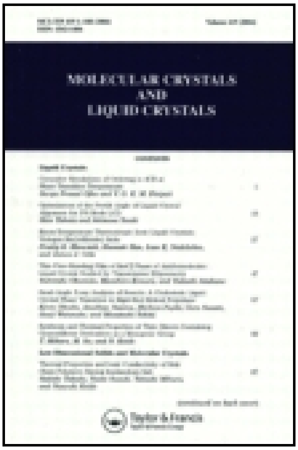

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Optical Microscopic Study of n-Propyl and n-Butyl Stearates in Their α-Phase

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Optical Microscopic Study of n-Propyl and n-Butyl Stearates in Their α-Phase

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As is well-known, many long chain aliphatic compounds, while solidifying from the liquid phase, undergo a first order transformation into a translucent waxy state before adopting a rigid crystalline form. This intermediate phase, called the α-phase, has been variously described in the early literature as: soft crystalline,[1] liquid crystalline,[2] ordered smectic,[3,4] smectic[5] and crystalline.[6] More recently, the author carried out a systematic study of the α-phase using optical, X-ray, infrared and NMR methods.[7–9] The study revealed that the molecules in the α-phase have an extended chain configuration and are arranged in layers with their long axes orthogonal to the layer planes; further, the molecules rotate freely about their long axes while being arranged in a hexagonal close-packed array within the layers. These facts led to the identification of the α-phase with the ordered smectic or the smectic B (S_B) phase.

In recent years, extensive optical, X-ray and miscibility studies have been carried out on the smectic phase and several polymorphic modifications of the phase have been distinguished.[10,11] In particular, it has been established that the S_B phase is of two very different types: The hexatic B phase which is a mesomorphic phase characterised by short-range in-plane positional order and long-range bond-orientational order,[11,12] and the crystal B phase having the usual 3-D positional order.[11,13] In fact, many of the S_B phases earlier regarded as liquid crystalline have now been shown to belong to the latter category.[13]

It is evident from these developments on the S_B phase that the description 'ordered smectic' is rather less specific. Thus the classification of the α-phase remains inconclusive and further work is needed to establish the true nature of this phase. This note concerns itself with the optical microscopic behaviour of the α-phase as observed in n-propyl and n-butyl stearates. Certain new textures are presented and their implications in regard to the identification of the α-phase are discussed.

n-Propyl stearate was of purity better than 99.7% and exhibited a monotropic metastable α-phase having a setting point of 28.8°C. n-Butyl stearate was more than 99% pure and showed an enantiotropic α-phase between 26.1 and 14.8°C. The samples in the form of thin layers sandwiched between glass plates were examined in transmitted light under a polarizing microscope equipped with a hot-stage. The temperature accuracy was ±0.1°C.

One of the textures that is readily observed at the onset of the α-phase consists of plates with rounded edges. These are extinct between crossed polarizers under normal illumination, but show birefringence in convergent light. That these are the homeotropic plates is evidenced by the positive uniaxial figure seen in the region under conoscopic observation. Figure 1a shows the plates as observed using a high power (oil immersion) objective. One of the characteristic features noticed here is the curvilinear, cusped border of the growing plates. This feature, as we shall see later, manifests itself prominently in the spiral-like growth patterns of the α-phase.

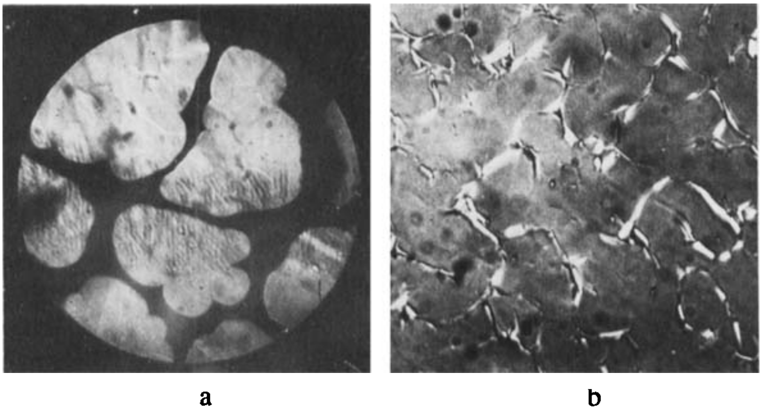

FIGURE 1 a) Homeotropic plates with curvilinear, uneven borders seen in n-butyl stearate using an oil immersion objective, convergent light, crossed polarizers, 25.5°C, 610 × ; b) Homeotropic plates of n-butyl stearate in contact showing rolled up borders, partially crossed polarizers, 25.5°C, 320 × .

When two homeotropic plates come in contact, a thin demarcation line is generally present at the boundary; quite often, the meeting edges tend to roll up and appear as a pair of birefringent bands (Figure 1b). These facts point to the presence of an order in the molecular arrangement within the layers of the plates.

The α-phase also exhibits the mosaic texture when it is obtained under rapid cooling conditions (Figure 2a). The specimen showing the mosaics is constituted of several monodomains of which some may be homeotropically aligned. Regarding the molecular orientation in other domains, there are two possibilities: The optical axes of the domains while being parallel or nearly parallel to the supporting surfaces may be randomly oriented in the plane of the sample. Alternatively, the optical axis of each of the domains may be oriented at some general angle to the supporting surfaces. The first of these possibilities, as we shall see below, describes the structure of the mosaics observed in the α-phase.

When the α-phase is obtained by slowly cooling the liquid, the 'tape' texture is obtained. In ordinary light, the tapes are recognized from their dark border lines as bands with rounded ends. Within each tape two black spots are also noticed which mark the location of the axes of curvature of the end parts. Figure 2b shows the appearance of a tape between crossed polarizers. The slow axis (parallel to the molecular long axes), as ascertained using a quartz wedge, is transverse to the length of the tape in its mid-region and radial in the rounded parts. Thus it appears that the tape is composed of a series of close-packed layers which are vertical to the supporting surfaces and which assume a cylindrical curvature at the two ends to form a closed arrangement.

When the liquid samples are rapidly cooled into the α-phase, numerous differently oriented and closely spaced tapes develop and fill the region. The closeness of the tapes prevents their full growth in that the terminal rounded parts are generally absent and only the homogeneously aligned areas are formed. These areas constitute the mosaic texture (Figure 2a). It may be noticed that at some of the mosaic-junctions in Figure 2a, a few narrow dark lines are present. This could be explained by considering the tape-walls as deviating slightly from being normal to the supporting surfaces.[11] The geometry of the mosaics depends on the density of nucleation of the tapes and the rapidity of their growth; between very small, irregular mosaics and large, nearly rectangular mosaics other variations are possible.

The tapes show an interesting melting behaviour hitherto unreported (Figure 2c). The molten regions at different points have a

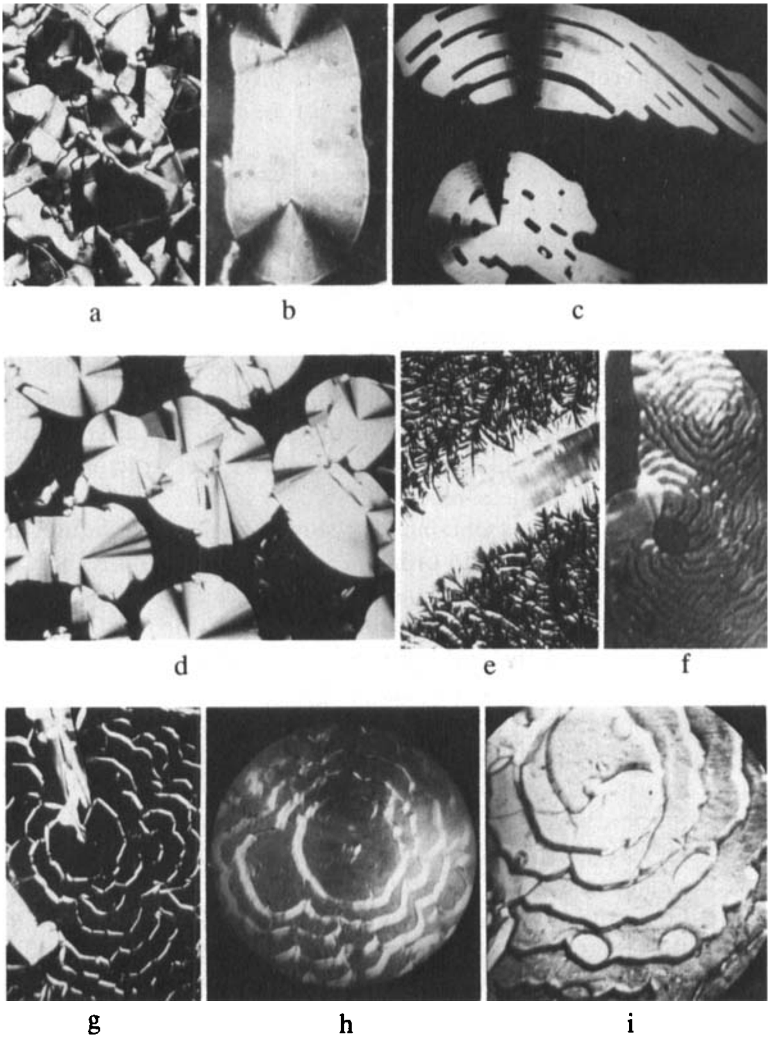

FIGURE 2 a) The mosaic texture in the α-phase of n-propyl stearate at 25°C, crossed polarizers, 190 × ; b) a tape with rounded ends in the α-phase of n-propyl stearate at 25°C, crossed polarizers, 1030 × ; c) tapes of n-butyl stearate in the process of melting, crossed polarizers, 360 × ; d) the fan texture of n-butyl stearate at 26°C, crossed polarizers, 510 × ; e) dendritic growth on either side of a tape in n-butyl stearate at 26°C, crossed polarizers, 180 × ; f) spiral growth centered upon an elliptical cavity, n-butyl stearate, 25°C, oblique illumination, nearly crossed polarizers, 520 × ; g) contours of steps in n-butyl stearate at about 18°C, crossed polarizers, 180 × ; h) growth steps in n-butyl stearate at 20°C, nearly crossed polarizers, oblique illumination, 270 × ; i) growth steps in the α-phase of n-propyl stearate at 25°C, partly crossed polarizers, oblique illumination, 720 × .

regular geometry with their long-sides parallel to the ordered layers. These regions widen as the melting progresses, but their geometry remains largely unchanged throughout. A greater melting along the normal to the molecular long-axes is perhaps indicative of a weaker force between the layers as compared to lateral intermolecular forces.

The homeotropic and mosaic textures happen to be the natural textures† common to both the α- and S_B phases.[10,11] The α-phase shows another natural texture which we shall call the fan texture (not in the sense of focal conic fan texture). Just as the mosaics in the α-phase are an aspect of rapidly growing tapes, the fans are predominantly an aspect of slow-growing tapes. In the first case the cylindrical terminations are generally not found while in the second they appear rather strikingly. Figure 2d illustrates a typical fan pattern. The dark regions in it between the birefringent parts are homeotropic regions and they are always a part of this texture; large areas showing exclusively fan-like formations are not found in the α-phase. The complexities associated with the fanlike formations are broadly explicable in terms of rolling of the tapes at their ends about the normal to the sample-plane (Figure 5, ref. 7), shifts in the axis of curvature of the layers, overlapping of different tapes and other types of defects and malformations none of which would involve bending of the ordered layers in three directions at once. Therefore, the fan texture here is quite different both in appearance and content from the standard focal conic fan texture (see, for example, Plate 8, ref. 11). It does closely resemble, however, the fan texture of the S_B phase of methyl 4′-n-octyloxybiphenyl-4-carboxylate[11,14] as it is shown in Plate 15, ref. 11. The fans of the smectogen form in a special way: As Gray and Goodby[11] describe it, the S_B is obtained from the S_A, which in turn separates from the liquid as bâtonnets and spherulites; these coalesce and tend to develop together as rod-like growths so that 'the fans form in rows and discs rather than individually.' These rows and discs are apparently the counterparts of the mid- and end-parts of the tapes of the α-phase.

Another feature of the fan texture of the smectogen (Plate 15, ref. 11) is that it is paramorphotic. This has been explained[11] as due to the ordered nature of the smectic layers which is not conducive to the direct formation of curved arrangements involved in producing these fans. It has been possible to see the fans only because this S_B

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†Natural texture is that which is spontaneously formed on cooling the liquid and which is not due to abnormal surface effects.[11]

phase is inherited from a precursor S_A phase to which the texture is natural. Although the α-phase also has a hexagonally ordered stratified structure, it can show the fans directly for two reasons: Firstly, the fans here do not appear to involve any focal conic domains at all and, secondly, the cylindrical curvature of the layers that is present here can be understood on the basis of the potentially flexible nature of the stearate molecules (as opposed to the rigid structure of smectogens).

It is relevant to mention here that the textural behaviour of the α-phase is not the same for all materials. Ethyl stearate, for example, shows the mosaic and homeotropic textures, but not the 'fan' texture; it shows birefringent needles and bands, but without the rounded ends. These facts, as also the others relating to the textural variations between the α- and S_B phases, only go to show that the macroscopic defect structures of structurally similar phases need not exactly correspond.

One of the textures commonly observed in n-butyl stearate, but not formed in n-propyl and ethyl stearates is that of moss-like or dendritic growths (Figure 2e). It occurs when the specimen is rapidly cooled. It also forms in some newly formed homeotropic regions. Moss-like texture has also been observed in the S_B phase which is obtained from the S_A phase of infinitesimally short temperature range; it comprises very small mosaic areas forming, during the S_{AB} transition, either directly in the liquid or in the originally homeotropic regions of the S_A phase.[11] Dendritic growth is a well-known phenomenon in all forms of crystal growth process. Its occurrence in strongly undercooled melts, in particular, is related to 'point effect diffusion.'[15] The sharp (paraboloidal) leading tips of crystalline dendrites facilitate the diffusion of latent heat and therefore grow preferentially in the direction of the temperature gradient, the growth-axis itself being a crystallographic axis. In Figure 2e, the texture is that of the finished form of growth and is too thick to reveal the finer features of the growth front. One conspicuous overall feature is that the dendritic 'arms' are more like oblong leaves; their 'stalks' appear, between crossed polarizers, as dark lines shading into the birefringent sides. In other words, the arms appear to be undulations or ridges on the homeotropic surface. The detailed structure and significance of this texture still remains to be understood. The absence of dendritic growth in ethyl and n-propyl stearates indicates that the greater flexibility of n-butyl stearate may be associated with its origin.

We shall now turn to some of the unique growth patterns observable in the homeotropic regions of the α-phase of both n-propyl and n-butyl stearates (Figures 2f to 2i). In Figure 2f complex spirals centered upon an elliptical cavity are shown; in the adjacent region another spiral-like growth pattern is seen. The edges of the steps are not simple vertical boundaries, for they are strongly birefringent between crossed polarizers while the rest of the field of view is dark (Figure 2g). The pattern in Figure 2h shows steps with curvilinear, uneven borders; the steps are broken up in places and the successive ones are seen to be interlinked in a manner to suggest a spiral like relief. In Figure 2i, many smaller steps appear to be forming from the larger ones; this situation is somewhat reminiscent of that of the degeneration of macrosteps observed by Dukova[16] in certain crystal growth processes. Even though none of the growth patterns of the α-phase reveals a continuous single spiral, the general character of these patterns is very different from that of the Grandjean terraces. They do not seem to be a stack of homeotropic plates having no interlayer correlations, since there is a continuity between successive steps, even if it be to a limited extent. In other words, the patterns are suggestive of dislocation promoted growth in the α-phase.

Evidence of translational order in the α-phase is also provided by polyhedral shape of uncovered droplets[7] and smears (Figure 3) on a glass slide. This cannot, however, be conclusive of 3-D order, since such shapes are not ruled out even when the structure is two-dimen-

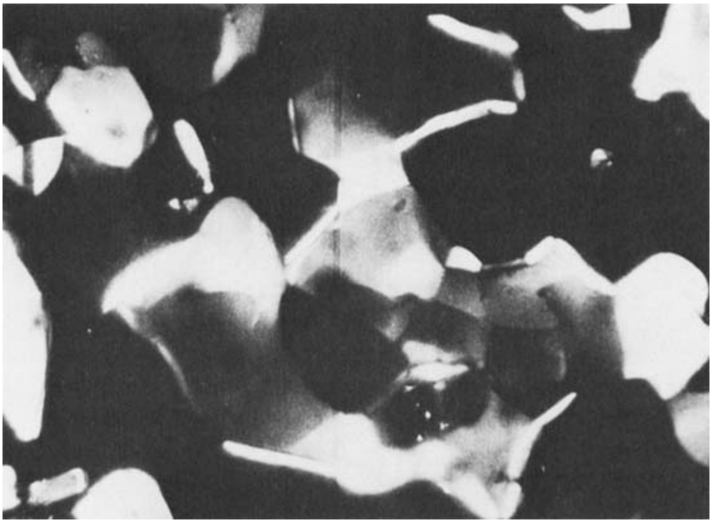

FIGURE 3 A smear of liquid n-butyl stearate on a glass slide cooled to the α-phase showing some plane faces and sharp edges on the free surface, 26°C, crossed polarizers, 460 ×. There is no sample in some of the darker areas.

sional.[17] But the appearance of boundaries between parallel or very nearly parallel tapes seems to furnish evidence of interlayer correlations. A photomicrograph of such boundaries in n-butyl stearate is given in Figure 4. Similar textures are also seen in ethyl and n-propyl stearates. The striated appearance of the junction region in Figure 4 points to a high degree of molecular distortion which is not expected in the absence of translational order between the layers.

To conclude, the stepped growth patterns and domain boundary features of the α-phase are consistent with the existence of a crystalline order in this phase. A definitive information about the crystallinity could be obtained from studies of the type conducted by Moncton and Pindak,[13] employing high resolution X-ray methods and free-standing film techniques. If the α-phase is indeed crystalline, then it remains to be understood as to how a spontaneous formation of cylindrical layers is possible in this phase. Seemingly, a simple way of overcoming this problem would be to envisage the rounded parts of the tape as consisting of many needle-like radiating crystals, while still regarding the straight parts as monodomains (so that they could appear as mosaics in rapidly cooled samples.) This picture raises other questions associated with the nature of the defects (linear or point) providing for multiple growth centres at the two ends of the tape,

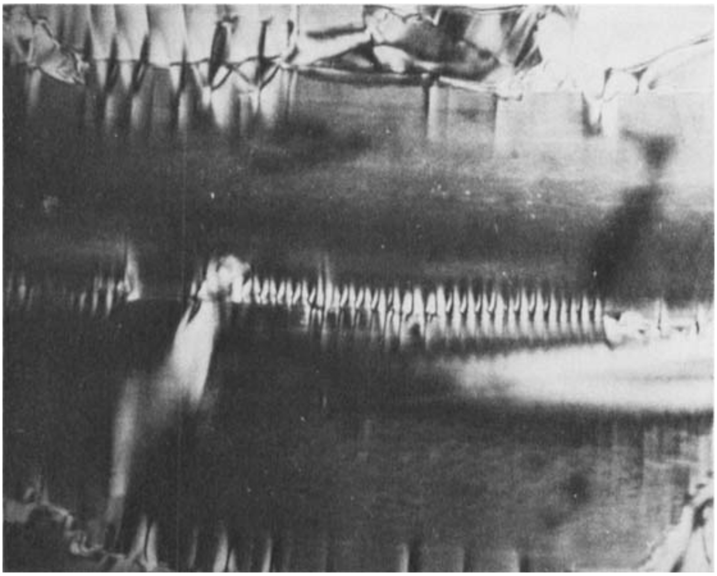

FIGURE 4 Parallel tapes in contact showing striated junctions, n-butyl stearate, 26°C, crossed polarizers, 600 ×.

the reason for the general absence of demarcation boundary between the central and terminal parts in well-formed tapes and so on. Further structural investigations on the tapes would be necessary to resolve these questions.

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