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Oblique Incidence Reflection Microscopy (OIRM) Study on Hydrocarbon Films

Studies on thin dotriacontane hydrocarbon in the form of thin films were made by employing Oblique Incidence Reflection Microscopy (OIRM). Information related to substructure and striations were discussed.

Keywords: OIR microscopy, hydrocarbons, thin films, defects, light scattering, striations

1. Introduction :

The organic crystal surfaces show a variety of features, some times simple and some times complex, resulting from growth process. If the desire is to obtain relatively smooth surfaces free from patterns, then it might become necessary to understand the factors and circumstances that are responsible for the occurrence of such patterns, so that proper controls could be applied.

Thin films of hydrocarbons could be used as dielectric films to shield electronic circuits, in order to protect them from humid environment. Such films are extremely cost effective. Calcium stearate films are known to have similar applications (MIKI et al 1985). Yet the presence of calcium metal ion can some times be undesirable. Hydrocarbon films are therefore the best choice. In fact the organic thin films have applications to protect insulators (VINCETT, ROBERTS 1980), resist films (GRUNFELD, PITT 1983), thin films with optical (SUGI et al 1979), and electronic (KAMURA et al 1976) properties.

Some of the observations on striations present on the as grown surfaces of thin hydrocarbon films were discussed in a previous report (PRASAD et al 1996). Rotation of film surfaces in a plane parallel to the microscope stage and around an axis normal to such plane, in combination with OIRM were employed in that study (PRASAD et al 1996). In the present study, in addition to the variability of horizontal angle (θ_H), the oblique incidence angle (θ_Z) was also varied, in the spirit of the work reported by VAND et al (1966) and TAJIMA et al (1976). Presence of several features, that were invisible in the usual transmission optical microscopy and patterns related to 3D structures of striations were detected. The details of the study and the interpretations advanced form this report. The study also beautifully illustrated the utility of OIRM technique, developed by the present authors, in exploring the films of hydrocarbons.

2. Materials and experimental methods

The hydrocarbon employed in the present work was Fluka made dotriacontane (n-$C_{32}H_{66}$). The solvent was high purity xylene. Experimental method was the same as that was used earlier (PRASAD et al 1996), except that the θ_Z, which had a fixed value in the previous study

(PRASAD et al 1996), was variable in the present work. The angle θ_z is the angle between the incident beam of light and the substrate (glass plate) that is present on the microscope stage. Necessarily, the contact point (where the light beam touches the substrate) happens to be on the vertical axis of the microscope.

A randomly selected area of film (near film edge) was subjected to microscopic examination at three different beam incidence angles (θz); 10^0, 15^0 and 22^0. The polychromatic beam intensity was kept very low and 90 minutes exposure time was used to record the image on 100 ASA B&W photo film.

3. Observations

The general appearance of the hydrocarbon film was recorded employing transmitted light mode, while keeping the polarizer and analyzer in parallel position. A triangle-like dark region (D), two crystals of hydrocarbon (A,B), edge of the film (E), and some faint layers were noticed (figure 1a). Transmitted light was switched off and oblique incidence at $\theta_z = 10^0$ was employed. At this angle of incidence, the two crystals (A,B) remained unseen (figure 1b). A modified edge (E1) appeared in place of regular film edge (E in figure 1a). Also in place of the dark triangle-like strucutre (D in figure 1a), a slightly irregular patch-like structure appeared (D1 in figure 1b) whose one edge coincided with the modified film edge (E1).

At θz = 15^0, the film edge was further modified into a thin, bright and slightly irregular line-like structure (E2 in figure 1b). The irregular patch-like structure D1 (figure 1b) merged with the newly appeared dark regions; its existence could be felt only because of the dicontinuity (D2 in figure 1c) that was noticed in the bright edge line.

Several interesting modifications took place when θz was changed to 22°. The edge of the film appeared as wide bright ribbon (E3 in figure 1d). However, it had a non-uniform texture. The lower part of the ribbon-like structure (E3) gave a faint appearance, having several coloured fringes (Q in figure 1d). The edges of growth layers (S2) were bright and appeared to be merged with (E3). The patch-like structure, seen in figure 1b totally disappeared from its location (indicated by the circle D3 in figure 1d). A set of a few short, thin and bright lines (J1 in figure 1d) were noticed, which did not show up at the other incidence angles (10° and 15°). In addition to these (J1) lines, some clear zig-zag lines (J2) were also noticed. The different features noticed in figure 1a to 1d were superimposed and a map (figure 1e) was obtained. Different positions of the edges of the film (E, E1, E2 and E3) could be noticed to be non-coinciding. Interestingly the positions of dark triangle-like structure (D) and the patch-like structure (D1) did not exactly coincide.

4. Discussion

The appearance of two crystal platelets in transmitted light (figure 1a) and their non-appearance in OIRM at θz = 10° (figure 1b) and several changes that appeared due to the gradual increase in θz clearly indicated that the features seen were due to light scattering from the interior of film and also by the interface between the two platelets and the film.

MORIYA and OGWA (1980) indicated two different situations occuring in light scattering; (i) images being independent of and (ii) sensitively dependent upon the direction of the light scattering vector and suggested that such a situation could occur when light scatterers (i) had a degree of spherical symmetry and (ii) when they were phase objects, respectively. From the discription provided by the authors (MORIYA and OGAWA: 1980) the meaning of “phase objects” seemed to be those with a refractive index which differed from its surroundings. In the present study it was noticed that images of different areas of the film were sensitive to the value of θz. However, in view of the fact that the areas D1, P1 (figure 1b) and E2, P2 (figure 1c), and E3 (figure 1d) did not differ in contrast in plane polarized light (figure 1a), it could safely be assumed that the entire area under observation (except area D in figure 1a) was of the same phase. As such areas D1, P1, E2, P2 and E3 which were sensitive to the value of θz could not be termed as phase objects. An attempt was made, in the following paragraphs, to interpret the observations made.

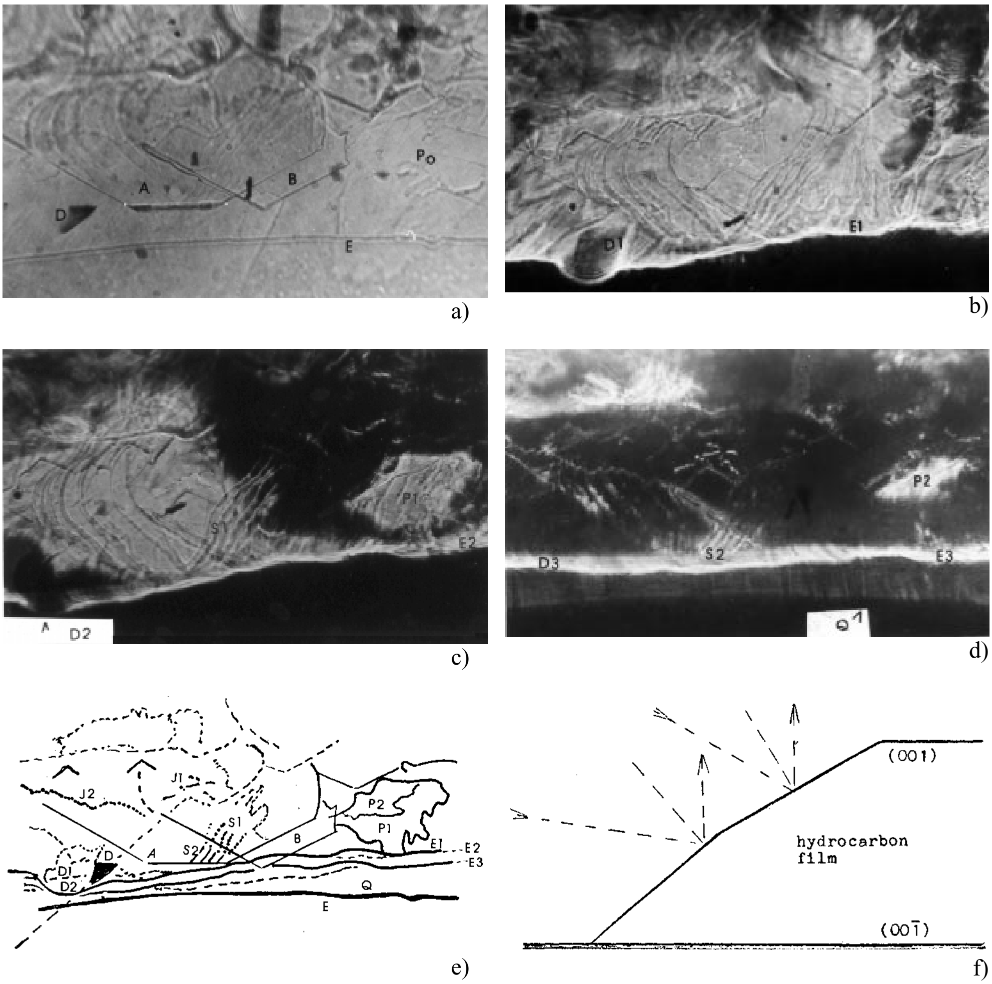

Fig. 1a: A thin film of C32 hydrocarbon. Photomicrographed when polarizer and analyser were in parallel position, Magnification 100x.
b: The same film, photomicrographed at oblique incidence angle (OIA) in verticle plane (θz) = 10°. Magnification 100x.
c: OIA (θz) = 15°. Magnification 100x.
d: OIA (θz) = 22°. Magnification 100x.
e: A map of the area of the film.
f: Model of a step consisting of two different crystallographic planes. If the step is burried under an epilayer, then it could generate an interface.

Since figure 1a was obtained in plane polarized light, the black colour of the area D (figure 1a) indicated that it was due to a half platelet present in the film in crossed position, i.e. with a rotation through 90°, with respect to the axis of the film (even though not a regular habit, some times hydrocarbons could crystallize as triangular platelets: see Ref: PRASAD and BHAGAVAN RAJU:1983). In all probability the triangular platelet was embedded into the film, during the growth process and such a situation would give rise to the formation of strain fields (around or in the vicinity of the triangular platelet), due to the curvatures developing in the layers of the film. The scattering vector at such curved layers would differ from that of rest of the surrounding film. As a result, the strained area could appear as dark, when the rest of the neighbouring film appeared bright. The occurrence of peculiarly shaped darker region, in the vicinity of D1 (figure 1b) might be the result of such a strain. It was interesting to notice that the area D1 showed its presence felt as area D2 in figure 1c and no trace of it could be seen in figure 1d. (The circle denoted by D3 indicated the location of strain field), however the bright ribbon was continuous. Such a situation could occur when the scattering vector of the layers in the strain field and that of layers in the bright ribbon happened to be parallel.

The appearance of edge E1 (figure 1b) its bright state as E2 (figure 1c) and transformation into wide ribbon-like structure E3 (figure 1d) at different θz values could be explained, with the assumption that it represented an interface or a step as showed in figure 1f. A thinner line-like (at θz=15°) and wider ribbon-like (θz=22°) appearance should be due to the fact that the interface or step was formed by two different crystallographic planes (figure 1f). It was fascinating that no trace of such a step was visible in the transmission optical photograph (figure 1a). The fringes in the Q area too remained invisible. There was continuity of fringes (present in the bright ribbon-like structure) into the Q area, in the form of faint bands. It might be due to the segregation of impurities at the terminal stages of the growth.

Some faint growth steps that were noticed in figure 1a became clearly visible in figure 1c and bright in figure 1d. Only a partial appearance of steps in figure 1d indicated that the growth steps, throughout their length, were not parallel to a plane; but were bent, through a small angle. The J1 and J2 that appeared with good contrast in figure 1d, represented (i) criss-crossing layers and (ii) a train of small steps respectively. In all probability they were burried inside the film.

The OIRM was also employed to study the striations. One particular case is presented here.

An isolated, slightly bent striation is shown in figure 2a. It was photomicrographed in polarized light and the darker patches were due to grains in different orientations. The striation was set at perpendicular direction to the incident beam, so that intensity of scattered light was maximum (PRASAD et al 1996). Then the striation was viewed at two θz values. Figure 2b and 2c correspond to θz = 42° and 30° respectively. The significant observation was that, the intensity was modified at different θz values, showing abrupt changes in the striation structure. We think that (i) presence of flat area between two segments of the same striation or (ii) changes in the orientation of roof-like corrugated structures (roof with different slopes at different points along its length) might be responsible for the appearance of discontinuities in the intensity of light, scattered by the striations.

Further observations made on the striations, employing OIRM technique indicated that several microstriations conjoin to generate a macrostriation. We believe that all the corrugated structures that appeared on the as-grown surfaces were striations and not cracks. Unless there is a severe thermal shock, probably cracks may not form in these long chain molecular lamellar systems.

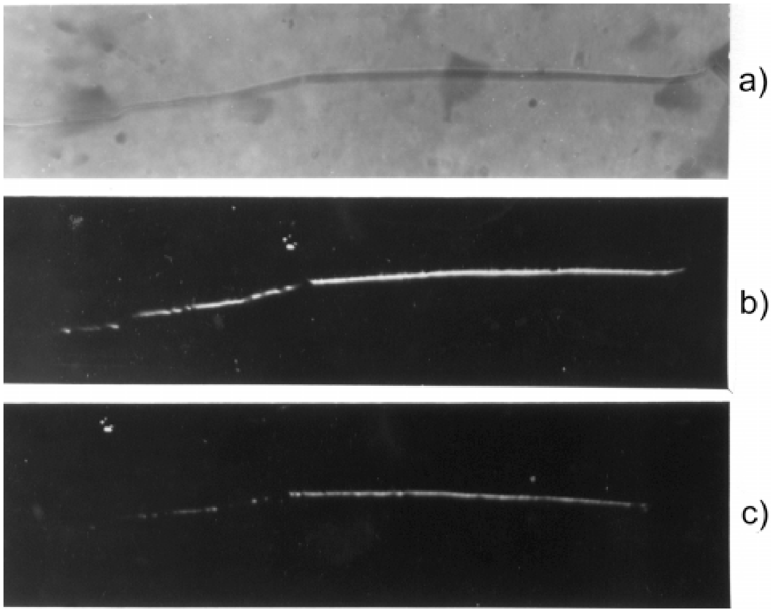

Fig. 2 a: Isolated striation in partially polarized light; optical transmission photograph. Magnification 100x
b: OIA (θz) = 42°. Magnification 100x
c: Discontinuities in the contour are more prominently visible at OIA (θz) = 30°

Conclusions

The study showed that the seemingly clear hydrocarbon films had a variety of defects, mainly due to their lamellar nature. The study also explicitly established that the OIRM has a great advantage over the conventional transmission optical microscopy, in exploring the lamellar crystalline materials. The OIRM technique has been employed in a study of heat induced modifications in hydrocarbon crystals and films. The findings shall be reported in a separate publication.

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