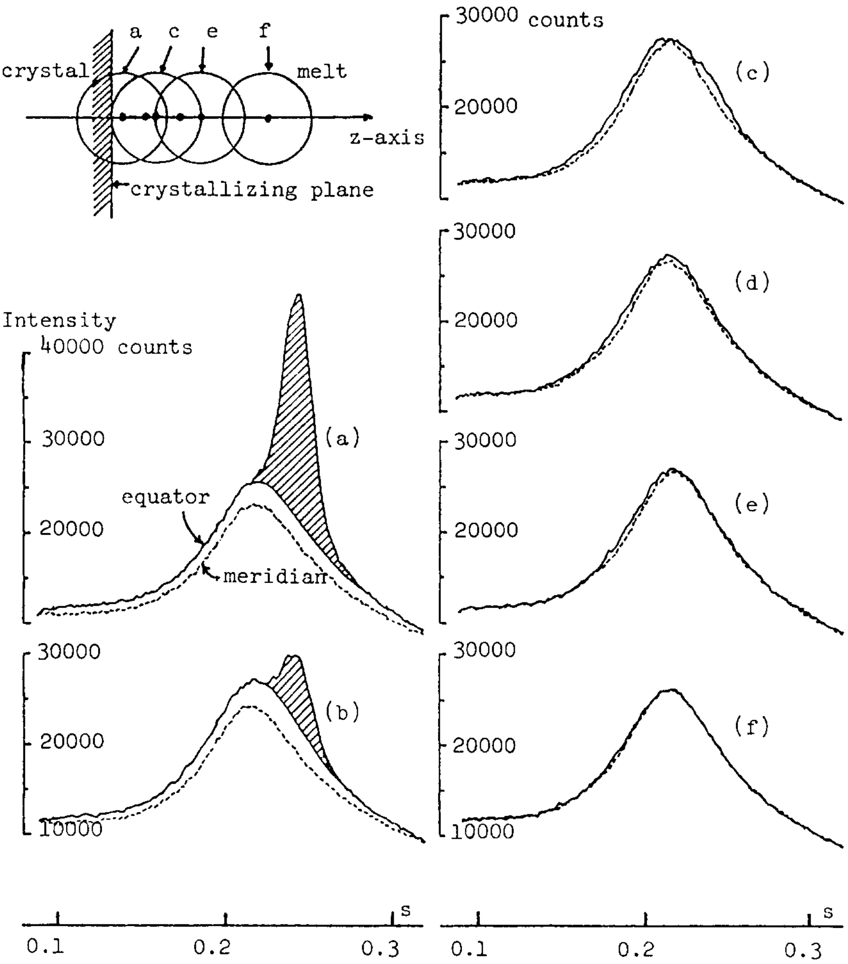

Fig. 2 Intensity profiles along equator (solid lines) and meridian (broken lines). The unit of the abscissa is $2\sin\theta/\lambda$. The positions of the incident X-ray beam are (a) 50 μm, (b) 150 μm, (c) 200 μm, (d) 300 μm, (e) 400 μm and (f) 700 μm. The irradiated regions are shown by the circles at the top of the Figure.

The anisotropy between equatorial and meridional intensities is defined by the following equation:

$$A=\frac{(\text{area of the equatorial peak})-(\text{area of the meridional peak})}{(\text{area of the equatorial peak})}$$

The peak area is integrated from $s=0.15$ to 0.30, where $s=2\sin\theta/\lambda$. The value of A is listed in the following TABLE as a function of the position of the incident beam.

TABLE

	(a)	(b)	(c)	(d)	(e)	(f)
Position(μm)	50	150	200	300	400	700
A	0.09	0.09	0.03	0.02	0.01	0.00

Above results show that the melt-state is isotropic at (f). During the crystallization in the temperature gradient, the anisotropy appears when the melt approaches to the crystallizing plane ((e)→(d)→(c)).

The primary peak from the melt mainly reflects intermolecular arrangements. If we suppose that the anisotropy of the peak intensity simply depends on the molecular orientation, the results show that the melt-molecules have weak orientation where the molecular chains are parallel to the z-axis. Existence of the molecular orientation strongly suggests that the melt-molecules are in the ordered state like nematic or smectic.

Supplementary experiments showed that the melt-state remains in the crystalline-side of the crystallizing plane, since the diffuse peak was still observed when the center of the incident beam was minus 200 μm. The values of A in (a) and (b) are three times larger than that of (c). This fact suggests that the remaining melt-molecules, which are in the highly supercooled state, are well oriented, since the incident X-ray is partially passing through the crystalline-side in (a) and (b).

Both the oriented melt-molecule and the c*-oriented crystalline molecule are parallel to the z-axis. Accordingly, both orientations seem to be closely related each other. However, the origin of the melt-orientation is not clear at this stage.

Additional experiments were carried out by small angle X-ray diffraction method. The weak meridional reflection was observed in the melt-state very near but not touching the crystallizing plane. This fact suggests the existence of the layer-like structure or smectic order in the melt-state. However, the reappearance of the above result is not perfect at this stage and more detailed observation is necessary to confirm the smectic state.

Morphological studies of the melt-state of n-alkanes have been carried out by small angle newtron scattering (DETTENMAIER 1978), polarized Rayleigh scattering (DETTENMAIER et al. 1977, STINSON and LITSTER 1970), Brillouin scattering (KRÜGER et al. 1981) and differential scanning calorimetry (DENNY and BOYER 1981, HÖHNE 1981), and both negative and positive conclusions have been reported as for the ordered state of melt-molecules. Our experimental results show the existence of the melt-orientation near the crystallizing plane, which suggests that the melt-molecules are in the nematic order.

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