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The nature of the lamellar overgrowth in polyethylene shish-kebab fibres as revealed by small-angle X-ray scattering and electron microscopy

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The melting, dissolution and crystallization behaviour of the lamellar overgrowth in polyethylene shish-kebab fibres have been studied by small-angle X-ray scattering and electron microscopy. SAXS experiments in which fibres were heated *in situ* demonstrated the irreversible reorganization of the lamellar overgrowth already at 60° C. Reorganization continued in an inhomogeneous manner until the fibre lost its porosity around 140° C. The morphology that developed upon cooling depended on the crystallization temperature as well as on the maximum temperature attained before crystallization. Transmission electron microscopy observations showed the influence of molecular weight on aggregation. The SAXS patterns obtained during *in situ* dissolution experiments disclosed that the lamellae dissolved in dodecane above 115° C. Recrystallization of the lamellae on to the backbones was almost complete within 10 min at 110° C. These high temperatures, as compared with single-crystal behaviour, indicate that the cilia nucleated with exceptionally high stem lengths on to the backbones. SAXS of fibres elongated to a maximum ratio of 1.5 at 90° C demonstrated the role of the lamellar overgrowth as a matrix between the elementary fibrils. The shish-kebab morphology could be restored after elongation by selective dissolution of the lamellae and recrystallization.

1. Introduction

Polyethylene (PE) shish-kebab fibres produced by means of the surface-growth method have outstanding mechanical properties [1, 2]. An improvement of the tensile strength of these fibres could be achieved by hot-drawing, and a strength of 4.7 GPa has been attained [3, 4]. The mechanical [3], rheological [4] and melting behaviour [5] of hot-drawn fibres, as well as X-ray data [3, 6], suggest that the lamellar overgrowth is transformed into extended-chain fibrils in the course of drawing.

In this paper we will present a study into the nature of the overgrowth, in order to obtain more insight into the molecular topology and its relation to macroscopic properties such as strength and drawability. The thermal and mechanical behaviour of shish-kebab morphologies have been investigated by several authors. Melting studies of stirring-induced shish-kebabs have been presented by Pennings and Van der Mark [7], who used DSC as the main technique. The response of similar samples to strain has been studied by Krueger and Yeh [8], by means of electron microscopy.

Tensile properties have furthermore been reported by Pennings *et al.* [9]. Keller and Willmouth [10] have investigated the melting and annealing behaviour of a variety of preparations. Grubb and Keller [11] have studied thermal contraction in order to find the distribution of crystallite lengths

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in shish-kebabs. Several aspects of the melting behaviour of surface-growth fibres have been examined by Pennings and Zwijnenburg [12]. A study of dissolution and recrystallization has been carried out by Pennings *et al.* [13]. A more extensive EM study of shish-kebabs subjected to dissolution treatments was presented by Hill *et al.* [14] and Hill and Keller [15] recently extended this work with *in situ* EM during melting and recrystallization.

For the characterization of shish-kebab fibres "as-produced", our group has used various techniques, including small-angle X-ray scattering (SAXS) [16–18]. In a previous communication [6], we have demonstrated, by means of SAXS experiments, the morphological changes that accompany melting and hot drawing. In this paper, more emphasis will be placed on the character of the original shish-kebab morphology. This work, therefore, provides new information in addition to the results of Hill *et al.* [14, 15]. It will be shown that EM and SAXS results are in good agreement.

2. Experimental details

2.1. Materials

Stirring-induced shish-kebab preparations were obtained from solutions of the linear polyethylenes Marlex 6050 ($M_w = 90 \times 10^3$) and Hostalen Gur ($M_w = 1.5 \times 10^6$). In the case of Marlex, mats of fibrillar crystals were prepared from a 5 wt% solution in *p*-xylene, by stirring at 100° C and 510 r.p.m. (paddle stirrer). For Hostalen Gur a 0.2 wt% solution in *p*-xylene was used, and crystallization was carried out at 110° C and a stirring rate of 930 r.p.m. (cylindrical stirrer). All preparations were washed in *p*-xylene at the crystallization temperature.

Samples for transmission electron microscopy were obtained by means of a stripping method which has been described previously [19]. The samples were heat-treated on the electron microscope grid. The latter was taken up in a sample pan of a DSC apparatus and maintained at the temperature of the treatment for 5 min under N_2 atmosphere. Subsequently the sample was cooled down to room temperature at a rate of 5° C min^{-1}.

The surface-growth fibres used as starting material in most of the SAXS experiments were prepared from a 0.5 wt% solution of Hifax 1900 in *n*-dodecane at 128° C, at a growth rate of 0.48 mm sec^{-1}. This sample will be referred to as fibre T1. Hifax is a linear polyethylene having an M_w of about 4×10^6 kg $kmol^{-1}$. In many cases the surface-growth fibre was washed in dodecane at 109° C before it was used; this will be indicated in the text. The effect of washing will be discussed in a later section. Drawn specimens of washed T1 fibres were obtained by means of a method described recently [4].

2.2. X-ray methods

SAXS measurements were carried out with the aid of a Kratky camera equipped with a proportional counter and an electronic step-scanner. Entrance slits of 20 and 40 μm were used. Cu$K\alpha$ radiation ($\lambda_x = 0.154$ nm) was produced by a Philips X-ray generator connected to a closed cooling circuit and operated at 45 kV and 35 mA. Monochromatization was achieved by using a Ni-filter and pulse-height discrimination.

The samples consisted of a continuous macrofibre wound regularly on a specimen frame in such a way that the fibre axis was perpendicular to the plane of the primary X-ray beam, which has a line-shaped cross-section. Consequently, the scattering curves recorded were slit-smeared meridional profiles. A correction for blank scattering was made in some cases only; this will be indicated in the legends to the figures. Fibres were subjected to heating, dissolution and crystallization experiments in an evacuated heating cell belonging to the Kratky set-up. The temperature was controlled by means of an electronic device coupled with a Pt-100 resistor near the sample. The construction of the heating cell, however, did not allow an accurate determination of the temperature at the sample position. The equipment was calibrated with an external thermometer inserted into the cell. SAXS curves were usually recorded at the temperature of the treatment; this will be indicated in the text. For the experiments in which the fibre was heated in solution, a specially designed cuvette was used, which is shown in Fig. 1. The actual container is formed by the Viton ring and the mica windows. The ring is slightly compressed when the screws are fixed and provides a good seal even when the cuvette is placed in vacuum at 130° C. Instead of mica, mylar windows may be employed if they are inert to the solvent used. Apart from easier handling, mylar has a much higher X-ray transmission than mica.

WAXD exposures were taken in a Statton camera on flat film; Ni-filtered Cu$K\alpha$ radiation was used.

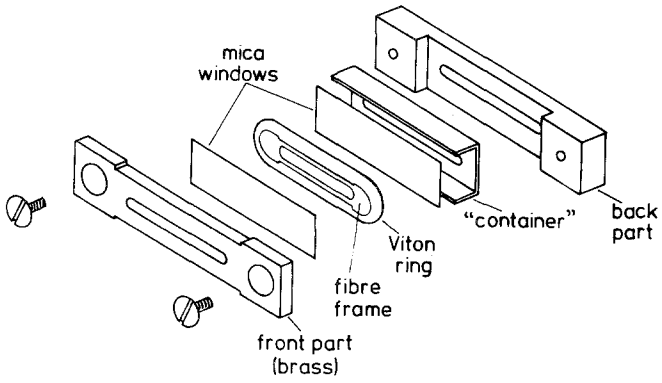


Figure 1 Exploded view of the cuvette used for measurements on fibres in solvent. External dimensions of the cuvette in mm: 70 X 13 X 10.

3. Results and discussion

3.1. Melting and crystallization phenomena in stirring-induced shish-kebabs

One of the most striking results found during our research on polyethylene fibres, is the similarity in thermal-mechanical behaviour between the various kinds of preparations, namely, stirring-induced fibres [7, 9], surface-growth fibres [1, 4, 12], and drawn gel-spun fibres [20, 21]. In this paper concerning continuous polyethylene filaments, the behaviour of the related stirring-induced material deserves attention, the more so since appropriate samples can be viewed directly in the transmission electron microscope.

The starting materials were prepared from Marlex 6050 and Hostalen Gur, respectively. A number of samples of these materials were subjected to a heat-treatment for 5 min, prior to examination in the TEM. The results are shown in Figs. 2 to 6 for the Marlex samples. Fig. 2 presents

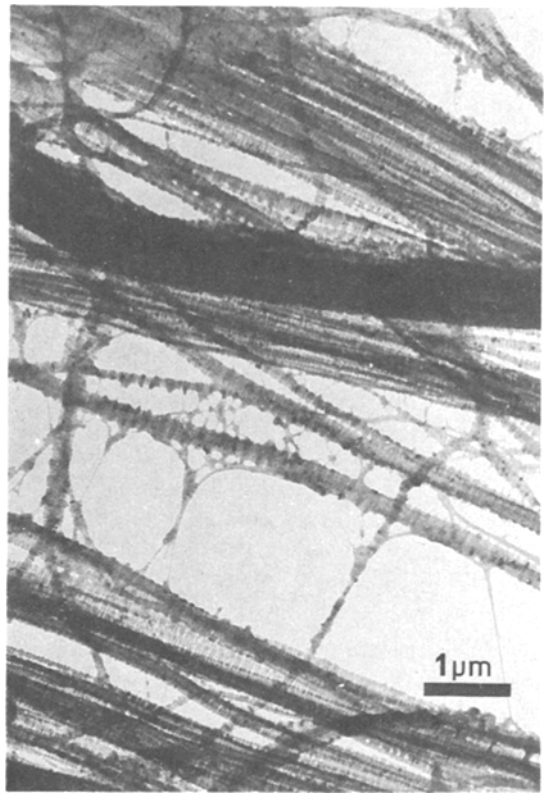


Figure 2 Transmission electron micrograph of polyethylene shish-kebabs, produced by stirring-induced crystallization from a 5 wt % solution of Marlex 6050 in *p*-xylene at 100° C, and heat-treated at 120° C for 5 min. Individual elementary fibrils can still be observed. At some places the lamellar overgrowth has formed "droplets".

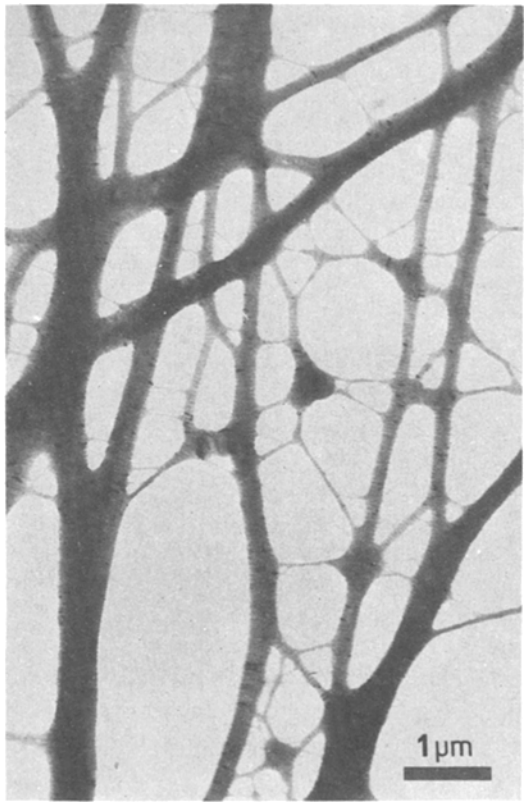


Figure 3 TEM of Marlex shish-kebabs heat-treated at 130° C for 5 min. The elementary fibrils have formed dense aggregates with a fine surface striation of 40 nm.

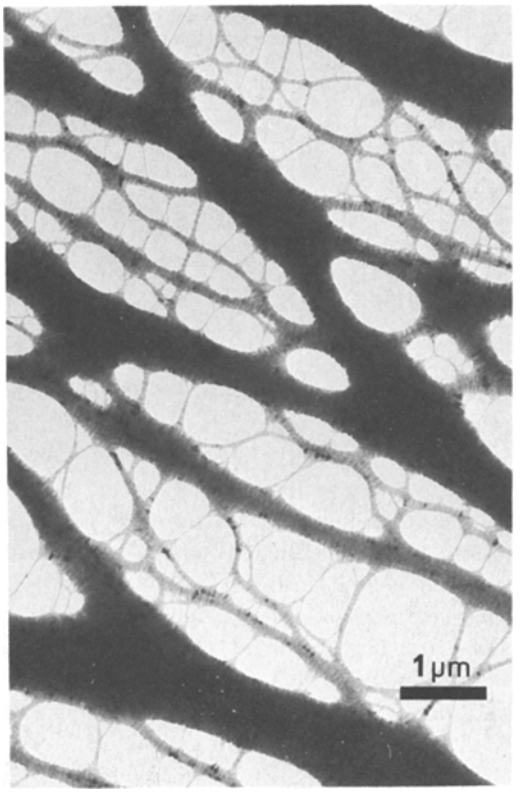


Figure 4 TEM of Marlex shish-kebabs heat-treated at 140° C for 5 min.

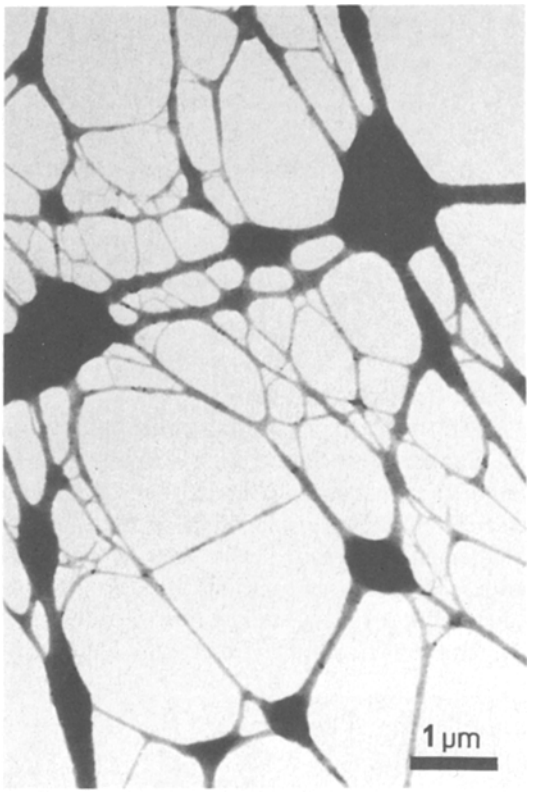
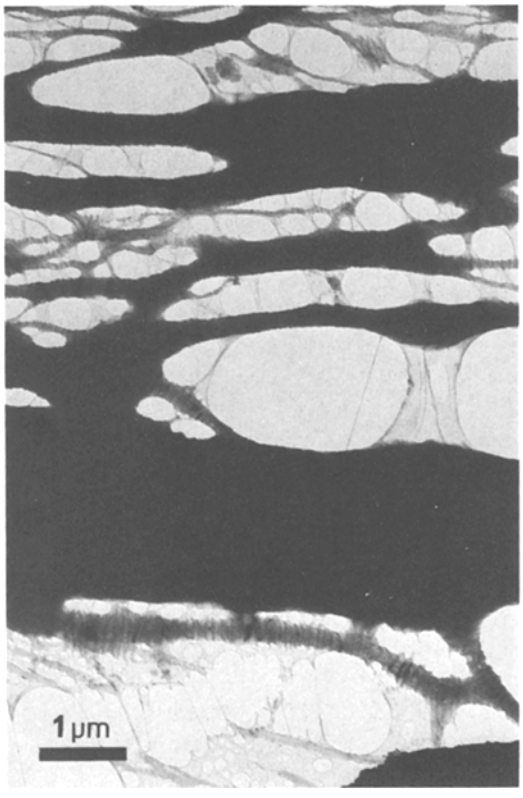


Figure 5 TEM of Marlex shish-kebabs heat-treated at 150° C for 5 min.

an electron micrograph of fibrils that received a treatment at 120° C. The onset of melting phenomena is obvious. The characteristic ordering of lamellae (with a period of ~ 40 nm) is still clearly visible along most of the backbones, but at other sites the overgrowth seems to have coalesced into "droplets". The sample has a very inhomogeneous appearance. In a sample heated to 130° C (Fig. 3), aggregation of elementary fibrils has clearly taken place. A fine striation is seen to cover all the thicker entities: the period is ~ 40 nm, and equal to the lamellar period on the original elementary fibrils. Fig. 4 was obtained from a sample heat-treated at 140° C. The striation is again observed, but seems to be less regular and coarser. When a sample is heated to 150° C, a further aggregation of material occurs, as can be seen in Fig. 5. The micrograph of Fig. 6, taken from a sample heat-treated at 160° C, suggests that very broad lamellae are found around the aggregates. Their separation appears to be somewhat larger than in the starting material.

A similar series of electron micrographs for the Hostalen Gur samples is shown in Figs. 7 to 12, but at a higher magnification. Fig. 7 presents the starting material at room-temperature. The overgrowth is somewhat irregular, and has an average repeat period of 45 nm. Fig. 8 shows a sample after a treatment at 130° C: the lamellae seem to have thickened, but are still clearly visible. Whereas in the Marlex preparations aggregates had already formed at this temperature, the Hostalen Gur sample still displays separate elementary fibrils. The lower degree of aggregation found is due to the high molecular weight of Hostalen Gur (more than ten times as high as that of Marlex) and the consequently very high melt viscosity. The formation of denser structures is clearly observed after heat-treatment at 150° C (Fig. 9); broad lamellae are found to have grown around the aggregates, with a period of ~ 60 nm. A sample kept at 170° C (Fig. 10) displays a similar morphology, but the period is somewhat higher, ~ 65 nm. Raising the temperature of the treatment produces more pronounced aggregation and correspondingly more extended lamellae, as is demonstrated by Fig. 11 (200° C) and Fig. 12 (230° C).

The main observations can be summarized as



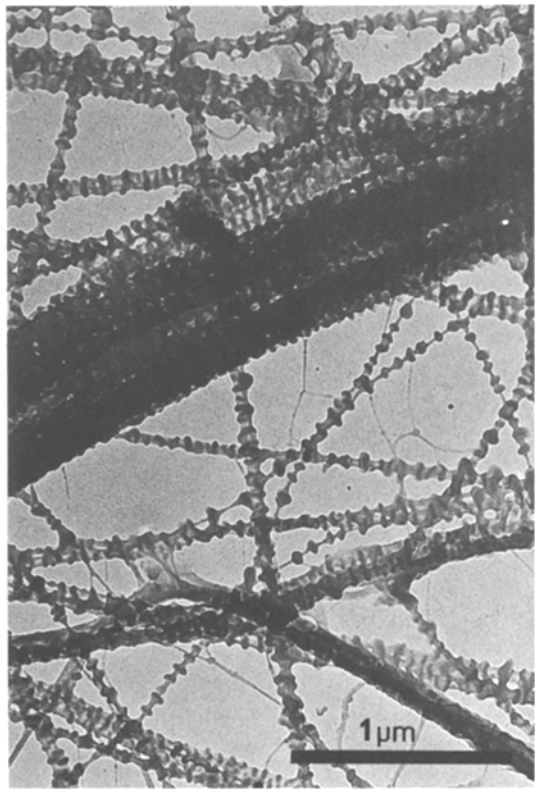


Figure 6 TEM of Marlex shish-kebabs heat-treated at 160° C for 5 min. Extensive lamellae with a more irregular character have formed around the aggregates.

Figure 7 TEM of polyethylene shish-kebabs produced by stirring-induced crystallization from a 0.2 wt % solution of Hostalen Gur in *p*-xylene at 110° C.

follows. Heating of shish-kebabs leads to the aggregation of the overgrowth on the elementary fibrils. In the 120° C sample of Marlex, the formation of droplets could clearly be observed. At higher temperatures, the elementary fibrils aggregate into thicker, dense bundles. After cooling, these aggregates as a whole are overgrown with lamellae, which are found to be more extended laterally for higher temperatures of sample treatment. The final overgrowth period is ~ 70 nm, somewhat larger than that on the original elementary fibrils in the starting material (~ 40 nm), but still in the range characteristic for shish-kebab preparations [16, 17, 22]. A remarkable result is the observation that the Hostalen Gur samples retain their fibrillar appearance up to temperatures over 200° C. In the Marlex samples, however, the molten material coalesces almost entirely above 150° C (note the globular appearance of the aggregates in Fig. 5). This striking difference demonstrates once more the extremely high melt viscosity of Hostalen Gur. Our TEM results on Hostalen Gur samples agree with those of Hill and Keller [15], who were able to show by *in situ* EM that the lamellae grow from droplet-like beads that surround the backbones at temperatures around 140° C.

3.2. Melting and recrystallization phenomena in surface-growth fibres

Surface-growth fibres were subjected to a heat-treatment under vacuum in the SAXS set-up, and scattering curves were recorded *in situ*. The results are shown in Figs. 13 to 17. A washed sample of fibre T1 was used in these experiments. The SAXS maximum for the starting material at 25° C (Fig. 13) denotes a most probable lamellar repeat distance of ~ 80 nm. The shift of this maximum to smaller angles with increasing temperature, which was found to be irreversible, indicates a redistribution of the lamellar overgrowth. This effect could clearly be detected at temperatures as low as 60° C (not indicated in Fig. 13), from which we have concluded that the lamellae are easily disrupted due to the contraction of taut tie-molecules between backbone

Figure 8 TEM of Hostalen Gur shish-kebabs heat-treated at 130° C for 5 min. Individual elementary fibrils with an overgrowth period of 45 nm are observed.

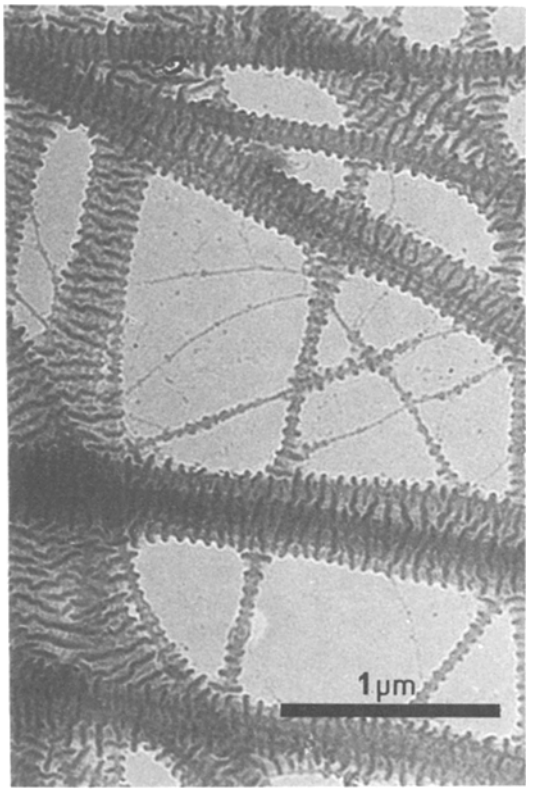


Figure 9 TEM of Hostalen Gur shish-kebabs heat-treated at 150° C for 5 min. Dense aggregates of fibrils are found, which display a fairly regular lamellar overgrowth.

and lamellae ("veil"). Close to the melting temperature, this leads to an aggregation of cilia into larger "beads". It should be emphasized that if melting of lamellae would occur in a random way and without reorganization, the SAXS peak would decrease in intensity and would not change its position until a stage when at least half of the number of lamellae has disappeared [23, 24]. The substantial decrease in scattering power above 135° C points to the disappearance of the voids when the lamellae melt completely and the fibrils aggregate.

Subsequent cooling of the fibres from 143° C to various temperatures results in the formation of periodic structures, as is shown in Fig. 14. SAXS curves were recorded at the temperatures indicated, after prolonged crystallization. The intensity level, however, rose only slightly above that of the "melt" at 143° C. The fibre, therefore, retained its dense, voidless morphology and the long period should be ascribed to a folded-chain structure grown from the melt of the lamellae. Note that the long period is remarkably high: ~ 90 nm at the higher temperatures to ~ 70 nm in the range 127 to 100° C. With decreasing crystallization temperature the intensity at larger angles increases, and eventually a second maximum is formed. This second maximum is certainly not a second order of the first peak, and it expresses the heterogeneity of the morphology, in which several long periods are realized. This is the result of different cooling rates in the sample during non-isothermal crystallization. It should be remarked here that, even after complete crystallization, the SAXS pattern was found to change when the temperature was lowered. This will be illustrated for an extreme case below.

The dependence of the long period on the supercooling, which was also found for shish-kebabs grown from solution [8, 13, 14], implies that cilia which protrude from the backbone at separated defect regions may become incorporated in one and the same lamella. At low temperatures crystallization of cilia is more likely to proceed in the vicinity of the defect region from which they emanate. The large span of the cilia will give rise

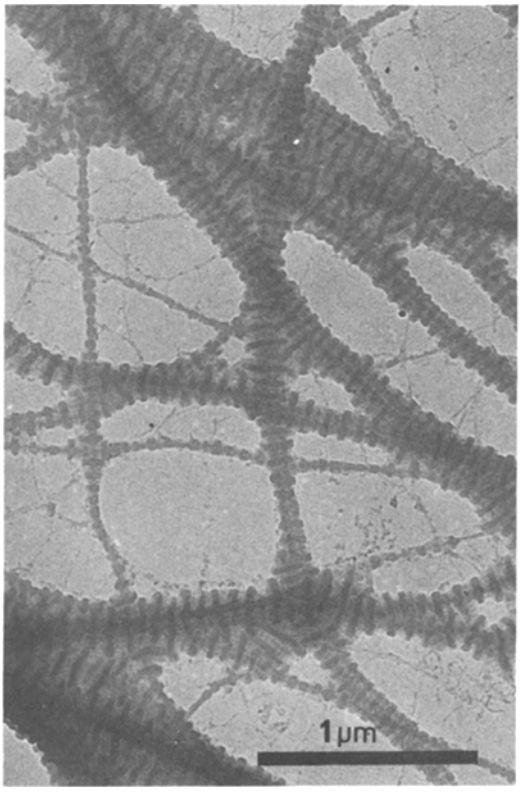


Figure 10 TEM of Hostalen Gur shish-kebabs heat-treated at 170° C for 5 min.

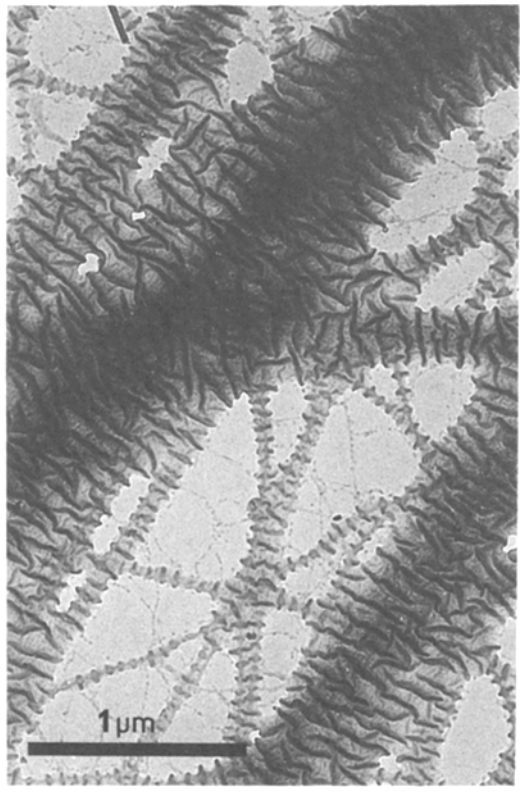


Figure 11 TEM of Hostalen Gur shish-kebabs heat-treated at 200° C for 5 min. The lamellar overgrowth on the thicker aggregates is very dense and more irregular than for lower temperatures of treatment.

to extended molecules being pulled taut during lamella formation, which, in turn, accounts for the disruption of the overgrowth upon heating. At the same time, long cilia are able to aggregate into larger beads around the backbone in order to reduce the surface free energy.

The developing morphology also depends on the maximum temperature, T_{max}, of the melt before crystallization. Fig. 15 shows the changes in the scattering behaviour after crystallization at 127° C, as a function of T_{max}. In order to evaluate these results, the scattering of the fibre "melt" (which hardly varied over the temperature range 143 to 162° C) was subtracted from the curves recorded after crystallization. Fig. 16 shows the results. There is a shift in the long period when T_{max} is increased from 143° C to 145° C, whereas for higher T_{max} the long period remains remarkably constant (~ 120 nm). This suggests that at temperatures slightly above 143° C, relaxation phenomena which result in longer cilia are occurring in the backbone [4]. The crystallization at 127° C seems to proceed more difficultly for higher values of T_{max}, as may be inferred from the curves C, D and E in Fig. 16. This could be due to a memory effect which is weaker for higher temperatures of the molten overgrowth. Hill and Keller [15] observed a less distinct lamellar morphology as a result of longer storage times at high temperatures, and suggested that this might be cuased by a higher degree of entanglement established in the melt. This point needs further SAXS-study.

Cooling from 162° C to a lower crystallization temperature, 121° C, again yields a very pronounced "semi-crystalline" long period (Fig. 17). The intensity distribution is found to depend strongly on the temperature of measurement, even after complete crystallization at T_{cr}. Fig. 17 demonstrates this effect, which was found to be reversible between room-temperature and T_{cr}. Similar phenomena have been observed for bulk polyethylene [25] and single-crystal mats [26, 27]. Changes in the peak intensity with temperature are to be expected because of the difference between the thermal expansion of the

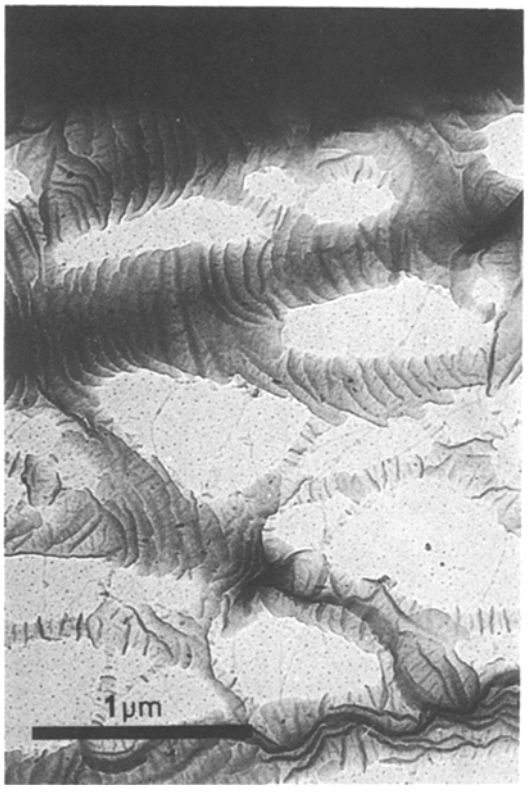


Figure 12 TEM of Hostalen Gur shish-kebabs heat-treated at 230° C for 5 min. The lateral extension of the lamellae is very large.

crystallites and that of the amorphous regions. Fischer [28, 29] has argued that the effect of thermal expansion cannot entirely account for the observations, and that changes in the thicknesses of crystalline lamellae and amorphous regions are involved as well. For shish-kebab fibres the situation is more complex. The "amorphous" regions in the semi-crystalline phase grown from the melt of the lamellar overgrowth will contain chain folds as well as tie-molecules. The tie-molecules will exert a retractive force upon heating because they tend to randomize their conformation. The behaviour of the amorphous phase, therefore, will depend on constraints such as the presence of extended-chain crystals or the external stress on the fibre. It has been found [7, 12] that extended-chain crystals may transform into a "hexagonal" phase which may persist up to 180° C, depending on external constraints. At 162° C, the maximum temperature reached in the experiments discussed above, the extended-chain backbones may therefore have been partly or completely molten. After the high-temperature experiments, the fibre was no longer tightly wound around the sample frame. Fig. 18 shows a WAXD-pattern of the fibre after the experiment at 162° C. Obviously relaxation processes have taken place: only a part of the material still displays the initial orientation. All this complicates the interpretation of the (slit-smeared) SAXS-curves. In a comparison of curves A and B of Fig. 17, however, it should be noted that the SAXS intensity at scattering angles around $b = 4 \times 10^{-2}\ \mathrm{nm}^{-1}$ (where the reduced scattering angle, $b = 2 \sin\theta/\lambda_x$) is lower at 121° C than at 25° C. This strongly suggests that a process at the interfaces between crystallites and defect regions is

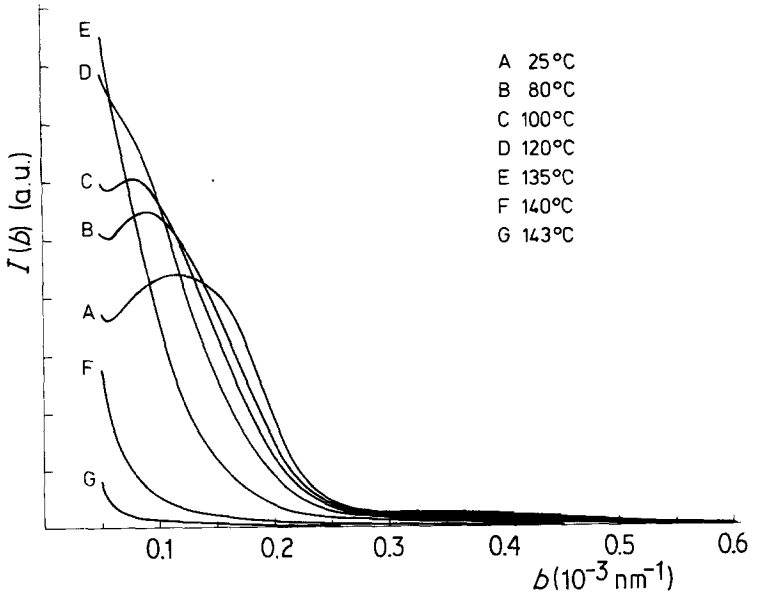


Figure 13 Heating of surface-growth fibre T1. Curve A: fibre at room-temperature; curves B to G recorded at the temperatue indicated, after several hours of exposure of the fibre to this temperature. (Meridional SAXS curves, no blank correction applied; $b = 2 \sin\theta/\lambda_x$.)

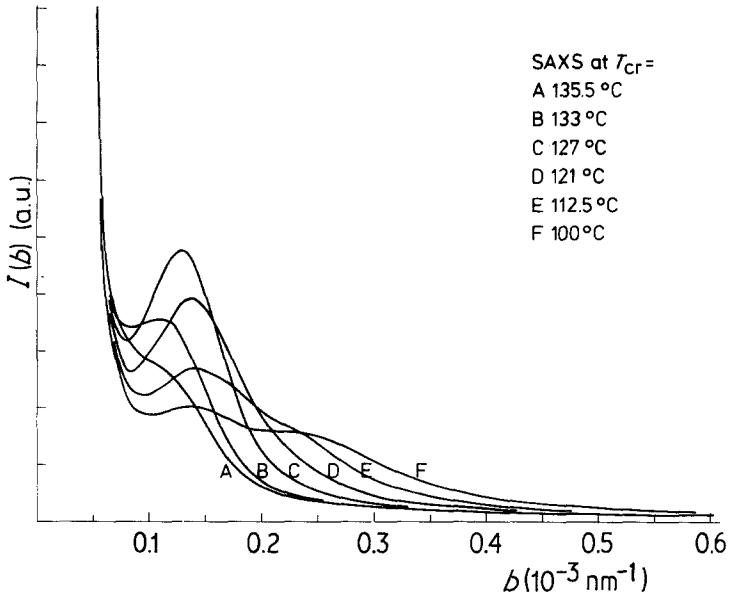


Figure 14 Crystallization of the lamellar overgrowth from the molten state. The surface-growth fibre T1 was maintained at 143° C for 30 min and then cooled to the temperature indicated. SAXS curve recorded at T_{cr} after prolonged crystallization. (Meridional SAXS curves, no blank correction applied; $b = 2 \sin \theta/\lambda_x$.)

involved. For this reason the observations are tentatively explained as being due to "surface melting" in a semi-crystalline structure in which the defect regions contain many chain folds and chain ends [28, 29]. The strong temperature dependence of the peak intensity will be partly due to a relatively short fold region (Fig. 19). The effects of thermal expansion and surface melting might be separated by means of quenching experiments.

3.3. Dissolution and recrystallization of the lamellar overgrowth

In the experiments discussed in the previous section, we have used a washed fibre as starting material. Washing was carried out in order to remove adhering polymer from the fibre. Although the fibre T1 was prepared from dodecane at 128° C, washing took place at 109° C in this solvent for at least one day, in which the solvent was refreshed once. The effect of this procedure is shown in Fig. 20. The substantial change of the lamellar period from 125 to 80 nm shows that the shish-kebab morphology has been affected. In view of the results to be discussed in this section, the decrease of the period suggests that the original lamellae crystallized isothermally at temperatures higher than 109° C. Quenching from high temperatures produces considerably shorter periods.

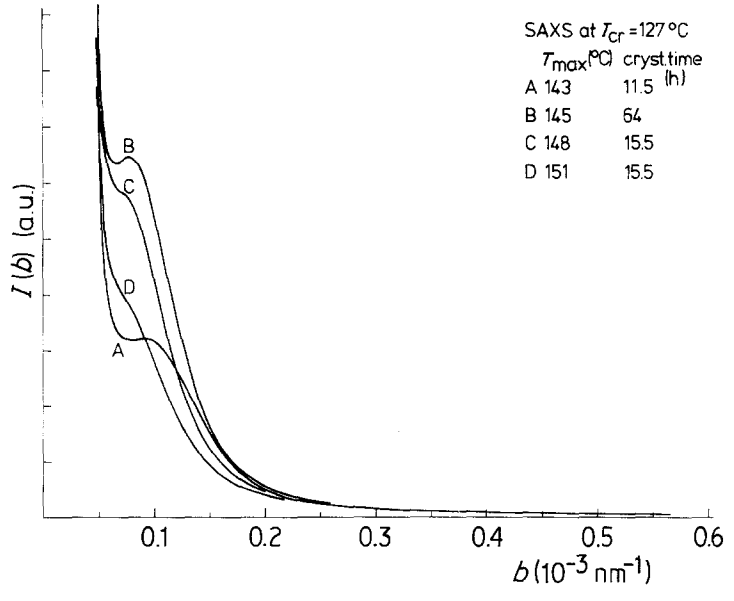


Figure 15 Crystallization of the lamellar overgrowth form the molten state. The surface-growth fibre T1 was maintained at T_{max} for several hours and then cooled to 127° C. SAXS curve recorded at 127° C after the crystallization time indicated. (Meridional SAXS curves, no blank correction applied; $b = 2 \sin \theta/\lambda_x$.)

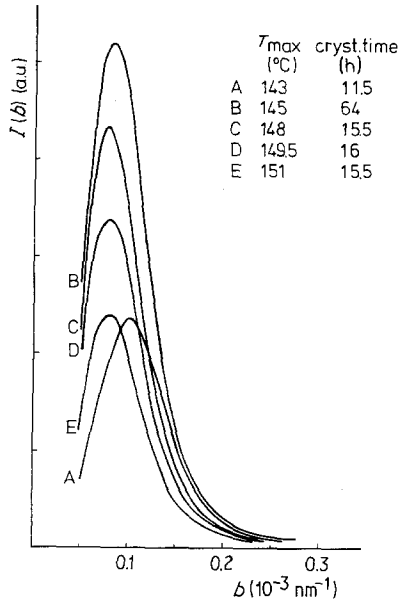


Figure 16 See legend to Fig. 15. The scattering curve of the fibre measured at various temperatures between 143° C and 162° C was extrapolated to 127° C and subtracted from the curves shown in Fig. 15. Curve for 149.5° C added. (Meridional SAXS curves; $b = 2 \sin \theta / \lambda_x$.)

(This was also found by Hill *et al.* [14], who used *p*-xylene as solvent). As will be demonstrated below, the lamellae do not completely dissolve at 109° C in dodecane.

The washing procedure also enhances the second maximum in the curve at $b = 3.5 \times 10^{-2}\,\mathrm{nm}^{-1}$. Its angular position is not simply related to that of the lamellar-period peak. A comparison with theoretical curves [18] suggests that it is a subsidiary maximum of the scattering of isolated lamellae. The scattering profile of a lamella of thickness, t, is given by [30]

$$I(b) = \text{constant} \times \left(\frac{\sin \pi b t}{\pi b t}\right)^2$$

The first side maximum is found for $b = 3/(2t)$. For the curves shown it follows that $t \approx 40$ nm. For this maximum to be observed the lamellar thickness must be quite uniform. Obviously, the washing procedure has resulted in a more regular and "open" overgrowth. The fact that the second order of the lamellar period is not observed is in accordance with the result that the lamellar thickness amounts to one half of the period.

We will now discuss dissolution experiments carried out in the SAXS set-up. These experiments were very exploratory in character; we hope to present a more detailed study in the near future, especially with respect to the temperature dependence of the phenomena involved. Nevertheless, these first experiments reveal some novel features, since the scattering curves were recorded *in situ* at various temperatures.

A fibre, wound on a frame, was placed in the liquid cuvette, which was filled with dodecane and heated in the high-temperature cell of the Kratky camera. Scattering intensities were lower by nearly a factor 70 as compared with experiments on a fibre in vacuum, since in dodecane the contrast is reduced by a factor 16 [17, 18], and since the transmission coefficient of the filled cuvette was about 22%.

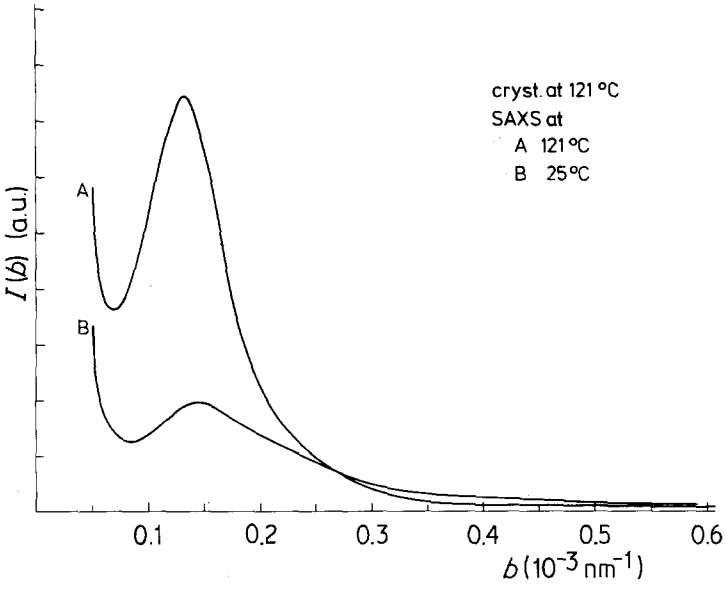


Figure 17 Crystallization of the lamellar overgrowth from the molten state. The surface-growth fibre T1 was kept at 162° C for several hours and then cooled to 121° C. SAXS curves recorded after crystallization at 121° C for 3 days, at 121° C and at 25° C. This sample had previously been used for the experiments of Fig. 15. (Meridional SAXS curves, no blank correction applied; $b = 2 \sin \theta / \lambda_x$.)

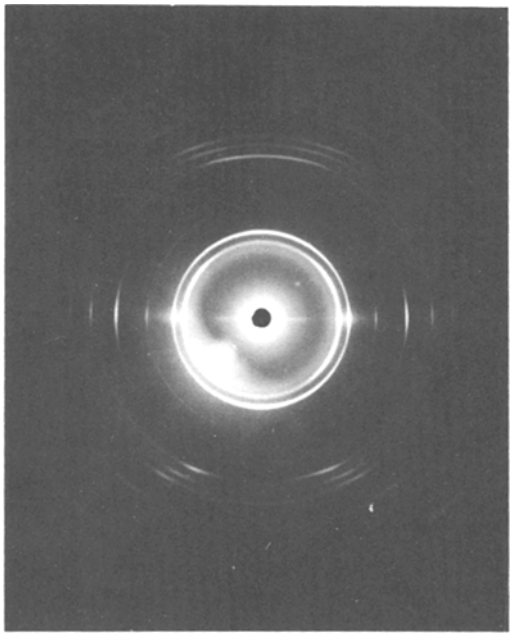


Figure 18 WAXD pattern showing the partial disorientation of the crystallites in surface-growth fibre T1 after the heating experiments of Figs 15 and 17. The fibre axis is vertical; it appears to have been slightly tilted out of the plane of the film.

An unwashed sample of a fibre prepared from *p*-xylene solution at 104° C was employed in the heating experiment. Fig. 21 shows the meridional scattering curves of this sample in dodecane. Blank scattering has not been subtracted. The intensity of the lamellar-period peak increases with temperature; its position does not change. At 115° C the peak is less pronounced and at 122° C only a weak shoulder is visible upon the background. This points to dissolution of the lamellae above 115° C.

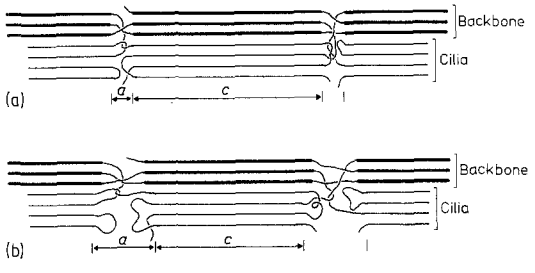


Figure 19 Surface-melting phenomena in the folded-chain phase which originates from the lamellar overgrowth and surrounds the backbones in heat-treated fibres. At 25° C (a) the disordered region (*a*) is much shorter than the crystallite length (*c*). At elevated temperatures (b), the length of the disordered zone has strongly increased. Chains that are not entangled contract, which gives rise to a gap of lower density.

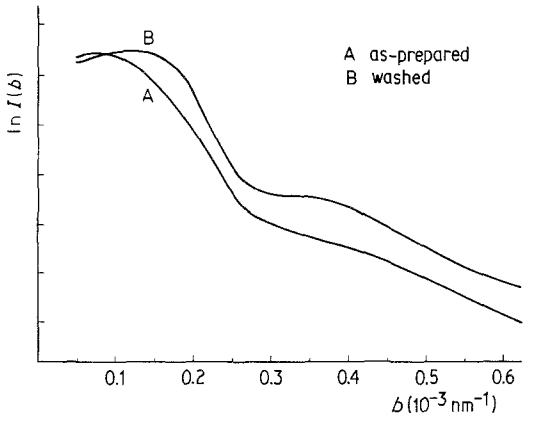


Figure 20 Meridional SAXS curves of fibre T1 before (A) and after (B) washing in *n*-dodecane at 109° C. (Logarithmic intensity scale; curves corrected for blank scattering; $b = 2 \sin \theta/\lambda_x$.)

A redistribution of the lamellar overgrowth, as was observed upon heating in vacuum, does not take place, nor does disappearance of the lamellae lead to a dense aggregate.

In this context, the results of crystallization experiments on single crystals should be mentioned. Single crystals were prepared by isothermal crystallization from a 0.02 wt % solution of Hifax in *n*-dodecane at 106° C. When the crystal

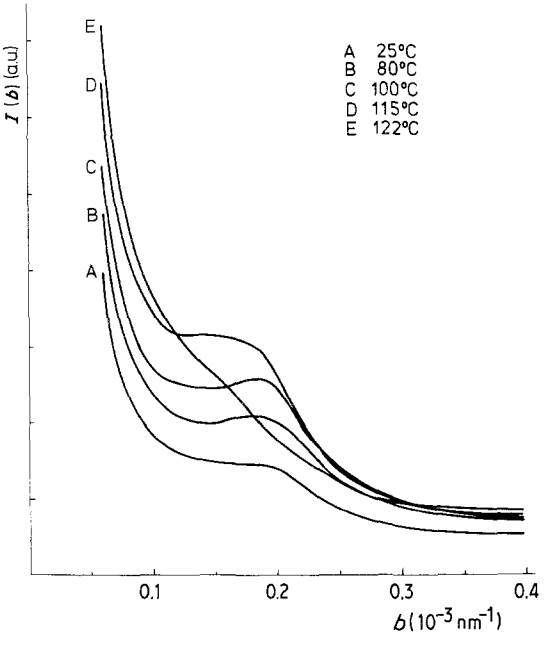


Figure 21 Heating of a surface-growth fibre in *n*-dodecane. At room-temperature curve A is found; curves B to E recorded at the temperature indicated, after 1 h exposure of the sample to this temperature. (Meridional SAXS curves, no blank correction applied; $b = 2 \sin \theta/\lambda_x$.)

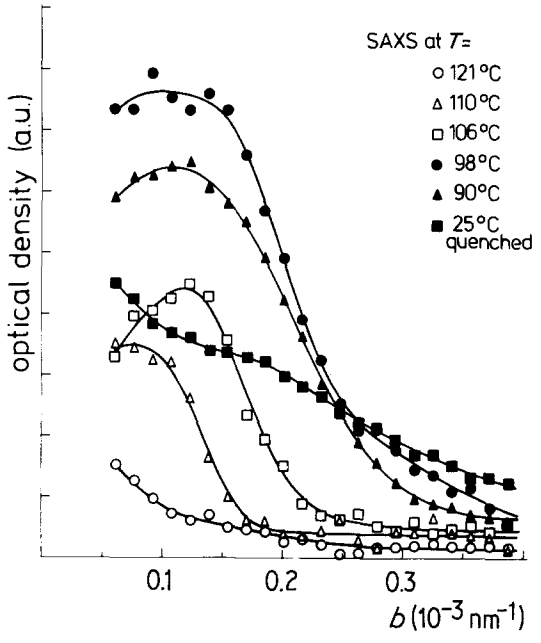


Figure 22 Crystallization of the lamellar overgrowth from the dissolved state. The sample of surface-growth fibre T1 in *n*-dodecane was kept at 121° C for 15 min and then cooled to the temperature indicated. After 10 min the SAXS pattern was recorded on film for another 30 min at this temperature. (Meridional SAXS curves, optical densities obtained from Optronics densitometer, no blank correction applied; $b = 2 \sin \theta/\lambda_x$.)

suspension was heated at a rate of 0.2° C min^{-1} in a flask in a thermostat bath, dissolution took place around 112.5° C. Crystals adsorbed onto the glass surface or the stirrer dissolved at higher temperatures, however. Gel-like aggregates, which formed under different crystallization conditions, were found to persist up to 116.5° C when heated at the same rate. These features reflect the strong influence of the very high molecular weight of Hifax on its properties. When a suspension of single crystals prepared at 106° C was heated in the SAXS set-up at a rate of approximately 0.25° C min^{-1}, dissolution was again found to occur between 112 and 113° C as indicated by a sharp decrease in scattered intensity. Crystallization could not be detected within 30 min at 106° C by this method. These results should be compared with those obtained for shish-kebabs during similar experiments, which will be described below.

A crystallization study was carried out in order to follow the behaviour of the dissolved cilia. A washed sample of fibre T1 was used in order to avoid the formation of loose single crystals, as these were found in the cuvette in large quantities when an unwashed sample had been used. The meridional scattering pattern was in this case recorded on photographic film in order to reduce the measuring time. The fibre in dodecane was kept at 121° C for 15 min and subsequently cooled to the crystallization temperature. By means of the X-ray counter tube it could be ascertained that after 10 min at the crystallization temperature the intensity became reasonably constant. The film was exposed during the subsequent 30 min. Fig. 22 shows the results. No blank correction was applied, but this correction might at most correspond to the curve for 121° C. Although the pattern on the film was still very weak after 30 min, its profile suggests that the lamellar overgrowth crystallized in shish-kebab fashion. The periodicity is ~ 80 nm in the range 106 to 90° C.

The experiments show that the cilia crystallize and dissolve at temperatures which are generally several degrees higher than those found for single crystals. This may be due to the fact that the cilia are attached to the backbone, as well as to the high local concentration of cilia around the fibrils. Both "localization" and "crowdedness' result in a reduction of the number of possible chain conformations and therefore in an increase of the free energy of the cilia [13, 31]. The influence of such factors on the dissolution temperature of very high molecular weight polyethylene was, in fact, demonstrated by the experiments on crystals from quiescent solution that were described above. In view of the small diameter of the cross-section of the backbone, 15 to 25 nm [16, 18], as compared with the length of the molecules, the properties of the backbone as a substrate for the cilia may be of greater importance than the effect of localization. In particular, nucleation proceeds more readily on strained substrates, which display surface dislocations that would not be stable without strain [32]. In the case of the backbones, thin bundles of taut molecules could be responsible for the higher dissolution and crystallization temperatures. Such long "primary stems" may promote that the cilia nucleate with an exceptionally high stem length on to the backbones. The same is suggested by the very long periods found upon crystallization from the melt (as was described in the previous section). The tapered shape of lamellae on shish-kebab fibrils may be largely due to this phenomenon.

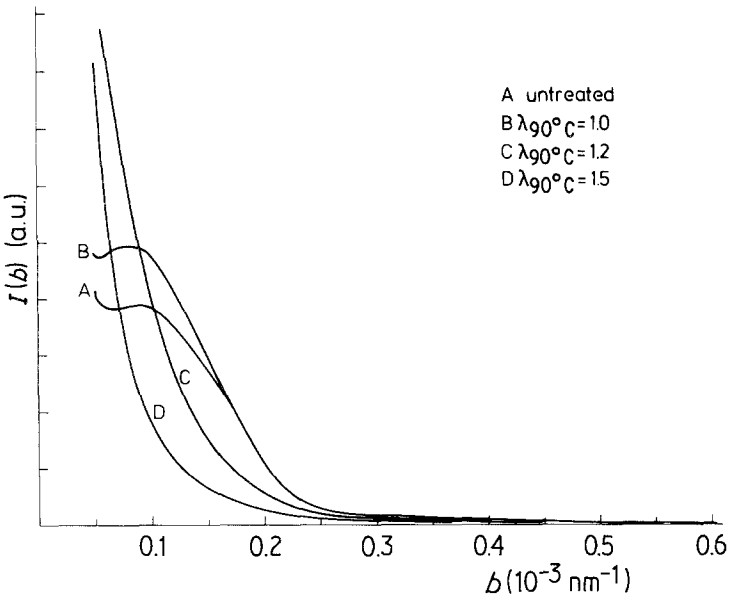


Figure 23 Changes in the morphology of surface-growth fibre T1 upon drawing at 90° C. Undrawn fibre (A) and fibres drawn to various ratios λ indicated in the figure (B to D). (Meridional SAXS curves, corrected for blank scattering; $b = 2 \sin \theta/\lambda_x$.)

Furthermore, Fig. 22 demonstrates that rapid cooling produces a more heterogeneous morphology with a shorter period (25° C quenched).

The results presented above are strong evidence for our view that the folded-chain overgrowth is not formed simultaneously with the backbones at the high temperatures of fibre growth. For polyethylene in *p*-xylene, which is more commonly employed as a solvent than dodecane, the corresponding temperatures of crystallization and dissolution are roughly estimated to be 10° C lower.

3.4. Behaviour of the lamellar overgrowth in a strained surface-growth fibre

In the framework of an investigation into the mechanism of hot drawing of surface-growth fibres [3, 4], we have also made a SAXS-study of drawn fibres [6]. This will be the subject of a forthcoming paper. Since the shish-kebab morphology is lost due to the aggregation of the elementary fibrils at temperatures above 135° C, the behaviour of the lamellar overgrowth upon hot drawing can no longer be easily observed by means of SAXS. In order to study the response of the overgrowth to mechanical strain, some SAXS measurements were made on fibres that had been drawn at 90° C. At 90° C the maximum attainable draw ratio was only 1.5. These results will be discussed in the context of this paper.

Fig. 23 shows the meridional scattering curves. Curve A represents the washed starting fibre T1. After a passage through the drawing apparatus at 90° C at constant length, a slight change is noticeable (B) in agreement with the results of Fig. 13. After drawing to a ratio of 1.2 the scattering profile has changed considerably (C): the maximum has completely disappeared, which indicates a disturbance of the ordered character of the lamellar overgrowth. The invariably high intensity indicates that the porous nature of the fibre has been preserved. Drawing to a ratio of 1.5 results in an even steeper continuous curve (D).

These SAXS curves indicate a strong deformation of the lamellae upon elongation of the fibre. If this deformation would occur only here and there in the sample, the peak intensity would not decrease so strongly, and the long period would still be detectable. The effects observed suggest that the morphology has changed throughout the fibre. The results are not in accordance, however, with a homogeneous (affine) elongation of the elementary fibrils, which is unlikely anyway. Instead, the observations suggest that the fibrils slide past each other, thereby shearing the lamellar overgrowth. In order to have this take place throughout the fibre, the backbones of the elementary fibrils should be of finite length, or should contain many weak spots that yield under a certain load. From this emerges a picture of the macrofibre in which the lamellae act as the matrix of a fibre-reinforced system. This is a direct consequence of the mechanism of fibre formation, in which an entanglement network of long chain molecules is stretched [33]. The elastically ineffective parts form the transverse lamellar connections between fibrils [34]. This view is sup-

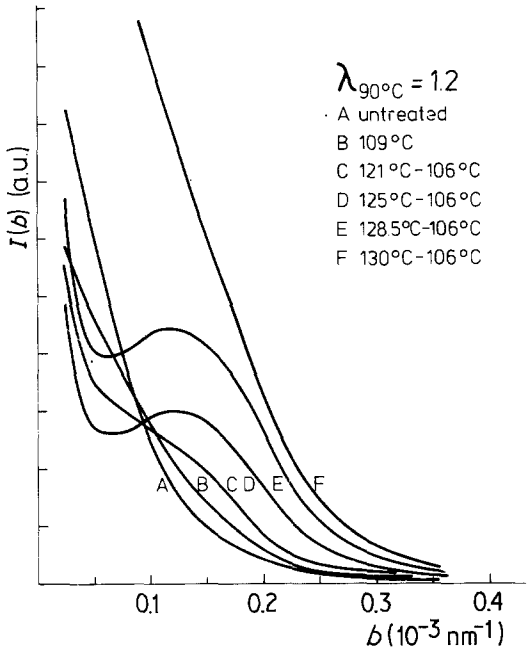


Figure 24 Recrystallization of the overgrowth in surface-growth fibre T1 drawn to a ratio of 1.2 at 90° C. For the curve referred to as 109° C, the sample was kept in *n*-dodecane at this temperature for ~ 16 h, and allowed to cool in ~ 30 min. For the curves 121 to 130° C, the sample was kept at this temperature for 30 min, subsequently stored at 106° C for 16 h and left to cool. After removal of dodecane with acetone or hexane and drying, SAXS curves were recorded at room-temperature. (Meridional SAXS curves, corrected for blank scattering; $b = 2 \sin \theta / \lambda_X$.)

ported by EM observations which show that many lamellae extend over several backbones [5, 9]. Furthermore, neighbouring lamellae around different backbones tend to intercalate [5, 18]. During elongation, these lamellae will become inclined with respect to the backbones and some may be stretched so as to form fibrils. Transverse fibrils have been observed on electron micrographs [3, 9, 33]. The low-temperature transformation of lamellae into fibrils is also demonstrated in the transmission EM work by Krueger and Yeh [8], who studied fibres grown by stirring-induced crystallization onto a mylar support film which was elongated afterwards. Zwijnenburg and Pennings [1] found a plateau in the stress–strain curve of fibres with extensive lamellar overgrowth; this also suggests the transformation into fibrils. Fibrils could be formed from a lamella connecting neighbouring backbones that slide past each other, but also from a lamella situated at a highly defected region that yields upon elongation, during with the lamellar material is incorporated into the backbone [6]. Both mechanisms could operate simultaneously if the backbones would branch and merge throughout the system. If the defect zones in the backbones that yield on elongation are not too far apart, the morphology will become too inhomogeneous to produce a SAXS maximum. A possible distinction between "shearing" and "reeling-in" mechanisms will be the subject of our future work on drawing.

The results of dissolution experiments carried out in this framework are shown in Fig. 24. The fibre drawn to a ratio of 1.2 at 90° C was kept in dodecane at various temperatures. SAXS curves were recorded on the dry fibre at room-temperature. There is a steady change in the SAXS curves. The formation of a shoulder indicates that more cilia dissolve upon each successive treatment so as to form lamellae upon cooling. (One more experiment was carried out at 115° C; the curve is omitted in Fig. 24 for clarity.) It appears that up to 121° C very few cilia are involved. At 125° C the amount is larger and a clear shish-kebab morphology (80 nm) is formed upon cooling. A similar SAXS curve, although of higher intensity, is found for 128.5° C. After a treatment at 130° C, which is substantially above the growth temperature of 128° C of the original fibre, the SAXS intensity is very much higher. This is accompanied by a change to a more shiny appearance of the macrofibre, and a tendency of the adjacent fibre turns on the sample frame to stick to each other. A WAXD pattern of the fibre at the end of the experiment is shown in Fig. 25. The over-all orientation is still very good. We conclude that at 130° C a substantial fraction of the fibre, including backbone material, becomes swollen and yields cilia, with the result that much larger lamella are formed upon cooling. Such an overgrowth may have a periodicity which is too large to be observed by the SAXS set-up used [10, 13].

The SAXS results show the re-formation of the shish-kebab morphology and indicate that the cilia in the elongated fibre are able to dissolve and disentangle at 125° C, i.e. only slightly above the dissolution temperature of the lamellar overgrowth. This suggests that during elongation of the fibre at 90° C the lamellae were stretched into fibrils but were not integrated into the backbones.

4. Concluding remarks

By means of SAXS measurements we have been able to show the morphological changes that take

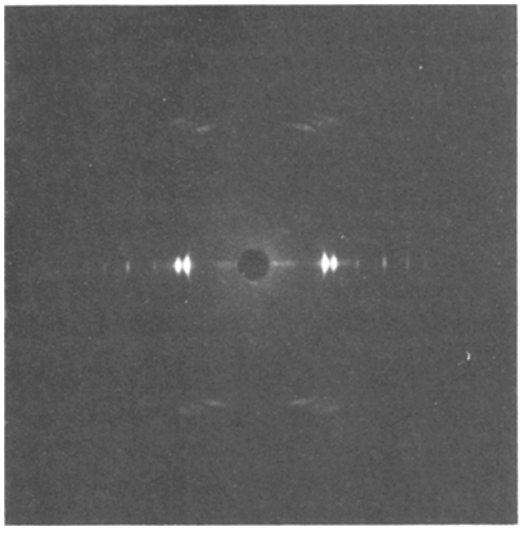


Figure 25 WAXD pattern of surface-growth fibre T1 after drawing to a ratio 1.2 at 90° C and subsequent recrystallization cycles in *n*-dodecane (Fig. 24).

place in shish-kebab fibres upon heating in vacuum and in solvent. Upon heating in vacuum, the aggregation of overgrowths into beads and of whole fibrils into thicker threads leads to densification of the fibres. In the more dispersed shish-kebab samples used for TEM, the presence of lamellae on the surface of aggregates can be assessed after cooling. In the case of heat-treated surface-growth fibres, the low SAXS intensity and its reversible temperature dependence suggest that lamellae are formed throughout a phase which is free of voids. Indeed, the observation that the scattering of such a sample does not vary over the range 143 to 162° C indicates that the aggregation is as complete as possible. The reorganization effects are not found upon heating in dodecane, which is a solvent for the material at high temperatures. The lamellae can be dissolved selectively and can be made to recrystallize as shish-kebabs at ca. 110° C. From these observations it is concluded that the reorganization in vacuum is due to the large surface area of the elementary fibrils, which results in a high free energy in vacuum. Apart from the lamellae, there may be a large contribution from the "veil", thin bundles of tie molecules, to the surface free energy.

The deformation of the lamellae between fibrils when a fibre is elongated can easily be observed by SAXS. This phenomenon supports the idea of highly entangled or even continuous cilia between elementary fibrils as a result of the fibre growth mechanism. If a model is considered in which the lamellae act as a matrix between the fibrils, an improvement of the mechanical strength could be achieved by a process which yields (a) a higher volume fraction of backbones, or (b) backbones of higher continuity and perfection, or (c) a matrix in which the applied stress is more evenly distributed. The latter mechanism is likely to account for the result that drawing at 90° C, during which the fibre remains porous, has been found to increase the tensile strength from 1.9 to 2.5 GPa [5]. Clearly, this involves a deformation of the matrix which results in fewer stress concentrations upon loading at room temperature.

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