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On the morphology of polyethylene crystallized from a sheared melt

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The morphology of linear polyethylene, crystallized from a sheared melt in the form of shish-kebabs, has been investigated by transmission electron microscopy following permanganic etching. The microstructure of lamellae crystallized transversely on a central linear thread changes systematically with crystallization temperature and shear rate. Higher strain rate produces more and longer filaments and aligns lamellar normals along their rows. At lower strain rate, lamellar habits resemble, but differ from, those characteristic of quiescent growth. Fold surfaces that are inclined to the chain axis *c* at lower shear rates become normal to *c* with higher shear, thereby adopting a state of higher energy. It is inferred from this and the high crystallization temperatures that their crystallization was not strain-free. The separation of adjacent lamellae and its decrease at higher strain rate are consistent with pressure from molecular cilia emerging from fold surfaces, in a similar way to the basic cause of lamellar divergence in spherulites.

(Keywords: polyethylene; crystal morphology; sheared melt)

INTRODUCTION

When polymers are crystallized from an oriented or strained melt, shish-kebab textures are usually a predominant feature of their morphology. This generic term refers to the product of a two-stage crystallization. The first stage is the extension of the underlying molecular network in response to applied stress, rendering it liable to nucleate and form filaments aligned parallel to the extensional strain. The second stage is development, on these core filaments as nuclei, of lamellar overgrowths. While the first stage is a direct response to applied stress, this is thought to be largely taken up by the resulting filaments, with the second (lamellar) stage of crystallization occurring under conditions in which strain is much reduced, perhaps to zero (see the review in ref. 1). It should therefore resemble lamellar growth from a quiescent melt at the same crystallization temperature.

In this paper we report observations on a series of polyethylene samples solidified under shear. All possess shish-kebab textures, but each of these differs according to the particular condition of its formation. The actual morphologies agree with general expectations according to the change in shear rate and the variation of lamellar habit with crystallization temperature. However, it is also shown that the lamellar habits differ from those found in quiescent growth and that they are affected and modified by the strain rate. As a consequence a more detailed understanding is achieved, leading to a more confident interpretation of the history of shish-kebab morphologies obtained in general circumstances.

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EXPERIMENTAL

The five samples examined are listed in *Table 1*. They are of a high-density polyethylene, $\bar{M}_w \sim 50\,000$, manufactured by BUNA, Germany. Crystallization, at one of two shear rates and one of three temperatures, was within a rotation rheometer. In this instrument, which has been described previously[2], the sample is contained between two parallel and coaxial circular glass plates, of radius 4 mm; the upper plate remains stationary while the lower can be rotated mechanically. The whole cell is mountable on the stage of a polarizing microscope for textural changes to be observed *in situ*. Quantitative measurements of the intensity of transmitted depolarized light may also be taken to provide a record of the development of orientation and crystallinity.

To prepare samples, polymer was introduced at the axis of the rheometer, heated to 170°C and homogenized (as judged optically) with a brief rotation. The controlled temperature was lowered to the chosen value and rotation commenced, after which the onset and progress of crystallization could be followed by light scattering. The shear rates quoted refer to the tangential velocity of

Table 1 Preparation conditions

Sample	Shear rate (s^{-1})	T_c (°C)
4	7.5	124.5
5	30	124.5
8	7.5	128.5
10	7.5	132.5
11	30	132.5

the lower plate at 3 mm radial distance, divided by the film thickness, which can be as much as 100 μm. Our study is complementary to previous work[3] in which equivalent specimens were examined optically regarding their textural development before, during and after crystallization.

ELECTRON MICROSCOPY

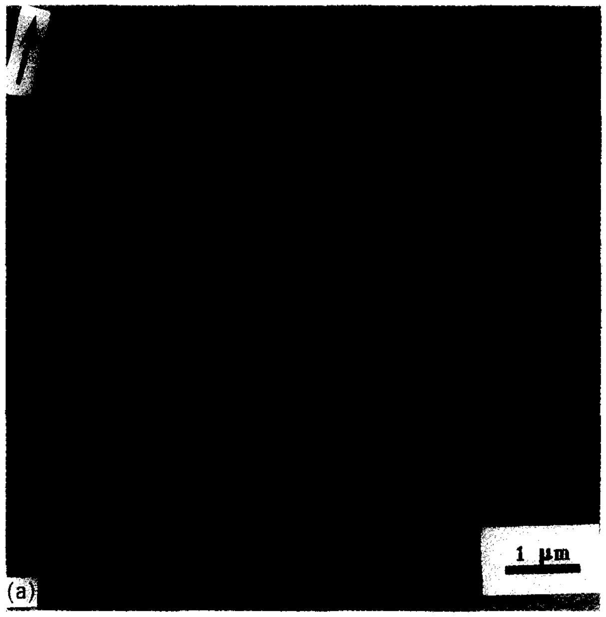
All photographs are of metal-shadowed carbon replicas of specimens after permanganic etching. To this end, the five samples were each etched at room temperature to expose internal surfaces, which were parallel to, but some 10 μm below, the plane of the disc specimens. The composition of the etchant was 0.7% w/v $KMnO_4$ in 1:2 H_2SO_4/H_3PO_4 (refs 4, 5). Subsequent washing according to published procedures[4], then standard two-stage replication produced the specimens used for transmission electron microscopy. The orientation axis is indicated on all micrographs by an arrow.

RESULTS

The principal features of interest are the distribution of shish-kebabs and their dimensions, together with the lateral size and habit of their lamellar component. In *Figure 1a*, which refers to sample 4, i.e. the lowest shear rate and crystallization temperature, individual shish-kebabs appear on the page as near-vertical columns, a few micrometres or more in length, a micrometre or less apart. The detail of *Figure 1b* highlights the associated lamellae, which are seen predominantly edge-on. Most traverse the width of the exposed shish-kebab, as is expected for growth from the central filament sharing with it a common chain axis, ***c***, direction. A few lamellae, however, lie parallel to the orientation axis (e.g. to the right of A), indicating the scale and extent of local inhomogeneity. When a presumed core happens to lie in the etched surface, e.g. AB, it has a width similar to the lamellar thickness and is linked to a sequence of transverse lamellae separated longitudinally by the equivalent of two to three lamellar thicknesses.

Of particular interest is the lamellar profile. Frequently, especially for narrow lamellae, this is approximately linear with undulations, but some (arrowed) are S-shaped (and approximately 1 μm wide). This profile is found in strain-free growth at this temperature[6], when viewed approximately down ***b***, the direction of fastest growth.

Figure 2a illustrates the morphology for the higher shear rate but the same crystallization temperature of 124.5°C (sample 5). Compared to *Figure 1a* the columns of shish-kebab are more numerous with more pronounced relief. They appear longer and are certainly closer together laterally. The lamellae, shown in detail in *Figure 2b*, are similar in thickness to those of the lower shear rate in *Figure 1* but now curved and S profiles are absent. There are still a few lamellae with traces parallel to the orientation axis but the great majority have linear traces normal to the shish-kebab. In addition there are some examples of shallow chevrons, e.g. at lower right above B. Compared to *Figure 1b* there is more core while lamellae are fewer in number, with their longitudinal separation often reduced to about one lamellar thickness. Indeed, towards the left-hand side, there is a column, ca. 0.5 μm wide, of contiguous lamellae (with low depth of relief); this is presumably a region near the core of a shish-kebab.



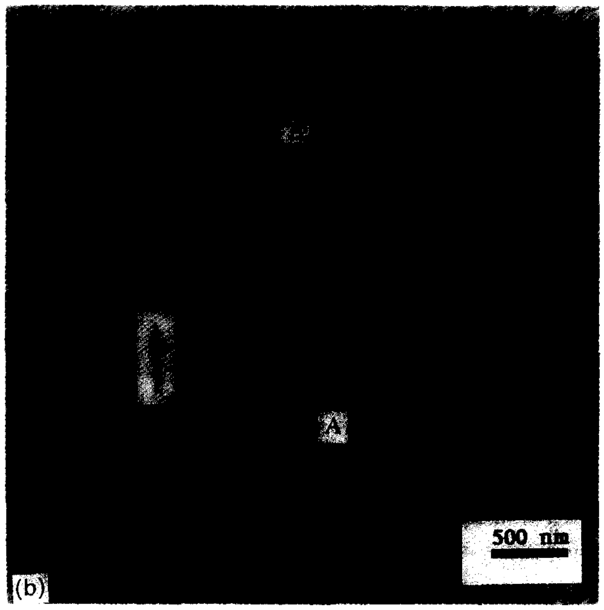


Figure 1 Morphology (a) and detail (b) of linear polyethylene crystallized at 124.5°C and 7.5 s^{-1} shear rate

The morphology changes again for sample 8. In particular, as *Figure 3a* shows, the lamellar width is much reduced. Nevertheless there is an area of considerable lateral lamellar continuity at the upper right where shish-kebabs are in close contact. The lateral separation is often much closer than in *Figure 1*, down to ~ 0.1 μm in places, with longitudinal extensions of 2 μm or more. When lamellae are examined at higher magnification (*Figure 3b*), their traces are seen often, though not always, to be inclined to the orientation axis, at angles of order 30°. This value is similar to the lamellar profiles recorded in earlier studies[6] for polyethylene of this molecular mass, grown from the quiescent melt at this temperature.

Inclined profiles are prominent for sample 10 (*Figure*

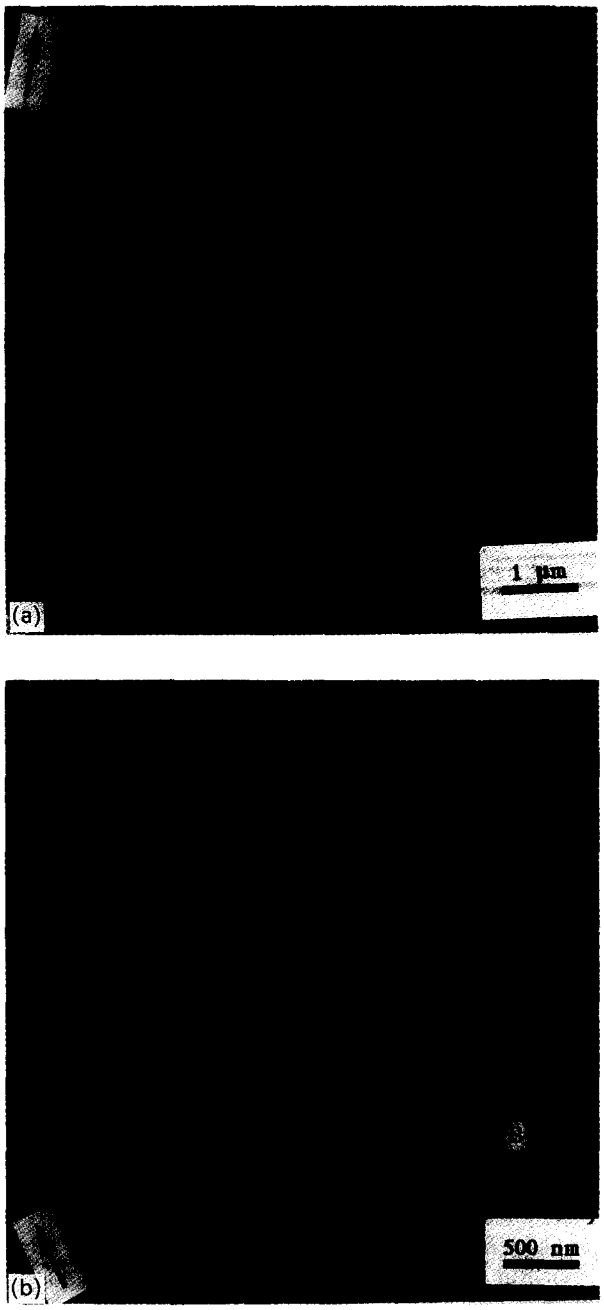


Figure 2 More shish-kebabs develop for crystallization at 124.5°C under the higher shear rate of 30 s^{-1} (a) and detail (b)

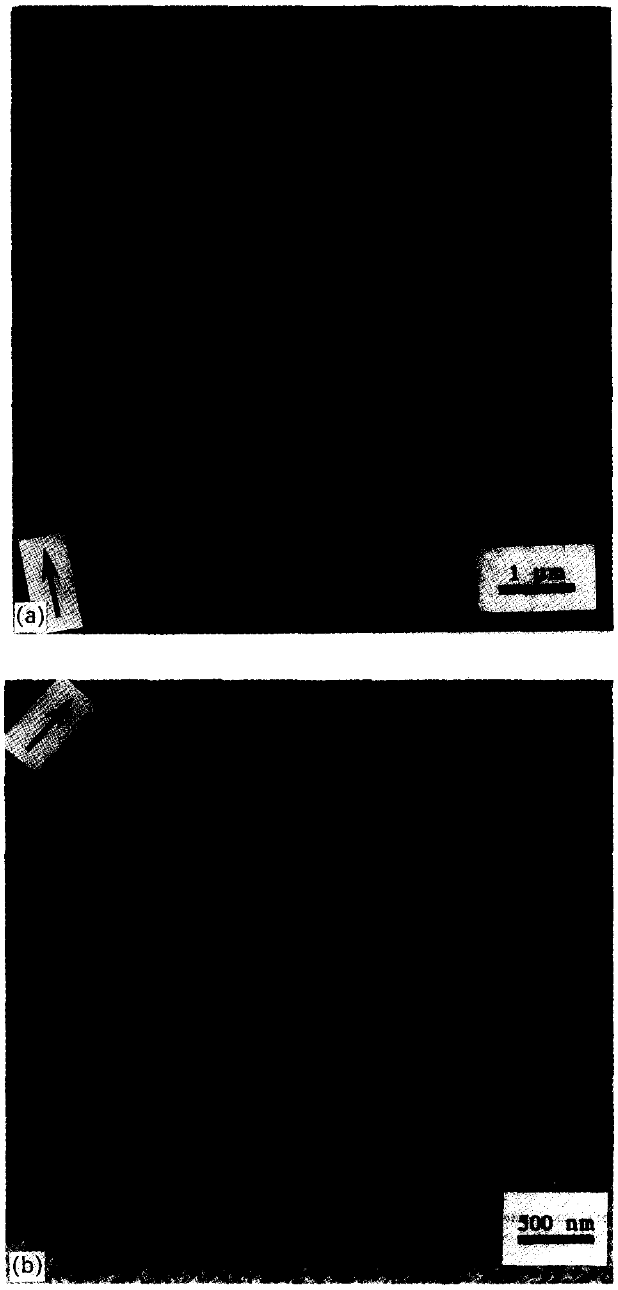


Figure 3 Shish-kebabs grown at 128.5°C and 7.5 s^{-1} shear rate are narrower (a) and contain inclined lamellae (b)

4a) although as *Figure 4b*—which illustrates a less regular area—shows, they are not universal. Note that at this lower strain rate the separation of lamellae is again one or more lamellar thicknesses. However, for sample 11, formed at the higher strain rate and highest crystallization temperature, inclined profiles have disappeared and, with a few exceptions, lamellar traces are normal to the shish-kebabs (see *Figure 5a* and detail in *Figure 5b*). Adjacent areas of sample 11 (which is less uniform that the others) have a different appearance. *Figure 5c* shows wide (~ 2 μm) regions of lamellae transverse to the orientation direction together with one or two displaying their top (fold) surfaces whose planes are substantially parallel to this axis, plus an occasional ridged lamella. The detail of *Figure 5d* identifies also, on the left, a single inclined trace at 30° immediately below the area of top surface and, on the right-hand side, regions where some lamellae lie almost parallel to the orientation axis together with a variety of profiles including ridged (to the right of R) and S profiles (below S). In *Figure 5c*, therefore, we appear to have a juxtaposition of, on the left, an oriented region associated with the applied stress and, on the right, one whose appearance is akin to that for crystallization from a quiescent melt albeit at higher supercooling[6].

DISCUSSION

Shish-kebab morphologies were encountered very early in studies of polymer textures and were soon recognized to result from crystallization under extensional strain (see ref. 1 for a review). They appear under a wide range of conditions, which extends across growth from

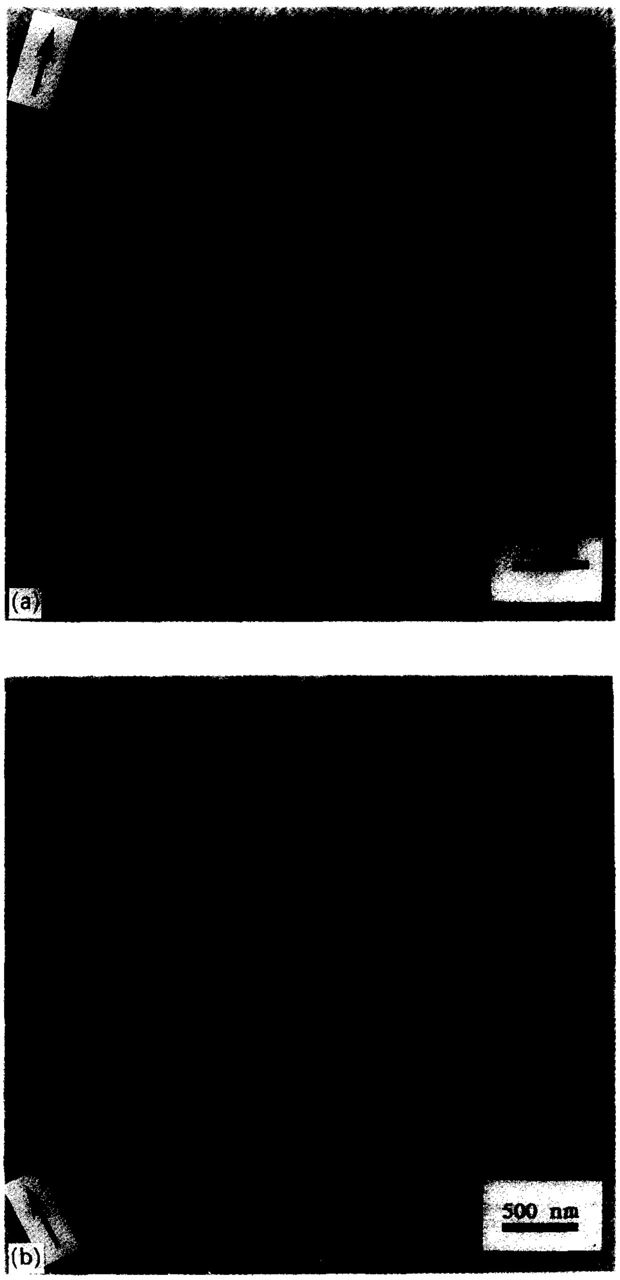


Figure 4 Inclined lamellar texture (a) and detail (b) in shish-kebabs crystallized at 132.5°C and 30 s^{-1} shear rate

solution and from the melt[7]. An early investigation of natural rubber crystallized while stretched[8] identified columns of lamellae aligned along the tensile axis (with individual layers normal to it), evidently deriving from a common linear nucleus; the number of such nuclei increased with applied stress. Several studies, especially those employing nitric acid to etch polyethylene, revealed similar columnar structures in oriented polymers[1]. In a wide-ranging investigation of how the nature of shish-kebabs varied with the applied strain during crystallization, Keller and Machin[9] examined films of crosslinked polyethylene, thin enough for transmission electron microscopy. They also found that, with increasing stress, the density of nuclei increased, together with the alignment of lamellae, but that the 'lamellar twisting typical of polyethylene' decreased.

The consensus of understanding reached following these and similar studies is that crystallization under strain occurs in two stages. First, linear (row) nuclei, consisting of chains with substantial extension, are formed parallel to the strain direction. Secondly, chain-folded lamellae grow on these epitaxially, sharing the same chain-axis orientation. Because the row nuclei, once formed, carry most of the applied load, the crystallization is expected to be effectively strain-free and to resemble the lamellar growth from quiescent systems[1].

In succeeding years the importance of purely extensional strain for increasing chain extension has been recognized[10]. Crystallization is facilitated when molecules are mutually aligned with no relative motion and do not rotate with respect to the extensional stress. Nevertheless, nucleation and oriented crystallization can be promoted by macroscopic simple shear stresses[11]. In our experiments it may well be that attachment of molecules at the external surfaces of what are macroscopically thin films effectively mitigates the internal rotation implicit in simple shear to allow the effects of extensional flow to be revealed.

The observations of this paper take the understanding of shish-kebab morphologies forward, taking advantage of two circumstances. In the first place the samples are of a typical polyethylene homopolymer that has been neither crosslinked nor prepared in very thin films to allow its observation. This is possible because of the development of techniques of permanganic etching for the examination of representative morphologies within melt-crystallized polymers[4,5]. Their use has produced the second advantage, namely a good knowledge of the lamellar morphology of polyethylene crystallized from a quiescent melt over a wide range of relevant variables[6]. One can, therefore, draw more authoritative conclusions concerning the crystallization conditions under which the lamellar component actually formed and show that, especially as shear rate increases, crystal habits are modified and fold surfaces assume higher energy states.

Our observations are, first of all, consistent with the expectation that higher strain rates will produce more nuclei, partly because of greater molecular extensions but also because of the involvement of a higher proportion of the longer molecules in the sample. This is evident by comparison of *Figures 1a* and *2a* and also *Figures 4a* and *5a* (LHS), which refer to crystallization at 124.5°C and 132.5°C respectively. It also appears that shish-kebab cores and hence nuclei are shorter at the lower shear rate: see especially *Figure 3a*. Such behaviour shows not only that greater extensional strain is being achieved at higher shear rates but also that crystallization has been able to proceed notwithstanding the application of a simple shear rather than a purely extensional stress.

Shish-kebabs with their linear cores and transverse lamellae are generally tangential to the disc-shaped specimen. When, therefore, lamellae are seen that are parallel to the rows (e.g. *Figures 1b*, *2b* and *5d*), it is likely that they have formed on a transverse nucleus, arising from transverse extension of the molecular network because of some local perturbation of flow.

The width of lamellae would be expected to decrease with both higher strain rates and higher crystallization temperatures. This is because size is determined by the ratio of nucleation to growth rates: more nuclei give

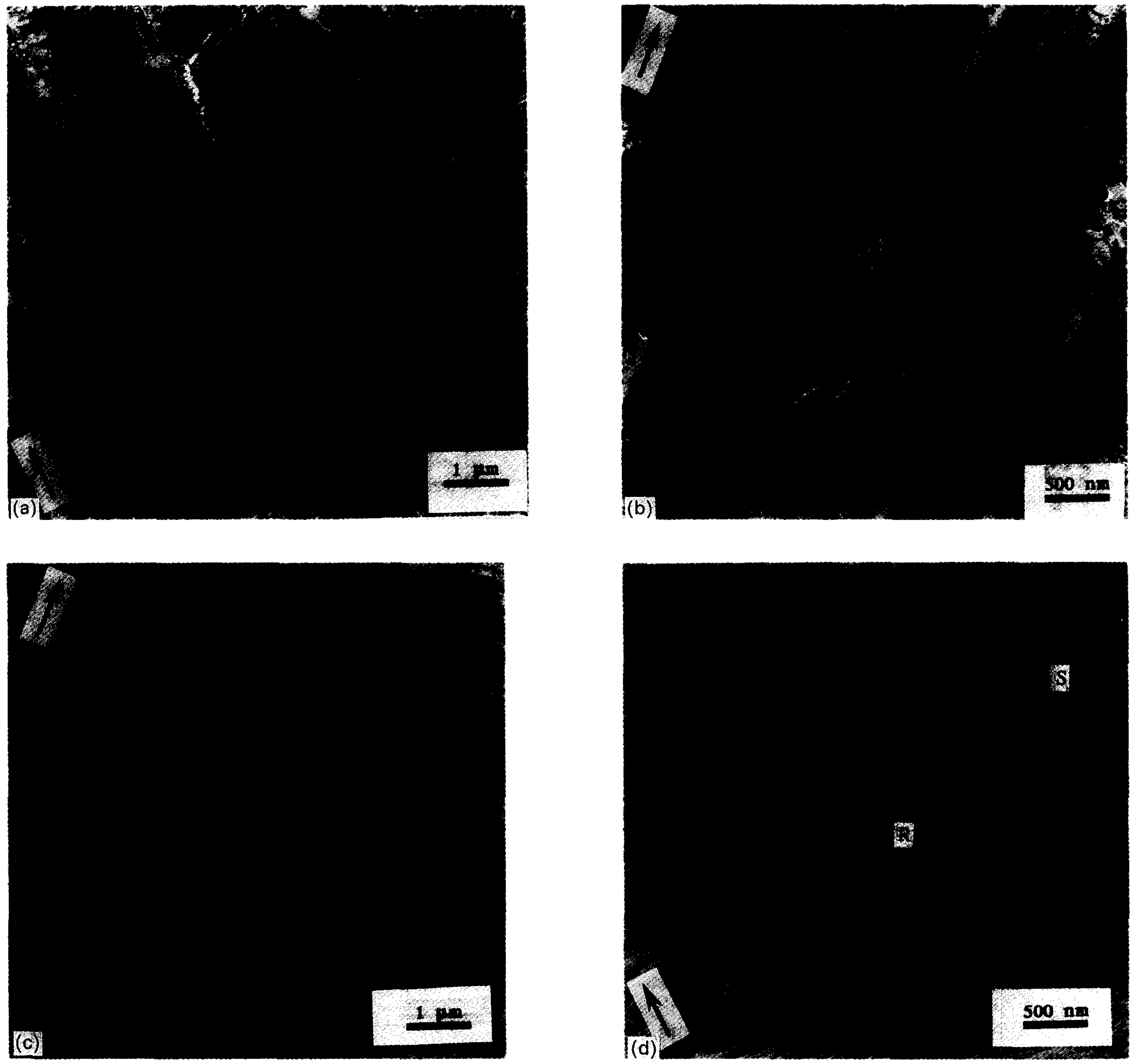


Figure 5 When crystallized at 132.5°C at $30 s^{-1}$ shear rate shish-kebabs have lamellar normals parallel to rows (a) and detail (b). There are also adjacent areas (c) and detail (d) in which lamellae develop profiles resembling those for quiescent crystallization, e.g. ridged (right of R) and S-shaped (below S)

smaller lamellae. As nucleation rate increases with strain rate while growth rate falls with rising temperature (i.e. less supercooling), the cited changes in morphology are anticipated. They are also observed, for example, in a comparison of *Figures 1a* and *2a* and *Figures 1a* and *3a* respectively.

Particular interest attaches to the shape of lamellae, especially to their profile and its relation to the chain axis direction ***c*** (indicated by the length of the core nucleus). One expects the photographs to show this principally in ***b*** projection because ***b*** is the fastest growth direction and consequently assumes the radial direction both in polyethylene spherulites and as here in shish-kebabs. Moreover, recrystallization on macroscopic fibres as nuclei proceeds with ***b*** as radius; other directions may be nucleated but do not propagate[12].

Polyethylene lamellae grown from a quiescent melt at 124.5°C from 50 000 mass polymer possess one of two profiles[13,6]. Those which form first, the dominant lamellae, are systematically curved and frequently S-shaped when viewed down ***b***, the fastest growth direction. Those which form later and occupy the space between the dominants are narrower and planar; they will also contain the shorter molecules within the sample. Concerning the present observations, it is known that lamellae which crystallize from row nuclei are effectively all dominants and, in other circumstances, have been observed all to have S profiles[14]. Here, in *Figure 1b*, there are just a few S profiles but most have more nearly linear, sometimes undulating, traces similar to earlier observations[9]. The comparative paucity of S profiles, even allowing for the consequences of fractional crystallization, demonstrates that in these experiments, while some lamellae grew in strain-free conditions, the majority did not.

Sample 5 (*Figure 2*), which was grown at the higher shear rate, has lamellar habits that show no curvature. They are not typical of growth under strain-free conditions at this growth temperature. Their fold surfaces are normal to the chain axis, as opposed to the preferred inclination of $\sim 35°$ for freely grown lamellae[13]. In consequence the surface energy will be raised, for which the strained conditions of growth must be responsible.

The preferred habit at 128.5°C and higher temperatures for polyethylene of this molecular weight is planar lamellae[6] with fold surfaces near $\{2\,0\,1\}$. *Figure 3b* shows a preponderance of lamellae with normals inclined to their rows but by rather less than the $\sim 35°$ of strain-free growth. Here and in *Figure 4b*, where there is a distribution of inclinations between 0° and 35°, the crystal habit is evidently being influenced by the strain field, with a tendency to reduce the chain inclination to lamellar normals and consequently to raise surface (free) energies.

With the imposition of the higher shear rate for sample 11, *Figure 5b* shows that the reduction of inclination is effectively complete and lamellae have become normal to rows. However, in the same specimen (*Figures 5c* and *5d*) are areas some micrometres in size, and adjacent to rows, in which lamellar habits are akin to those formed in quiescent conditions at lower temperatures. Here (*Figure 5d*) are S-profiled and ridged as well as planar lamellae. The growth temperature of 132.5°C is at least 2 K higher than the effective maximum value for this molecular mass under quiescent conditions and 5 K or more above that giving a similar growth rate and/or comparable lamellar profiles without applied strain. The melt must, therefore, still be subject to significant strain to increase the effective supercooling (by decreasing the entropy of the melt), even though the flow pattern has become heterogeneous.

The final point to discuss is the separation between adjacent lamellae of the shish-kebabs. The trend of our observations is that the separation decreases with strain rate (compare *Figures 1b* and *2b* and *Figures 4b* and *5b*) and near the centre of the row (*Figure 2b*). A recent paper[15] has suggested that the cause of the frequent separation between lamellae of a shish-kebab is the pressure of uncrystallized molecular cilia protruding from fold surfaces. This is an extension of the suggested origin of the divergence of dominant lamellae intrinsic to the development of spherulites[15,16]. Such cilia will have a rubbery modulus and will readily be compressed with the application of stress. Our observations are qualitatively accounted for on this basis. Nevertheless contiguous lamellae have recently been observed in the recrystallized component of compacted fibres[14], an analogous system to row nucleation. This is probably related to crystallization conditions that are likely to approximate to constant volume, leading to the compression of molecular cilia by raised hydrostatic pressure. A consistency of interpretation would thus underlie crystallization in the different circumstances.

CONCLUSIONS

This paper has shown the following:

The morphology of shish-kebabs crystallized from a sheared melt of linear polyethylene changes sytematically with growth temperature and strain rate.

The increased number and length of filaments with higher strain rate is in accord with expectation.

At higher strain rate, lamellae are planar with normals along their rows raising their surface free energy, but at lower strain rate inclined and S-profiled habits are present. The modified habits and the inferred increasing supercooling at high crystallization temperatures both imply that lamellae in shish-kebabs have not grown under strain-free conditions.

The longitudinal separation of lamellae present at low strain rates and its absence at high strain rates may be rationalized in terms of the properties of molecular cilia emerging from fold surfaces, thereby extending the explanation offered for the essential divergence of lamellae creating polymer spherulites[15,16].

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REFERENCES

1 Peterlin, A. *Pure Appl. Chem.* 1973, **8,** 277
2 Melior, J.-P. PhD Dissertation (Teltow-Seehof), in preparation
3 Moneva, I. T., Sokolov, A., Melior, J.-P., Hirta, R. and Michaeilov, M. Proc. 13th Disc. Conf. Prague, 1990, p.70 and in preparation
4 Olley, R. H., Hodge, A. M. and Bassett, D. C. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17,** 627
5 Olley, R. H. and Bassett, D. C. *Polymer* 1982, **23,** 1797
6 Bassett, D. C., Hodge, A. M. and Olley, R. H. *Proc. R. Soc. (A)* 1981, **377,** 39
7 Bassett D. C. 'Principles of Polymer Morphology', Cambridge University Press, Cambridge, 1981
8 Andrews, E. H. *Proc. R. Soc (A)* 1964, **277,** 562
9 Keller, A. and Machin, M. J. *J. Macromol. Sci.-Phys. (B)* 1967, **1, 41**
10 Frank, F. C. *Proc. R. Soc. (A)* 1970, **319,** 127
11 Grubb, D. T. and Keller, A. *J. Polym. Sci., Polym. Lett. Edn.* 1974, **12,** 419
12 Kabeel, M. A., Bassett, D. C., Olley, R. H., Hine, P. J. and Ward, I. M. *J. Mater. Sci.* 1995, **30,** 601
13 Bassett, D. C. and Hodge, A. M. *Proc. R. Soc. (A)* 1981, **377,** 25
14 Olley, R. H., Bassett, D. C., Hine, P. J. and Ward, I. M. *J. Mater. Sci.* 1993, **28,** 1107
15 Bassett, D. C. *Phil. Trans. R. Soc. (A)* 1994, **348,** 29
16 Bassett, D. C. in 'Comprehensive Polymer Science-1' (Eds C. Booth and C. Price), Pergamon, Oxford, 1989, p.841