their response to the requirements (i) and (ii) in comparison with the low T_g structures synthesized so far.

EXPERIMENTAL

Equation (1) has already been tested for elastomers subjected to small variations of chain regularity[1]. Data available in the literature also allows us to extend the validity of equation (1) for cross-linked elastomers.

Gent's data[8,7] on crystallization of 1,4-*trans*-polyisoprene and 1,4-*trans*-polychloroprene with different cross-linking density (v) fit equation (1) well, as shown in *Figure 3* for the case of *trans*-polyisoprene, showing a decrease of T_m^0 only as v increases. These ΔT are plotted (*Figure 4*) together with those found experimentally by Gent[8] for 1,4-*trans*-polyisoprene and those obtained for polybutadienes with different 1,4-*cis* content (BR–U and BR–Ti are polymerized with uranium

and titanium catalyst, respectively) and crosslinked using different recipes (DCP = dicumylperoxide; Sulfasan R = 4,4'-dithiomorpholine).

The validity of equation (1) for elastomers strained at different elongation ratios (α) was also tested using Gent's data[7] on 1,4-*trans*-polychloroprene as shown in *Figure 5*. showing an increase of T_m^0 only with α.

The differences, ΔT, between T_m^0 for $\alpha \neq 1$ and T_m^0 for $\alpha = 1$ as a function of α, together with the experimental ΔT obtained by Gent[7] and reported in the same paper are plotted in *Figure 6*.

Of course, the fact that the slope of equation 1 does not depend on enthalpy of fusion ΔH_u, which is different for different elastomers, does not mean that it is not important for elastomer crystallization.

The influence of ΔH_u should play a very important role in determining the variation of T_m^0 as a function of elongation as represented by the well know equation due to Flory:

$$\frac{1}{T_{m,1}^0} - \frac{1}{T_{m,\alpha}^0} = \frac{R}{\Delta H_u}\left[(6/m\pi)^{1/2}\alpha - \frac{1}{m}\frac{\alpha^2}{2} + \frac{1}{\alpha}\right]$$

where m is the number of equivalent freely jointed links per network chain.

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On lamellar organization in banded spherulites of polyethylene

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INTRODUCTION

One of the central problems in polymer materials science is to understand the lamellar organization within spherulites. Until very recently little progress had been made in this area for more than a decade but the introduction of two new morphological techniques has radically altered the situation. For example, elsewhere[1] we have described the highly ordered lamellar organization shown by polyethylene spherulites of intermediate molecular weight grown very slowly under Regime I conditions[2]. This consists of radiating sheets, composed of alternating {201} facets, growing out along b as spherulitic radius. A preliminary, as yet unpublished, survey of polyethylene spherulites grown under other conditions has shown that

the above is an optimum morphology in the sense that lamellae are less ordered in all other cases examined. In particular the regular facetting tends to disappear and is replaced at lower crystallization temperatures by sheets whose end-on profile (i.e. viewed down b) is approximately a shallow S. Lamellar lengths along the radius also decrease. This note concerns further aspects of lamellar organization in banded spherulites, as typically produced by quenching molten polyethylene, and especially the queston of whether they contain ribbon-like lamellae helicoidally twisted about the radius.

Detailed optical[3-6] and X-ray[7] studies in the past reached the conclusion that the molecular orientation in banded spherulites of polyethylene rotated continuously about the b axis

in travelling along a radius. The corresponding lamellar geometry has still not, however, been determined. There is little beyond Fischer's famous photograph[8] showing that the optical banding corresponds to an alternation of regions having radial lamellae lying successively in and perpendicular to the plane of the page. All this evidence in combination with what has been believed to be a radial fibrosity has led to the well-known airscrew model according to which the spiralling molecular orientation is accommodated within helicoidally twisted lamellar ribbons lying parallel to the radii. Two such airscrew-like lamellae are depicted in the figure of Kawai[9] which has been widely reproduced despite the obvious problems of packing greater numbers of helicoids that this particular representation would entail. Keller and Sawada[10], in their studies of banded polyethylene spherulites degraded by nitric acid uncovered some lamellar stacks which were apparently compatible with this twisted lamellar model. They also con-

Figure 1 Banded spherulites of polyethylene in a 5 μm section viewed optically between crossed polars and crossed quarterwave plates

cluded that the twisting airscrew units were built of 'crystals of length comparable with one or half a turn . . . stacked in a roof tile fashion along the spherulite radius'. Other workers[11] have queried whether there is complete twisting around the radius and have suggested a partial twist model. Helicoidal twisting has also been questioned by Bevis and coworkers[12] and by Kanig[16]. We are now able to show that lamellar orientation does spiral about the spherulitic radius but that this is achieved by interleaving sequences of curved lamellar units, with slightly different azimuthal orientations about the radius. These have a length of about 1/4 to 1/3 of the band period and are themselves substantially untwisted.

MATERIALS AND TECHNIQUES

The material used was commercial polyethylene chip (Marlex 5, Phillips Petroleum) containing spherulites with an optical banding between crossed polars of a few μm spacing (*Figure 1*). Samples of this material have been examined electron microscopically using the two new techniques of staining by chlorosulphonation[13] and permanganic etching[14]. For staining, individual pellets were immersed in chlorosulphonic acid at 60°C for 5 h and then treated with uranyl acetate; the details are as described previously[15]. Sections of stained pellets, nominally 200 nm thick, were examined in transmission. The complementary technique of etching with the permanganic reagent of Olley, Hodge and Bassett[14] was used on cut surfaces of pellets, i.e. those left after the passage of a glass microtome knife. Etching was for 15 min at 60°C; etched surfaces were replicated in 2 stages and these replicas also examined in transmission.

RESULTS AND DISCUSSION

Banding, similar to the optical banding of *Figure 1*, can be seen in stained sections at low magnification in the electron microscope. At higher magnifications, individual lamellae can be identified edge-on. These are normal to the blacker regions. The staining technique adds electron dense atoms at lamellar surfaces so that the dominant contrast is when lamellae are seen edge-on, i.e. parallel to the electron beam. Accordingly, the staining technique tends to provide a selective view of morphology, because although lamellae with other aspects are also present in the sample, their image when not parallel to the electron beam is diffuse and may be unrecognizable, as we have discussed in detail elsewhere[15]. Advantage can, nevertheless, be taken of this selectivity to delineate those regions where lamellae share a common orientation (parallel to the electron beam) in an analogous way to that in which dark field electron microscopy maps out regions of common molecular orientation.

Consider *Figure 2*, 4 micrographs taken from a more extensive sequence, which records the results of tilting a stained section from −45° to +45° about an axis presumed to be the spherulitic radius in projection, i.e. the mean direction of lamellae in the 0° (untilted) position. This shows that the regions in which lamellae are edge-on change as the specimen is rotated; the marker point serves as a reference. The complete sequence shows that the change is a smooth one with a 'band' of edge-on lamellae progressing as the specimen is rotated. There is a continuous rotation of lamellar normals when travelling along the radius, which parallels the optical[3-6] and X-ray[7] finding of a continuous change of molecular orientation in identical circumstances. This conclusion does not depend on whether the section is diametral or not, but only on the essential observation of a continuous advance of a 'band' on rotation. If the section is diametral (or strictly, if the spherulitic radius lies in its plane) then the advance will be linear with rotation angle; if not, plotting these two quantities against each other will give a sigmoid curve (which is the case for *Figure 2*). This provides, therefore, an experimental means of diagnosing the position of a section within the spherulite.

Figure 2 and *Figure 3* (which is an enlargement of part of the untilted specimen of the same sequence), are also informative in other respects.

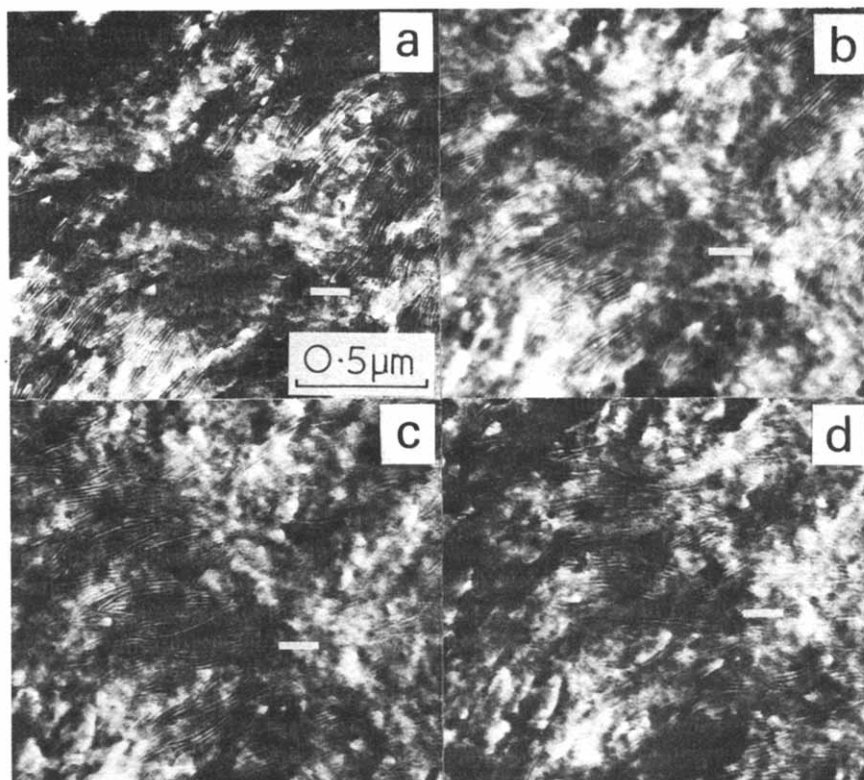(1) The number of lamellae in one band appearing edge-on at the same

Figure 2 Four figures selected from a tilt sequence in which the stained specimen was rotated about the line normal to the bands, i.e. approx. *SW* to *NE* on the page. The smooth shift of the regions in which lamellae are visible edge-on is most easily detected using the reference point, to the left of the marker in each photograph. The tilt angles are (a) 36°; (b) 12°; (c) −12° and (d) −36°
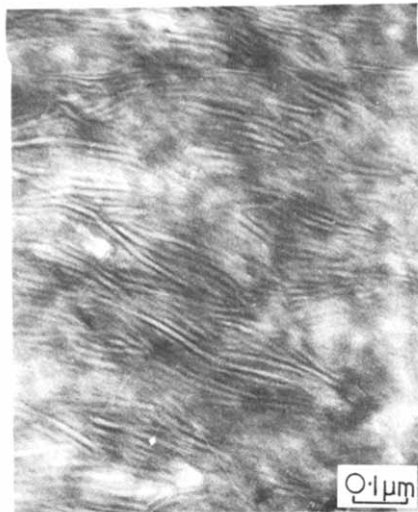
Figure 3 An enlargement of the untilted (0°) photograph in the previous sequence showing how lamellar images cease abruptly with little or no indication of twisting

time fills only a moderate fraction of the space available causing a band to look gappy. The gaps are filled, as the specimen is rotated, by other lamellae which, must, therefore, have a different azimuthal orientation about the radius and are generally also translated along it. It follows that, at any given radial position, there are lamellae whose normals are mutually rotated about the radius and that these lamellar units interleave along the radial direction. The spread of different azimuthal orientations at the same radial position covers a range of about 45° to 60°. This follows because simple geometry shows that the ratio of this value to 180° must be equal to that of the lamellar length to the band period. In *Figure 2* lamellar lengths are about 1/4 to 1/3 of the band period, whence the above figures result.

(2) No firm indication has been found that such lamellar units are helicoidally twisted around the radial direction. The evidence here is two-fold. Firstly, as a section is tilted, it is generally not the case that the image of a particular lamella translates along the radius as it would if it were twisted; instead other lamellae to the front and sides come into view. When twists have been seen, they have amounted to no more than ~6°. Secondly the images of lamellae end rather abruptly (*Figure 3*); their outline would gradually become wider and more diffuse if there were a twist, as we have shown elsewhere[15]. There is little sign of this effect here and on two grounds, therefore, we conclude that lamellar units are substantially untwisted.

(3) If this last argument is taken fur-

ther, the relatively large angle over which lamellae appear to be sideways-on without their edge contrast becoming diffuse suggests that lamellae may be curved around the radius i.e. *b*. *Figure 4*, a replica of an etched cut surface, confirms directly that this is so, at least in some cases. Close inspection of the shadow contrast in those regions where lamellae are approximately flat-on shows that not only are lamellae curved around *b* but also the sense of curvature tends to reverse giving lamellae a shallow S-shaped profile when viewed down *b*. We have also found this feature in non-banded spherulites grown at e.g. 120°C. *Figure 4* has many features in common with Fischer's classic surface replica[8], but being derived from a random cut of the interior, shows that such morphologies are indeed characteristic of the whole spherulite. It also substantiates the existence of a range of lamellar orientations at a particular radial position showing lamellae splaying apart rather similar to the leaves of a partly opened book and that such stacks appear to start at varying positions along the radius.

(4) The orientation of lamellae in a band is not always normal to a band, but can be inclined by 30° and more to this direction. For untilted sections, the difference in magnification required to resolve lamellae on one hand and bands on the other means that, without elaborate precautions, one identifies the (projection of the) spherulitic radius with the average direction of

lamellae. Even so, there is appreciable spread around this mean; *Figure 3* reveals ~30° variation and in *Figure 2d*, which is tilted, there are very pronounced differences of lamellar orientation by a similar amount.

The variation is thus undoubtedly real, but in tilted sections one also needs to consider whether the section was off-diametral in interpreting the magnitude of inclination of lamellae to the tilt axis. It is readily shown that if the true radius is inclined to the plane of the section by θ, then a rotation through ϕ will incline lamellar lengths by α to their original direction (the tilt axis) where

$$\tan \alpha = \tan \theta \sin \phi \qquad (1)$$

Even if the tilt axis is misaligned to the spherulitic radius in projection by unrealistically large amounts, values calculated from equation (1) are relatively little affected. The systematic changes predicted by equation (1) are not, however, sufficient to account for the observed changes of inclination of lamellae to a band on rotation. Many lamellae in *Figure 2d* are inclined by ~45° to the band normal whereas for the opposite tilt in *Figure 2a* lamellae have remained parallel to the band. Similar asymmetries have been observed in diametral sections, in neither case would they be expected. It seems clear, therefore, that the inclination of lamellae to the band can vary from point to point along a radius.
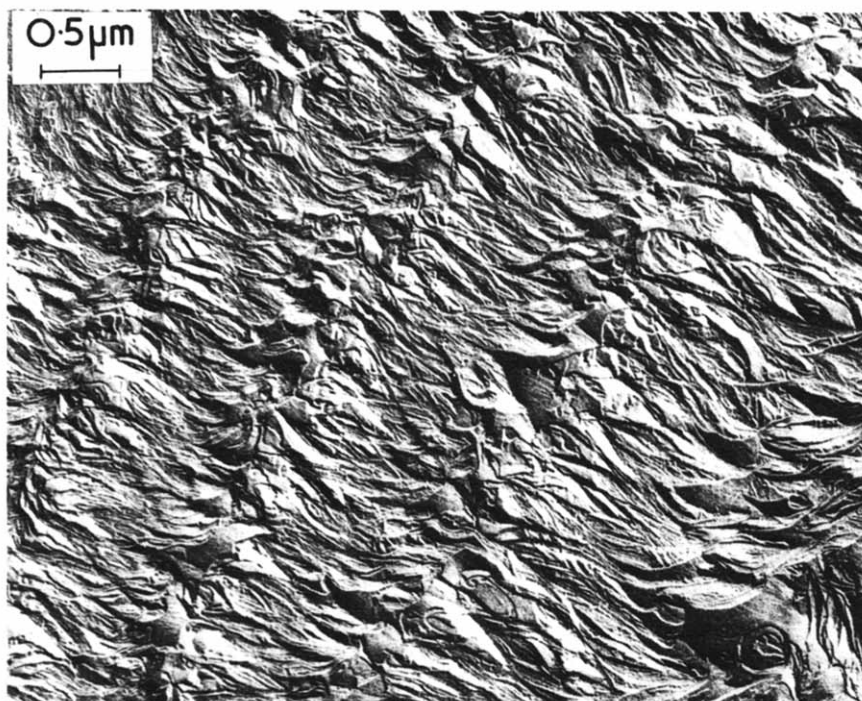

Figure 4 Replica of an etched cut surface of a banded polyethylene spherulite. Note the curvature of lamellae about the radius and the varying angles lamellae make with the radius

Many of the main elements in the lamellar packing of banded polyethylene spherulites are now becoming clear. A spiralling change of average lamellar orientation along a radius has been found but no airscrew-like ribbons, the twist being accommodated by an interleaving sequence of substantially untwisted lamellae. These lamellae are, however, generally curved about the radial *b* direction with at least the dominant ones in the structure having a shallow S-shaped profile perpendicular to *b*. Principally what is still missing is a precise understanding of how these lamellar units are mutually related. We have found no evidence to support the roof-tile packing suggested by Keller and Sawada[10] but the main factor is what happens to the simple interleaving of *Figures 2* and *3* in directions out of the plane of the paper. *Figure 4* and related photographs suggest that this is a complicated multiply-connected arrangement. However, the dimension perpendicular to the page is not explicitly revealed in *Figure 4* and there is reason to believe that the morphology is still more complicated than is immediately apparent. Although most of the previous deductions are directly confirmed, as already described, it is noteworthy that the radial extent of lamellae in the flat-on regions is approximately the third of a bandwidth previously inferred, whereas in edge-on regions continuity appears to extend about twice as far. For consistency with the staining results it must be assumed, therefore, that this apparent continuity masks changes of orientation going into the plane of the paper. It is, moreover, interesting to compare *Figure 4* with the scanning micrographs which led to the suggestion of the partial twist model[10]. The inevitable suppression of fine detail in these seems to us to have oversimplified the morphology in misleading ways.

Finally we comment upon the capability of the lamellar geometries described of accommodating twisted crystallization. It is useful to begin by analogy with the well characterized texture of polyethylene spherulites grown at low supercoolings[1]. In that case spherulitic texture is created by the first-forming or dominant lamellae between which there are channels subsequently filled in by subsidiary laminae. There are no radial fibres as such but a fibrous pseudoperiodicity is given to a cross-section normal to a radius by the pattern of interstices between the major sheets. The texture indicated, moreover, that a once-dominant lamella could beome subsidiary to an adjacent lamella and *vice versa* during the dynamics of growth and that when the 2 lamellae were growing along slightly different directions in space, this afforded a natural means of accommodating the small-angle branching necessary to fill space. Almost certainly the textures of other polyethylene spherulites form in a rather similar way. There is one very important difference, however. Whereas lamellae form under optimum conditions in Regime I with crystallographic {201} facets, at lower temperatures, and certainly for banded spherulites, dominant lamellae are shallowly curved about the radius, i.e. each possesses different azimuthal orientations about the radius within itself. Furthermore, the subsidiary S-shaped lamellae do not pack parallel (in contrast to the tendency for the ridged sheets of Regime I) but can be in contact only at one point (in a cross-section) with the remaining parts mutually splayed and thus rotated around *b*. This feature can be seen in *Figure 4*. In other words, in proximity to one lamella there are others growing with different azimuthal orientations. The geometrical possibilities exist, therefore, by which a change in the relative dominance of lamellae, or of parts of the same curved lamella, can cause growth to proceed with a changed azimuthal orientation. It seems from related work that this already happens at growth temperatures of, say, 120°C but that the changes of azimuth only become coordinated sufficiently to give optical banding when growth is sufficiently rapid in relation to molecular transport.

Under such conditions there will also be an asymmetry in growth because the conditions which caused one lamella to cease being dominant will also tend still to be present and so to mitigate against it resuming dominance at the next change. Successive changes could thus continue in the same sense, which is possibly relevant to the origin of twisting growth. Such considerations are, however, beyond the scope of this paper whose immediate concern is to demonstrate that the average lamellar orientation spirals about the radius of a banded polyethylene spherulite and that this is achieved by the interleaving of short, probably curved, lamellae which themselves are not substantially twisted.

ACKNOWLEDGEMENT

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