# A new route to high modulus polyethylene by lamellar structures nucleated onto fibrous substrates with general implications for crystallization behaviour*

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In the case of recent experiments with polyethylene involving nucleation of lamellar crystals along flow induced fibrous substrates unexpectedly high modulus (up to $10^{11}$ N/m$^2$) filaments were obtained in spite of the fact that the samples consisted predominantly of lamellar material. This finding has led to reconsideration of the requirements for high moduli in general providing explanation for our observation and indicating new routes for the attainment of high moduli. In brief, the principle is that high modulus need not require complete chain extension and can be generated by lamellar crystals. We identify the following conditions as necessary: (1) the lamellae are all parallel; (2) the plane normals are along the tensile direction; (3) the straight chain segments within the lamellae are also parallel to the tensile direction (hence perpendicular to the lamellar surfaces); (4) the lateral extension of the lamellae in all directions is large compared to the lamellar thickness; (5) there is intimate and strong contact between consecutive lamellae piled onto each other; (6) there is interlocking between lamellae in lateral contact. It is shown how and why these conditions are fulfilled by our lamellar samples of ultra-high modulus while additional reasons for the observed stiffness are being looked for. It is noticeable that samples based on lamellar morphology have advantages over the more usual high modulus material of purely fibrous nature as obtained along more conventional routes. The issue of modulus apart, the lamellae of tapering thickness in our samples (the morphological feature meeting requirement 6) imply the presence of folds of unprecedently short stem lengths which raise new issues in crystallization studies, notably relating to crystallization of chains in confined spaces, and opens up avenues towards the visualization of space filling by lamellae in bulk samples in general.

## INTRODUCTION

The values of modulus and strength in the chain direction of polymer crystals are known to be very high due to covalent bonding along the chains, whilst the moduli perpendicular to the chain direction are typically two orders of magnitude lower: hence near perfect chain orientation is a prerequisite for the achievement of high modulus and tensile strength in the bulk polymer. Nevertheless conventionally oriented materials do not begin to approach the theoretical values in spite of the evidence that the samples are practically perfectly oriented, with the chains along the fibre direction.

Ever since the recognition of chain-folding this has been attributed to the fact that near perfect *c*-axis orientation can be realized by stacks of lamellae or chain-folded blocks with straight stem directions all parallel[1]. In the light of this, recent efforts have been directed towards the achievement of high chain extensions in addition to chain orientation. Most research has been made along three distinct directions: orientation of chains in the solid state by ultra-drawing[2,3] or extrusion[4] of crystalline material; prealignment of chains in solution followed by subsequent crystallization[5,6] and the analogous process in the melt, where the chains are usually aligned by an extrusion process[7,8].

Considerable progress has been made by the first two techniques, but alignment and crystallization from the melt, although successful for the study of fundamentals has not led to high modulus products.

The prime reason for this lies in the fact that if solid fibres with the desired properties form in abundance they block the flow system, or conversely if they are sufficiently few in number to pass through the extrusion orifices, lubricated so to speak by the still uncrystallized melt, they represent too small a fraction of the total material to enhance the modulus of the resulting product significantly.

To quote figures for the relevant scale of modulus: estimates of the modulus along the chain direction in the crystal vary between 2.4 and 3.6 x $10^{11}$ N/m$^2$ [9,10]. Unoriented bulk polyethylene has a Young's modulus of about $10^8$ N/m$^2$, conventionally drawn fibres have a modulus along the draw direction of about 5 x $10^9$ N/m$^2$. The new improved methods of hot drawing and the latest fibres crystallized from stirred solutions have moduli in the range 5–10 x $10^{10}$ N/m$^2$. All these highly chain-extended materials suffer the disadvantage that they fibrillate very easily.

Here we shall report a new principle leading to the attainment of ultra-high modulus. The material prepared is of a predominantly lamellar morphology, and is far less prone to fibrillation. In addition the results raise some new issues as regards bulk morphology and chain folding in general.

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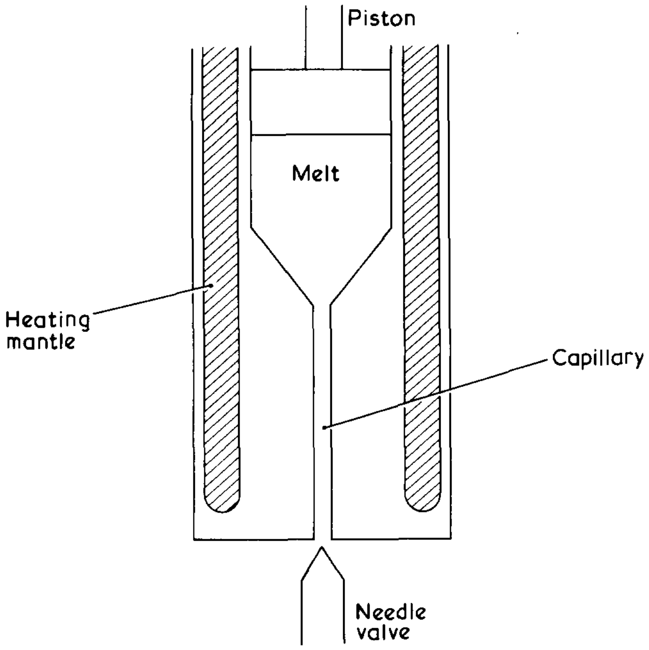

*Figure 1* The extrusion apparatus

## SAMPLE PREPARATION AND PROPERTIES

The new findings have arisen through studies of solidification in capillaries during melt flow, as a follow up to the original studies of Van der Vegt and Smit[11] and Porter and cowoi-kers[12]. Under these conditions crystallization can occur at higher temperatures than usual and the resulting products can have much improved moduli[13]. Our original objective was to isolate the two processes involved in the formation of such products, namely flow-induced crystallization, and subsequent solid-state extrusion of the crystallized product.

The method pursued is developed from that originally used by Porter *et al.*[12] and has been described in detail elsewhere[14]. Here some of the essentials will be briefly recapitulated. The apparatus consists of an Instron melt rheometer, with capillary die. The exit of the die is blockable by an external needle valve as shown in *Figure 1*.

Firstly melt extrusion conditions are set up (typically, for a 1 cm diameter barrel and a 1 mm capillary using rigidex 9; the plunger rate is 0.1 cm/min for a temperature of 142°C and a barrel pressure of $10^7$ N/m$^2$).

These particular conditions are arrived at by studying the flow system using a glass capillary, and are known to be favourable for the production of fine fibrils in the melt[14]. The onset of formation of fibrils is accompanied by a slight rise in pressure.

When a set degree of fibrils has formed the capillary exit is blocked by the needle valve. The fibrils still represent only a small fraction of the material, attempts to increase the volume fraction of fibrils invariably results in self-blocking in the capillary, and poorly controlled solid state extrusion.

The pressure is allowed to rise at a controlled rate, up to $2 \times 10^8$ N/m$^2$. This results in the crystallization of the remaining polymer. The assembly is cooled under pressure, and the extruded plug removed.

The measurement of Young's modulus along the extrusion direction presented special problems. Great care is necessary to avoid errors due to end-effects in these comparatively low aspect ratio, highly anisotropic samples. This difficulty was obviated by high resolution photography of the specimen[14] with appropriate reference marks on its surface, during a tensile test. Analysis of the photographic negatives then yielded a direct measurement of the distribution of strain along the surface of the sample. It was found that nearly 90% of the overall strain applied to the sample was accommodated in the end regions. Near the sample centre the strain was uniform over about 3 cm, it was this region which was used in the determination of moduli. A typical stress–strain curve is shown in *Figure 2*. The modulus measured in this way lies typically in the range 5–9 x $10^{10}$ N/m$^2$. Wide-angle X-ray diffraction (*Figure 3*) and optical birefringence measurements indicated practically perfect *c*-axis orientation.

The remarkable fact, however, was that such samples were almost entirely lamellar in structure, as shown by intense meridional low-angle X-ray maxima in the region of 300 Å (*Figure 4*) and by strong low-frequency Raman scattering peaks, corresponding to the *LA* mode vibration of the straight stems (*Figure 5*). The lamellar morphology was ultimately verified by electron microscopy of ultra-thin sections, stained by the Kanig technique[15]. A 'shish-kebab' structure was revealed (*Figure 6*) with lamellar overgrowths forming the greater part of the material, all aligned and per-

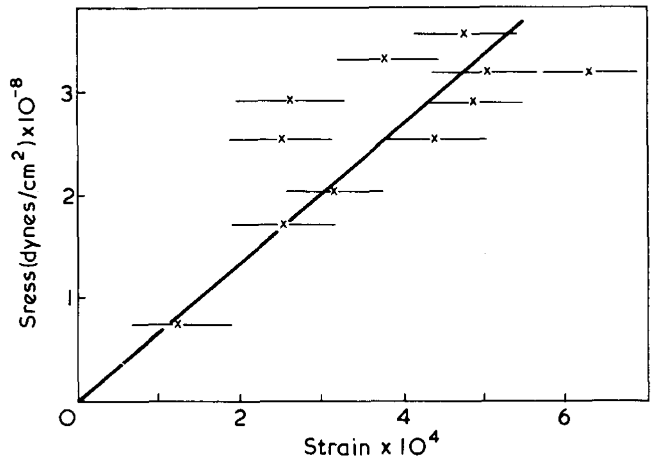

*Figure 2* Stress–strain curve of a high modulus fibre parallel to the extrusion direction used for determination of modulus

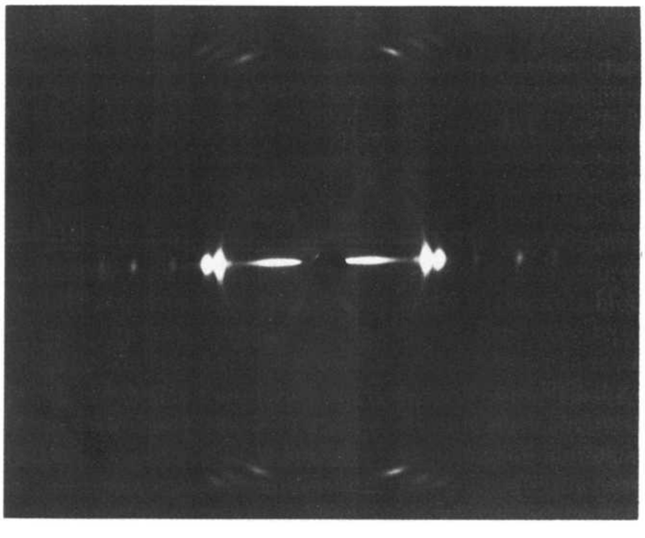

*Figure 3* Wide-angle X-ray diffraction pattern with the extrusion direction vertical

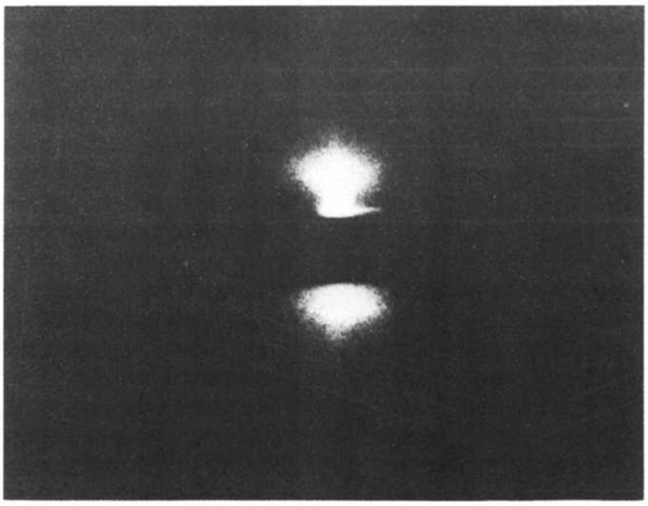

*Figure 4* Low-angle X-ray diffraction pattern, extrusion direction vertical, corresponding to a spacing of about 300 Å

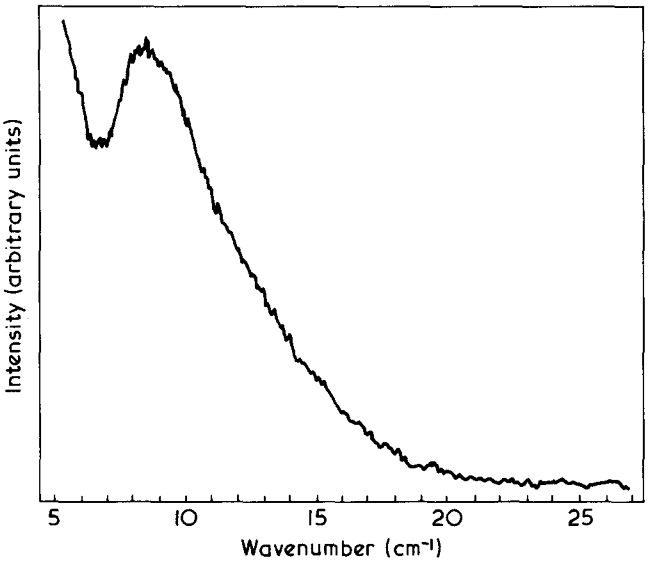

*Figure 5* Raman *LA* mode peak, corresponding to a straight stem length of about 400 Å

pendicular to the extrusion direction. The overall shish-kebab arrangement is best seen in specially heavily stained samples (*Figure 7*) which allow the central backbone to be revealed due to the fact that it appears to be singularly resistant to stain. The lamellar structure itself is clearly apparent but as comparison with a lightly stained sample reveals strongly swamped by the staining agent. For fine structural details in the lamellae the lightly stained samples as in *Figure 6* are therefore more appropriate; however here the backbone itself remains invisible.

This material does not contract as it is heated up towards the melting range, as opposed to the familiar contractile behaviour of highly drawn, or solid-state extruded material. The samples are most amenable to the hot stage microscopic test described in ref 16. *Figure 8* shows the view in the polarizing microscope as the sample is heated. Long macrofibres of birefringent material can be seen, which progressively disappear as the temperature is raised. These fibres are still capable of forming crystal nucleation centres on cooling even after the melt has been heated to 160°C.

*Figure 6* Electron micrograph of a thin section cut parallel to the extrusion direction (arrowed). The structure is stained by uranyl acetate. The fine striated structure corresponds to lamellae seen edge on, where the stained amorphous regions appear dark

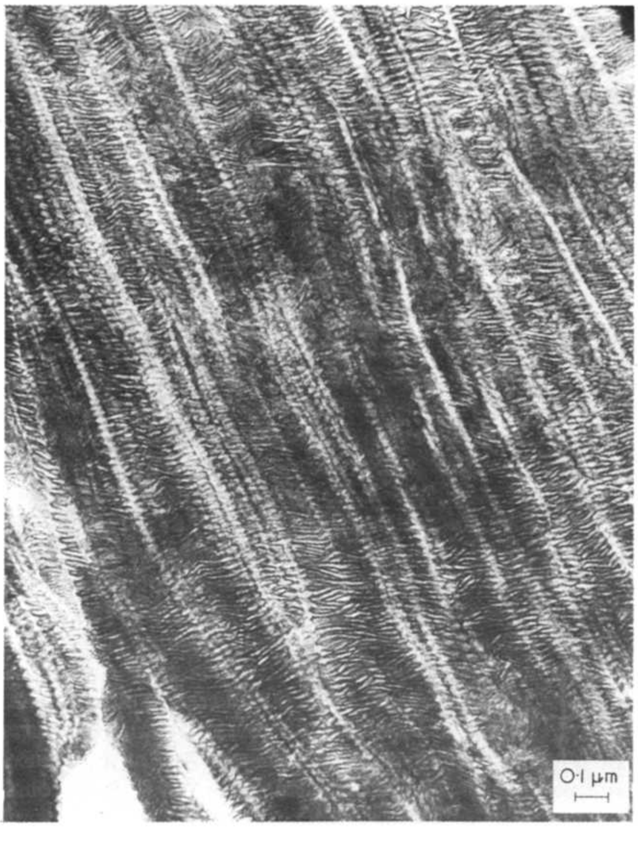

*Figure 7* Electron micrograph of a more heavily stained sample revealing the overall columnar structure with central backbones

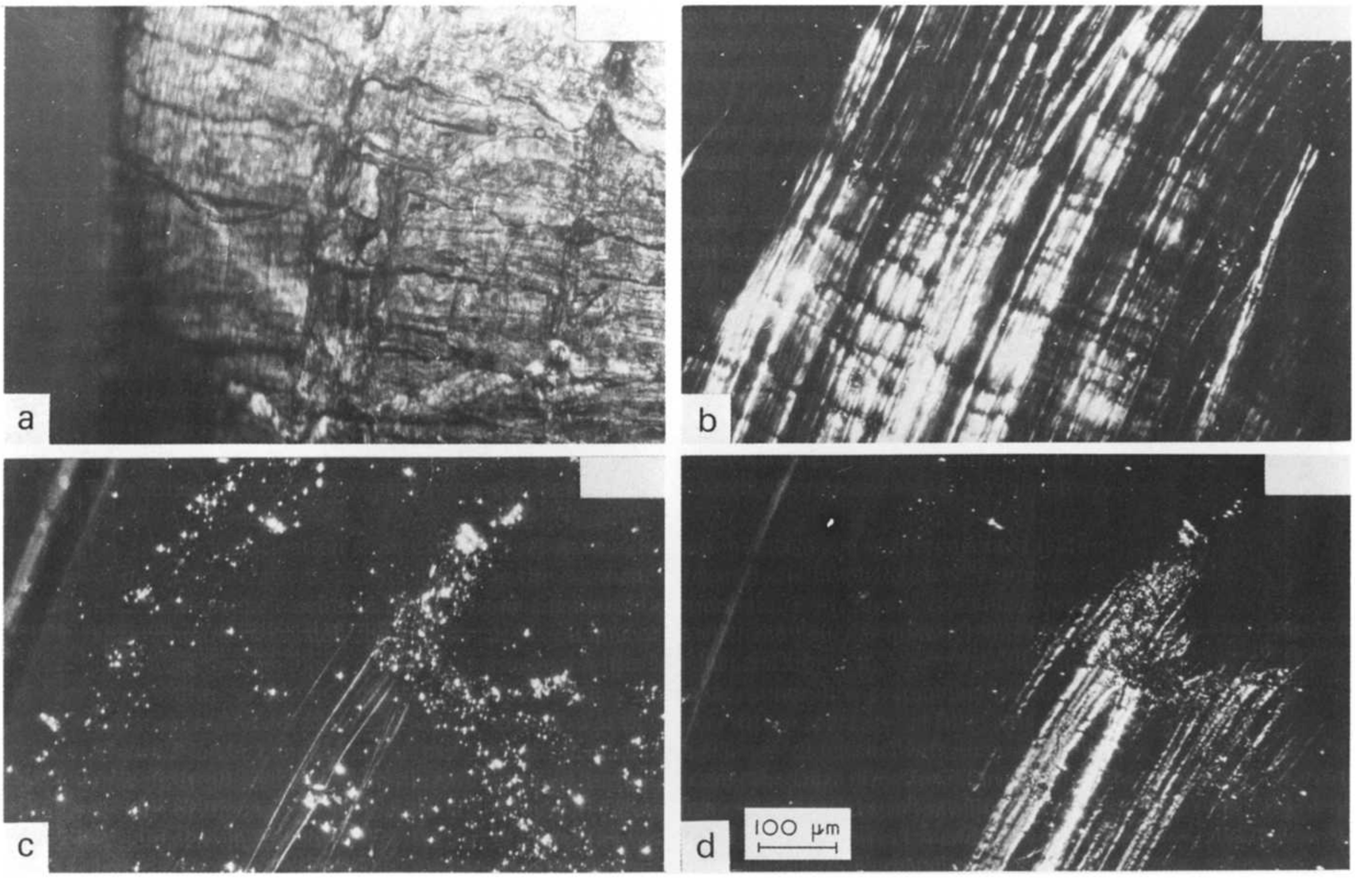

*Figure 8* Micrographs of the structure taken in the hot stage of a polarizing microscope. (a) At 133°C, there is little change from room temperature; (b) at 138°C, the specimen consists of birefringent rods in an isotropic matrix of the melt; (c) at 142°C, some rods persist; (d) at 130°C, after cooling from 142°C, rapid recrystallization occurs nucleated by the remaining rods

It should be pointed out that the combined occurrence of flow induced fibre formation and pressure rise during the subsequent quiescent crystallization were required for the achievement of the high modulus. As already mentioned[14] the quantity of fibres in itself was insufficient, and application of pressure on its own was ineffective (incidentally, the pressures are below those required for the formation of the familiar extended-chain crystals).

## MECHANICAL PRINCIPLES

In this section we shall discuss the mechanical principles of lamellar composite systems in general, and in particular how these relate to polymer systems. Our starting point will be the mechanical behaviour of a parallel layer composite consisting of alternating layers of stiff and compliant material. Such a model can be appropriately applied to lamellar semicrystalline polymer systems. In the present case the crystalline lamellae are considered as the stiff material, whilst the amorphous polymer lying between lamellae is the compliant material, as shown in *Figure 9*.

For tensile deformation perpendicular to the layer planes the two types of layer are coupled in series, i.e. they will both bear the same stress. However, they will not be able to extend as they would independently under this stress due to mutual constraints. Specifically the more compliant layer will be prevented from contracting laterally by its attachment to the stiffer layer, this will in turn reduce its extension parallel to the stress direction.

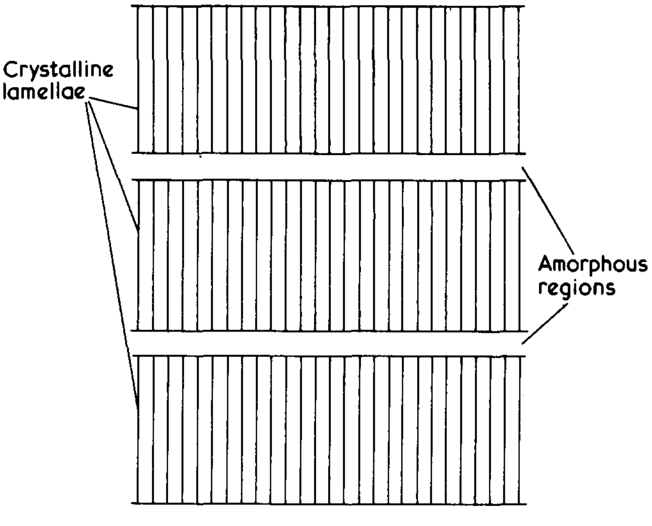

*Figure 9* A diagrammatic representation of a lamellar polymer in the arrangement appropriate for our samples

A similar problem in elasticity has been studied by Gent and Lindley[17] for the two dimensional case of a long 'lath' of rubber joined on its upper and lower surfaces to rigid end blocks as shown in *Figure 10a* and for the more appropriate three dimensional system of layers of discs shown in *Figure 10b*. They assumed a specific deformation of the rubbery material, and showed that the effective Young's modulus of the system could be much enhanced.

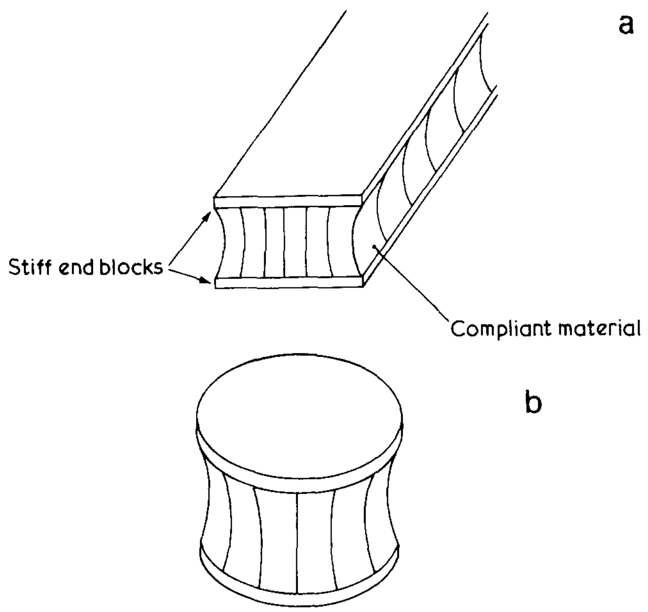

***Figure 10*** Models of lamellar structures of finite lateral extension as used in elasticity theories. (a) Two-dimensional 'laths'; (b) three-dimensional stacked discs

Arridge has solved exactly the two dimensional case by the Fourier series method[18] and his solution corresponds closely with Gent and Lindley's for thin lamellae and incompressible rubber (Poisson's ratio = 0.5). As the Poisson's ratio deviates from 0.5 (that is the bulk modulus is considered non-infinite) the overall effective modulus is reduced.

Treating the situation at its simplest a rubbery domain constrained from contracting in two dimensions (equivalent to lamellae of infinite lateral extent), stretched in the third dimension will exhibit a stiffness characteristic of its bulk modulus rather than its Young's modulus in that direction.

Now consider semicrystalline lamellar polyethylene. Unoriented amorphous polyethylene has a Young's modulus of the order of $10^8$ N/m$^2$. However, the bulk modulus of amorphous polyethylene at room temperature has been estimated by extrapolation of measurements made on the melt to be $3.5 \times 10^9$ N/m$^2$. This value agrees well with that reported by Parkes and Richards[19]. A rough calculation based on series coupling of stiff lamellae and rubbery amorphous material for a crystallinity of 75% predicts a Young's modulus of about $1.4 \times 10^{10}$ N/m$^2$ This is a minimum value ascribing only rubber-like properties to the amorphous material, and the maximum possible thickness to the amorphous layer.

Parallel lamellar structures have been realized before; why then have the moduli of these materials not approached even this figure? It follows from the previous section that the polymer chains are required to be perpendicular to the lamellar surfaces. In most previous studies of polyethylene at any rate, this was not the case: the chain segments were inclined in the lamellae. An example of such a structure is shown in *Figure 11*. This is an electron micrograph of a thin section of oriented polyethylene, prepared by drawing, rolling and annealing[20,28]. The lamellae are arranged in stacks with a double orientation of lamellar normals giving this unique herringbone pattern. Wide-angle X-ray diffraction shows the polymer chains to be highly oriented, parallel to the stacking direction, and hence tilted in the lamellae. This is shown diagrammatically in *Figure 12a*. Tilting of chains in the lamellae can also lead to a structure of lamellar normals parallel to the fibre axis, with the chains tilted[21] as shown in *Figure 12c*, or to a structure between these two extremes (*Figure 12b*). When tensile stress is applied to such systems along the fibre direction in the case of *Figure 12a* there will be easy shear along the oblique lamellar interface (lamellar slip), in the case of *Figure 12c* there will be easy shear along the chains within the lamellae (chain slip).

Either effect will prevent the achievement of a high modulus. For the full reinforcement of the system to be effective the situation as in *Figure 9* must pertain. How then does the present material fulfil these requirements?

The first point to note is that the initial crystallization products are fibrous crystals induced by elongational flow. It is these fibres which provide an epitaxial substrate for the crystallization of the rest of the material; this is substantiated by the fact that the crystal orientations are identical in the two consecutive crystallization processes, as revealed by X-ray diffraction.

This 'row-nucleation' effect is a well recognized feature in the crystallization of melts involving flow[25]. *Figure 13* recapitulates the essentials. Both *Figure 13a* and *13b* represent columns of crystallized lamellar material, in each case nucleated by a long central fibre. In *Figure 13a* the lamellae twist as they would in a spherulitic system leading to randomization of the *c*-axis with respect to the fibre axis. In *Figure 13b* the lamellae are all parallel with the *c*-axes all uniformly aligned along the fibre direction. Clearly the conditions of *Figure 13b* are a prerequisite for a high modulus system. In earlier works[25–27] textures (a) and (b) were attributed to low and high stress during crystallization of a stretched network system. This does not apply in the present

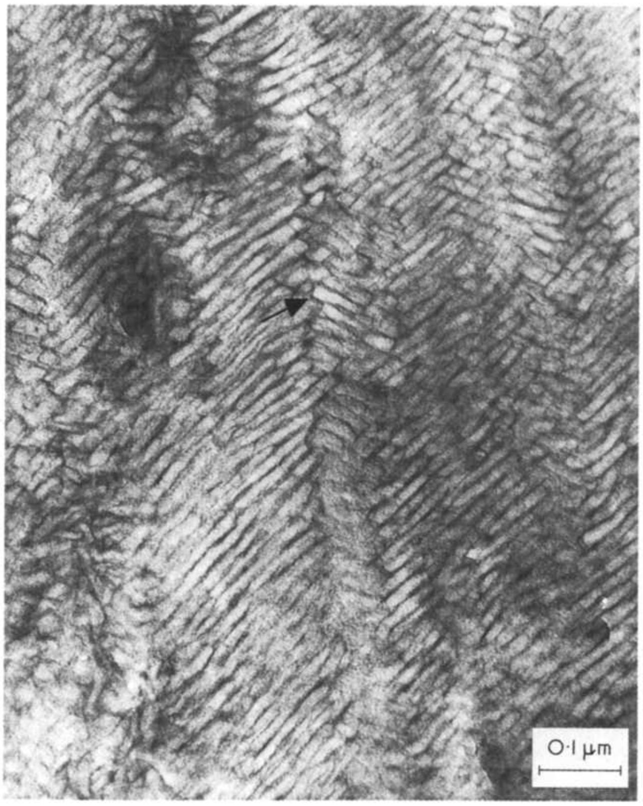

***Figure 11*** Electron micrograph of a thin section of drawn, rolled and annealed material, stained in uranyl acetate. Here the chain direction is vertical with inclined lamellar surfaces, giving the characteristic herringbone pattern[28]

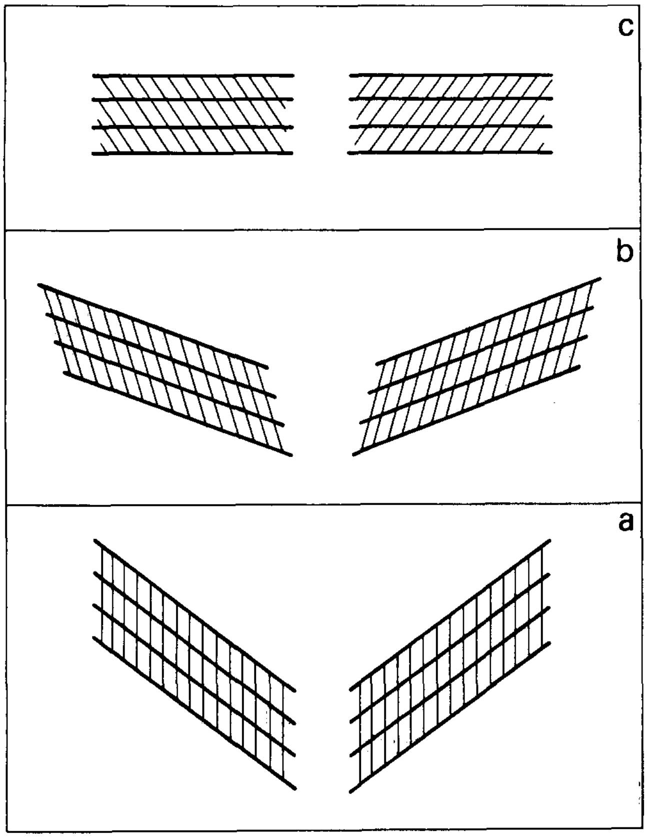

*Figure 12* Diagrammatic representation of lamellar systems in which the chains are not perpendicular to the lamellar normals. (a) Chains parallel, lamellae tilted corresponding to *Figure 11*. (b) Intermediate case between (a) and (c). (c) Lamellae parallel, chains tilted

case, since the nucleated lamellar crystallization occurs under essentially unstressed conditions.

We believe that twisting is prevented in the present system by the close proximity of microfibril nucleation centres, which in the present case are only about 1000 Å apart. This limits the size of the crystal overgrowths and the surface area available for nucleation and ensures that each nucleation event produces a whole new layer of crystal, so that the whole overgrowth is crystallographically coherent. Even special considerations apart, twisting would be impossible on this scale without unrealistically large lattice strains. Thus nucleation by the pre-existing fibril nuclei in itself ensures initial crystal *c*-axis alignment in the lamellar overgrowths, whilst the closeness of nucleation prevents twisting and preserves the crystal orientation throughout growth.

The requirement of both chain segments and lamellar normals being parallel to the fibre direction is necessary for the achievement of a high modulus, but not sufficient. The 'hard elastic' fibres[22] appear to fulfil these conditions, and yet their initial Young's modulus along the fibre direction is not much greater than that of unoriented material. It has been shown that these materials deform by a process of bending or recoverable shear of lamellae between comparatively few tie points; it is this process which is responsible for the high strain recoverability of these polymers. In order to achieve a high modulus, therefore, we must specify the additional condition that the bonding between layers should be sufficient to prevent disruption on the application of stress. At present little is known about the bonding between lamellae in the present system, but at the very minimum the lamellae are tied at the shish-kebab backbones, which in itself imposes a frequency of tie points about 100 times greater than that observed in the 'hard elastic' fibres.

It is noteworthy that the observed modulus of our material is considerably higher than achievable by an amorphous–crystalline alternating layer structure based on the preceding considerations involving the bulk modulus of the amorphous component, a difference beyond the uncertainties in the conventional parameters used. Consequently further sources of stiffening are required. Such may arise through two classes of effect. Firstly, that the amorphous component as sandwiched between crystal layers is not adequately represented by its bulk properties, which raises issues as regards its molecular structure. Secondly, the system is not purely a stack of lamellae but contains additional features as the lamellae are pinned to fibres at one end and intermeshed with other lamellae at the other (see below). The mechanical consequences of these additional features, beyond those attributable to simple lamellar stacks, are unknown and are at present receiving attention.

Oriented lamellar systems are commonly composed of microscopic columns of lamellae; in the present case these are the 'shish-kebab' structures. The existence of these structures creates further discontinuities in the form of columnar boundaries. It will be apparent that for achieving high modulus and strength there should be no weakness due to intercolumnar shear, which would drastically reduce the overall modulus due to poor transferral of stress to the columns in a way closely analogous to that described by shear lag theory for composites[23]. However, our material is locked together by a unique interpenetration of tapering lamellae growing from adjacent shish-kebab backbones. This removes weaknesses which are inherent in the intercolumnar boundaries and, as already stated, may perhaps have further consequences for the mechanical behaviour. The tapering itself

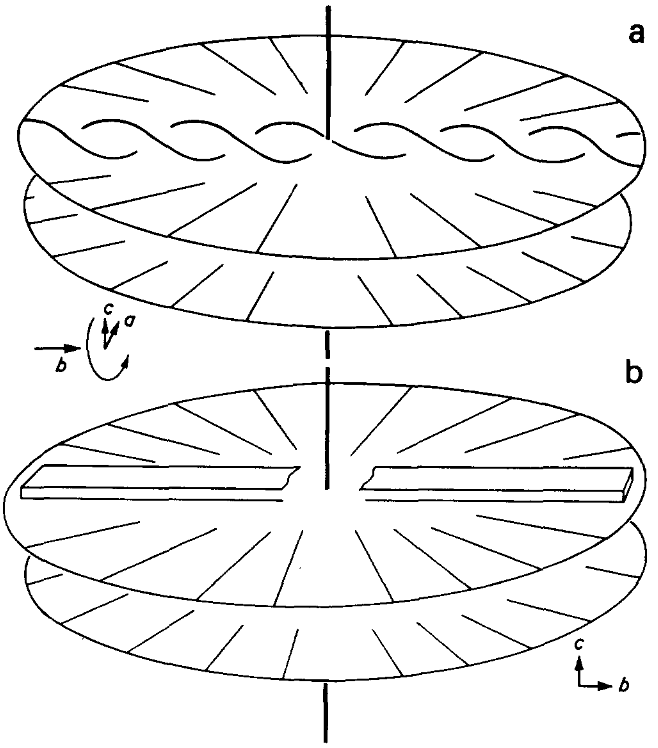

*Figure 13* Diagram of a row nucleated structure. In (a) the overgrowths twist as they grow outwards, randomizing the *c*-axis direction. In (b) the lamellae do not twist, and the *c*-axis is preserved parallel to the nucleating fibril[25]

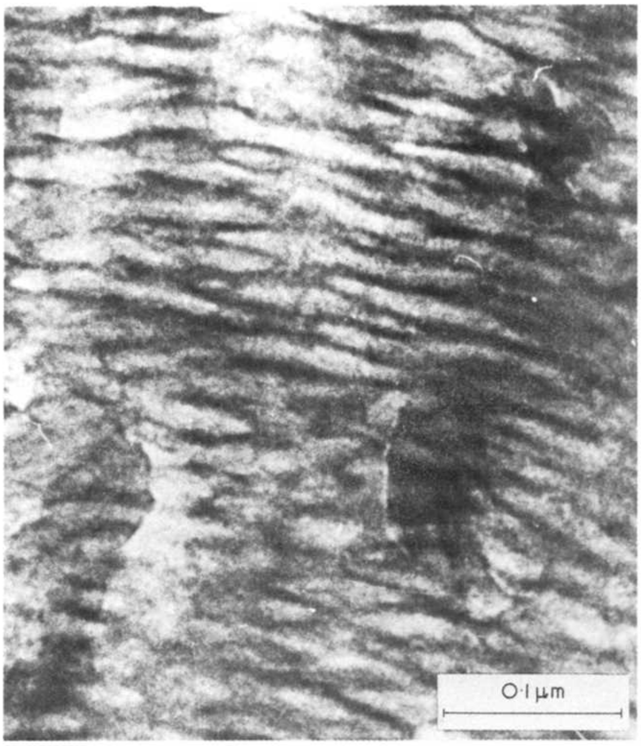

*Figure 14* A high magnification electron micrograph of a lightly stained section, showing interlocking tapering lamellae

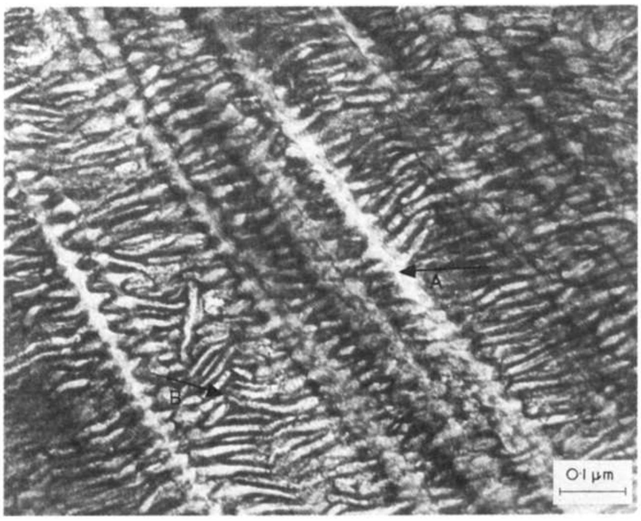

*Figure 15* A high magnification electron micrograph of a more heavily stained section permitting the observation of the backbone structure of the shish-kebab, shown arrowed at A. Arrow B shows a region where the nucleating fibrils are comparatively far apart, allowing the lamellae to randomize their directions

has also implications for the crystallization process and is more fully discussed in the next section.

## TAPERING LAMELLAE

It will be recalled that during crystallization of the lamellar overgrowths the pressure in the rheometer is allowed to increase in a controlled fashion. The rise in pressure results in an increasing supercooling during crystallization of the overgrowths, which produces tapering lamellae, and this in turn results in interpenetration of lamellar overgrowths from adjacent microfibril nuclei. Tapering perpendicular to the chain direction has been implicit in the special 'herringbone' morphology of drawn, rolled and annealed polyethylene of ref 28 where it was noted that the lamellar edges were inclined to the chain direction which was vertical throughout, a corresponding feature being arrowed in *Figure 11*. Tapering has also been observed in lamellae of high pressure crystallized chain-extended material[24].

The interpenetration of layers is an observed fact as can be seen in the high magnification electron micrograph (*Figure 14*) where the layers form interlocking wedges. This effect together with the possibility of tie molecules between lamellae of adjacent shish-kebabs removes the weakness inherent in the column boundaries of fibrillar material.

The interpenetration of lamellae from adjacent columns has two extra potential advantages. Firstly, it will help to ensure that the lamellae grow perpendicular to the nucleating microfibrils, keeping the overall lamellar normals parallel to the fibre direction (in the case of tapering lamellae the lamellar normals are considered as normals to the centre lines of the lamellae). Secondly, the interpenetration further helps to prevent lateral contraction of the material on straining along the fibril direction. *Figure 15* shows a more heavily stained section where shish-kebab backbones can be clearly seen as the stain has penetrated further into the structure. It is notable that in regions where the nucleating microfibrils are fortuitously far apart (over about 2000 Å separation) there is a tendency for the lamellar overgrowths to meander and disorient themselves (arrowed) whilst close packing of microfibrils results in well aligned interpenetrating overgrowths.

A computer model has been developed to describe the crystallization process, and here we will briefly discuss its predictions, which clarify the overall view of the structure.

The model is based on two pre-existing extended chain substrates, lying parallel to each other, and representing the flow induced microfibril nuclei. The computer simulates random nucleation events onto these substrates by depositing 'lamellae' with fold lengths and frequency appropriate to the supercooling and substrate length as determined by kinetic nucleation theory, each nucleation event is considered to produce a complete layer of crystal. *Figure 16* shows the computer prediction for lamellae grown at constant super-

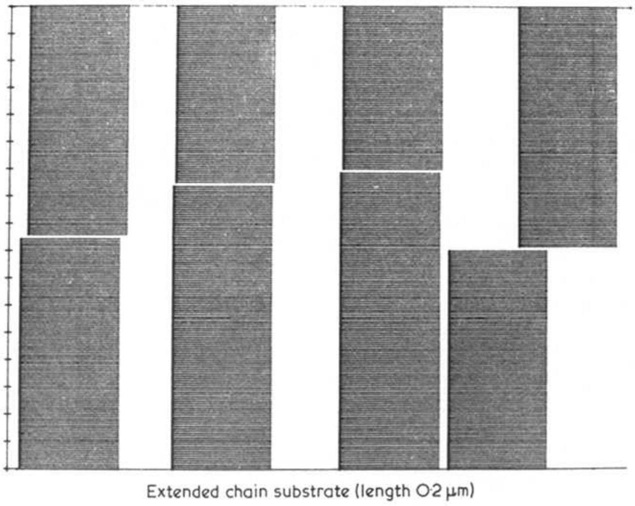

*Figure 16* Computer predcicted growth from two adjacent row nuclei (horizontal) at constant supercooling, the striated areas represent lamellar overgrowths

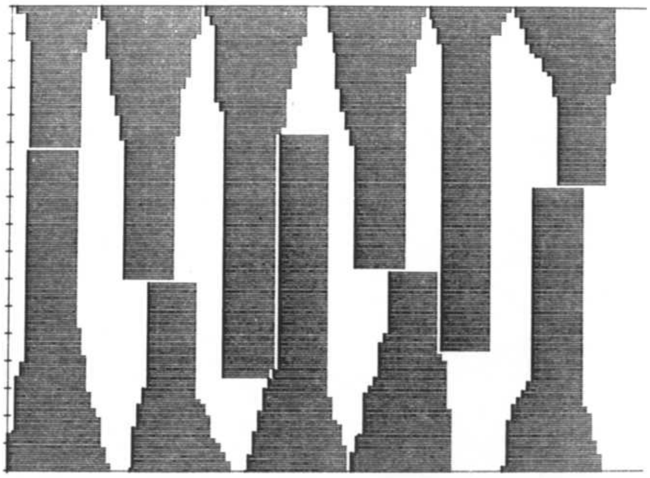

*Figure 17* Computer prediction for growth as in *Figure 16* but at a steadily increasing supercooling

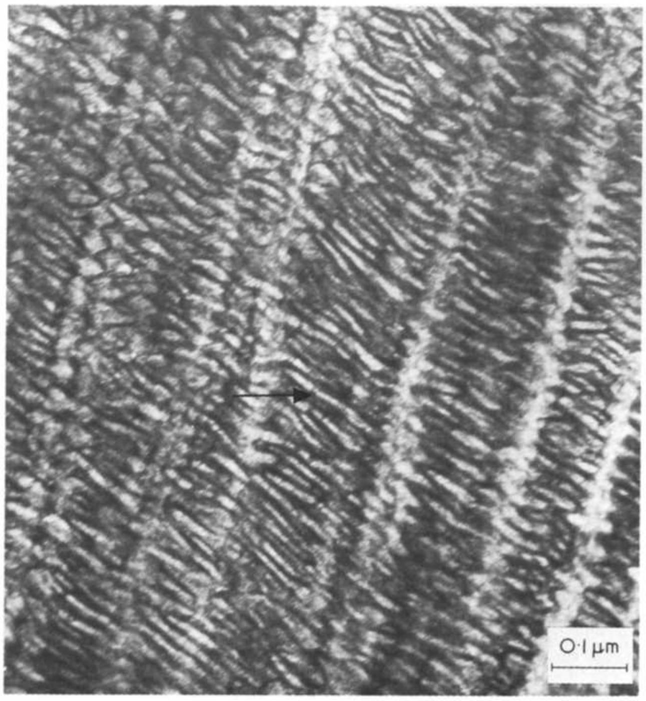

*Figure 18* Electron micrograph showing that in the absence of adjacent row nuclei the lamellae do not taper to a point, but continue to grow at a fold thickness characteristic of the maximum supercooling, see arrowed region

cooling. The lamellae grow until they impinge upon lamellae from an adjacent nucleus. We can clearly see that little interpenetration of lamellae is predicted. We are left with a weak intercolumnar boundary region.

Now look at the case where the supercooling is allowed to increase during crystallization at the rate employed in our experiments, shown in *Figure 17*. Now the lamellar thickness and the nucleation rate both depend on the effective supercooling. We can see that the extra room created by the reduction in lamellar thickness has enabled significant interpenetration of lamellae. It is interesting to note that there are still large volumes of uncrystallized material, which are prevented from crystallizing by their dimensions being smaller than the equilibrium fold thickness and the non-availability of long enough substrates.

However, the electron microscopy shows that whilst in some instances the taper reduces to a limiting value of about 200 Å (*Figure 18*) which is consistent with a realistic limiting layer thickness corresponding to the final stages of crystallization, in most cases the taper continues down to a point, as far as is visible in the electron microscope, corresponding to a thickness of less than 40 Å (*Figure 14*). As there is no evidence for discontinuity in the layers, nor any departure from perfect crystal orientation in the X-ray diffraction patterns there is no evidence for supposing that the chain orientation alters within the tapers. This means that the fold lengths must be unprecedently short at the ends of the tapering lamellae. Such short lengths have never been envisaged by crystallization theories. We believe that the remaining material crystallizes slowly to fill the interstices with non-equilibrium fold lengths.

Allowing the computer to complete crystallization with short fold lengths we have the final picture shown in *Figure 19*. A perspective view of the structure we envisage is shown in *Figure 20*. Thus there are two sources of taper. The first is due to crystallization during increasing supercooling, this occurs before overlap between columns and in the absence of spatial constraints, and tends to a limiting value. The second is imposed by the spatial constraint that the lamellae, if they are to continue growth, must grow into the tapering interstices between lamellae from adjacent columns. In our samples the two processes occur consecutively giving rise to a more or less continuous wedge shape. It appears to be this situation which produces optimum, interpenetration of the lamellar overgrowths of adjacent columns.

## CONSEQUENCES FOR CRYSTALLIZATION

The presence of fold lengths of less than 40 Å has many significant implications for our understanding of crystallization. In the first instance it raises the whole issue of crystallization of chain molecules in confined spaces, because clearly this must be involved in the layer interstices where the short fold length develops. Such interstices must arise in all melt crystallization including spherulitic growth and their existence has been previously postulated[24]. Thus the present observations are relevant to the general issue of space filling by grow-

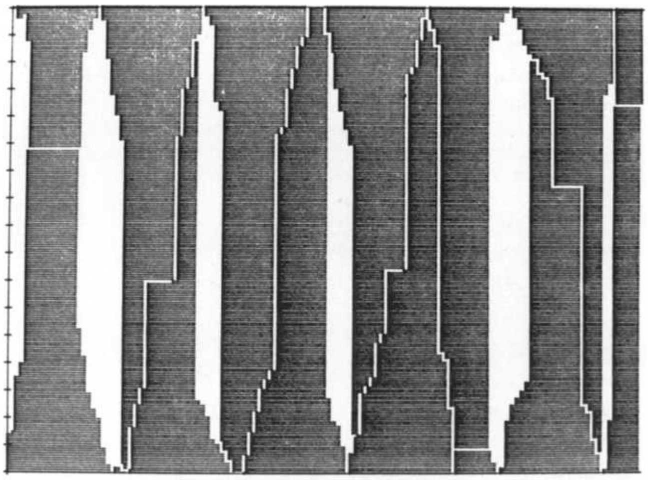

*Figure 19* Computer prediction for growth at increasing supercooling as in *Figure 17* followed by crystallization of non-equilibrium fold lengths in the interstices

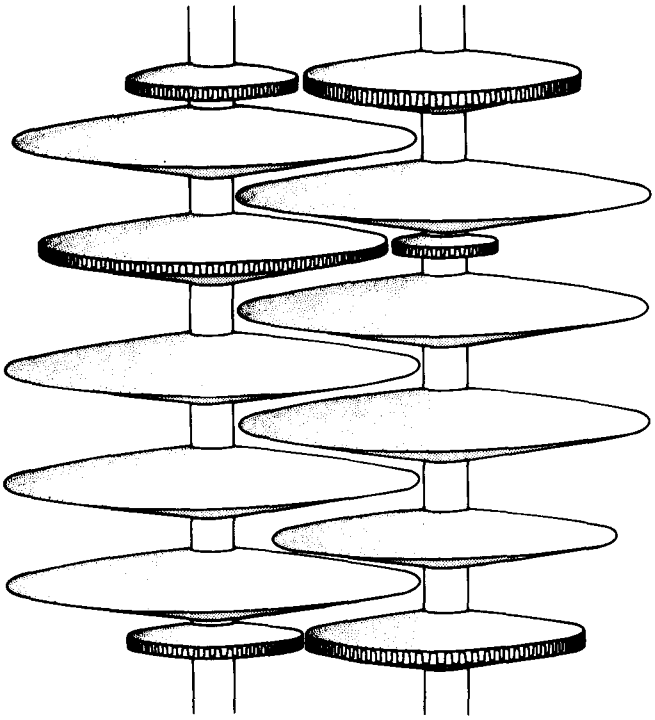

*Figure 20* A computer generated perspective view of the structure. Shading and a suggestion of chain-folding have been added

ing lamellae. (It has also arisen in ref 28 in connection with features at layer edges referred to above in connection with *Figure 11.*) The existence of such unexpectedly thin sections of lamellae must affect all experimental techniques by which the layer thickness is measured, such as low-angle X-ray scattering or low frequency Raman spectroscopy, by creating a natural distribution of thicknesses and other complicated superimposition of thicknesses (interference functions for X-ray work).

Finally the tapering lamellae will also affect polymer properties. We have been able to attribute a low melting point tail in the d.s.c. endotherms of such material (*Figure 21*) to melting out of the interstices which are thermally less stable due to their small crystal size*. Also a very slow recrystallization of these regions has been observed (typically 5 h crystallization at 40°C) from the d.s.c. exotherm (*Figure 22*). Thus we identified in concrete structural terms one source of melting effect which can occur at very low temperatures and thus contribute to the low temperature tail of thermograms even under more general circumstances, and similarly identified one source of slow change in properties at temperatures where crystallization is otherwise not expected to occur. Indeed a very conspicuous effect of the latter kind has been reported lately where certain hot-drawn fibres could even increase their moduli on storage at ambient temperatures (the 'self-stiffening effect' of ref 29); this may well have its origin in the presently described effect.

## CONCLUSION

The principal purposes of this paper are to announce the achievement of some of the highest modulus material obtained so far by solidification from the melt. and to discuss the principles underlying it. The origin of the effect follows readily from simple composite mechanics. It relies upon the creation of a parallel lamellar structure with the straight chain directions all along the lamellar normals. The achieve-

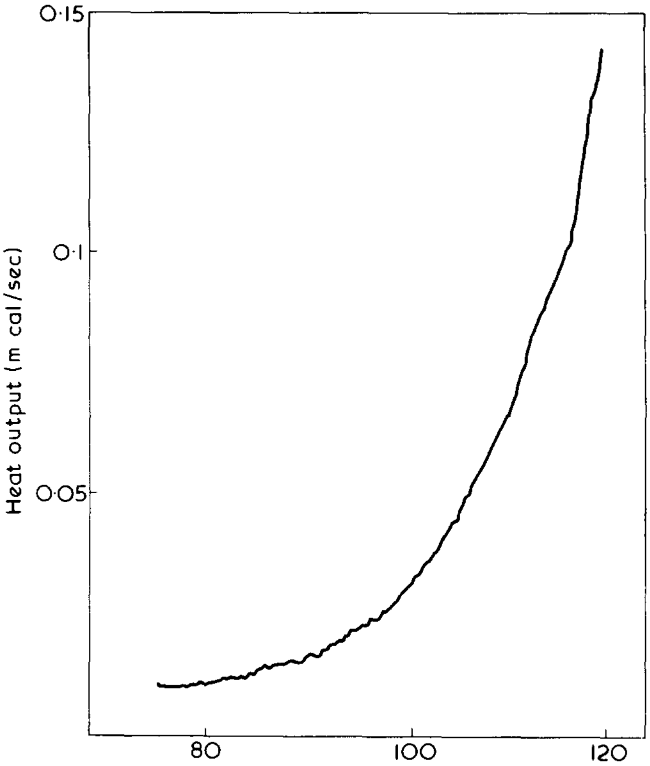

*Figure 21* The low temperature end of a d.s.c. melting endotherm. We associate the melting effects arising at unusually low temperatures with the tapering ends of the crystals

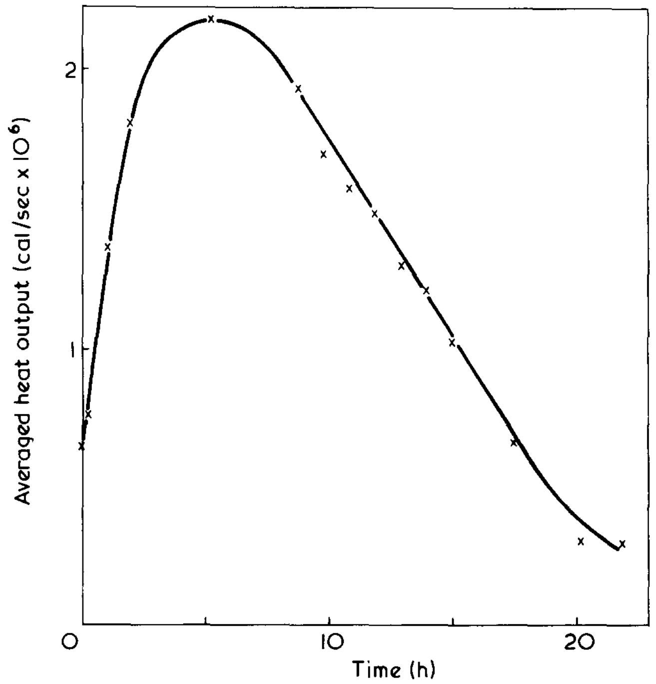

*Figure 22* Heat output as measured from d.s.c. recrystallization exotherm at 50°C as a function of time for a sample heated as in *Figure 21*. Over the long times of crystallization some base line drift occurs, so that values of heat output are subject to considerable error

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* We are aware that molecular weight segregation towards the end of crystallization will also contribute to such effects[30]. Nevertheless the taper itself is not due to the low molecular weight material accumulating in the interstices as the taper width of 40 Å or less is much below the chain length of low molecular weight material such as could be present in the appropriate quantities.

ment of this texture is based on nucleating the lamellae in close proximity to each other along parallel chain aligned fibrous crystals. The fibrous crystals are themselves produced by elongational flow-induced chain extension, and serve merely to set the pattern for the subsequent lamellar crystal growth, being insufficient in number to have a significant influence on the properties in themselves.

An additional factor is the intimate interlocking of adjacent row nucleated columns, which is produced by the tapering lamellae due to increasing supercooling which is itself a consequence of the rising hydrostatic pressure during lamellar growth. It is noteworthy that the resulting product does not share the common disadvantages of ultra-high modulus material obtained along other known routes, namely they are dimensionally stable against thermal treatments, in particular they do not contract even in the melting region, further and chiefly they are not prone to fibrillate as do the usual highly chain-extended high modulus products.

The recognition of tapering layer thicknesses of less than 40 Å raises new issues as regards the crystallization and properties of melt crystallized materials. These include crystallization of long chains in confined spaces, and a new outlook on space filling by lamellar structures with direct consequences for thermal properties and crystallization kinetics.

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