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A USAXS study of melt processed PE with a shish-kebab structure: the influence of temperature on the long periods

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The changes in the two axial long periods of injection moulded oriented linear polyethylene (PE) with a shish-kebab structure have been investigated as a function of temperature by ultra-small angle X-ray scattering (USAXS) using synchrotron radiation. The aim of the present study is to investigate the origin of both periodicities and to establish whether both scattering maxima are mutually related. The gradual transformation of the initial two long periods, $L_1 = 36.4$ and $L_2 = 65.7$ nm, measured at room temperature to the final single long period $L_f = 120$ nm at $T = 130°C$ has been demonstrated on high molecular weight oriented PE samples. The detection of such high long periods (up to 150 nm for these samples) has been possible, for the first time, thanks to the use of the new high resolution USAXS beam line at the DORIS-bypass, DESY. On the other hand, low molecular weight PE shows, at room temperature, one long period corresponding to an oriented structure with a wide lamellar distribution. The coherently diffracting domains in the chain direction and the mean orientation of the lamellae derived from the azimuthal scanning of the SAXS profiles have also been examined as a function of temperature. The changes of the long period L_1 with temperature are shown to be independent from the changes of the L_2 periodicity. From the results it is concluded that the oriented shish-kebab structure, in the high molecular weight samples, consists of two separate populations of lamellar stacks with the layer normals parallel to the injection direction. During annealing only the thinner lamellae increase in thickness until they reach the size of the thicker ones at about $T = 130°C$. For higher temperatures than $T = 137°C$ the scattering maxima vanish suggesting that the lamellae melt. Finally, after cooling from the melt the lamellae crystallize epitaxially on the preserved oriented shish fibrils and both stacking periodicities L_1 and L_2 appear again. © 1997 Elsevier Science Ltd.

(Keywords: polyethylene; USAXS; shish-kebab fibrils)

INTRODUCTION

Elongational flow injection moulding is a processing method which yields high strength materials due to the self-reinforcing capability of the highly oriented fibrils[1,2]. The morphology of these oriented materials is described as that of shish-kebab fibrils[3,4]. It consists predominantly of oriented shish cores along the injection direction and laterally grown stacked lamellae with the layer normals in the same direction. Extensive work has been previously performed on shish-kebab structures obtained from other processing routes. These generally involve an induced orientation by crystallizing the material under shear or extensional flow. In this respect, the work of Pennings *et al.* on hydrodynamically induced crystallization from solution[5,6] and the investigations of Keller *et al.* on the extrusion of PE just above the melting point[7,8] are well known. We have investigated the changes in crystal orientation of the crystal stacks as a function of temperature by real time X-ray wide angle diffraction[9]. Additionally, the influence of molecular weight and melt temperature upon the microstructure, as revealed by small angle X-ray scattering (SAXS) has been examined[10]. The SAXS pattern of the higher molecular weight ($\bar{M}_w \sim 478\,000$) linear PE oriented samples shows, at room temperature (25°C), two meridional maxima corresponding to two distinct periodicities of about 32 and 55 nm respectively[9–11]. On the other hand, the low molecular weight (LMW) material ($\bar{M}_w \sim 50\,000$) essentially shows, at room temperature, just a single long period of about 30 nm throughout the sample. The appearance of the lower long period has been associated to the stacks of lamellae while the presence of the higher periodicity has remained unclear until now[10,12].

The purpose of the present study is to investigate the origin of both periodicities and to elucidate whether both maxima are mutually related. For this reason we have followed the changes occurring in both long periods, L_1 and L_2, in real time, as a function of temperature up to the melting point. This investigation has been possible thanks to the recent development of a high resolution (~ 300 nm with the present setting) ultra-small angle X-ray scattering instrument (USAXS) which is available at the DORIS-bypass (DESY, Hamburg).

EXPERIMENTAL

Materials

Two linear PE samples having low (LMW) and high (HMW) molecular weight, were selected for this investigation (*Table 1*). Oriented PE bars with a square cross-section of 4 × 4 mm were prepared by elongational flow injection moulding. The influence of processing

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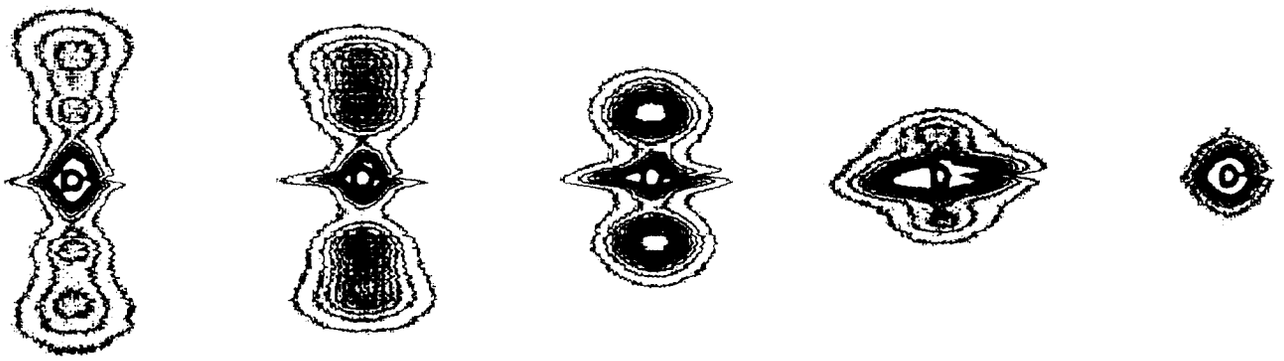

Figure 1 USAXS patterns from HMWPE obtained at various temperatures, from left to right: 25°C; 120°C; 130°C; 135°C; 150°C

parameters on the properties of the oriented materials has been reported in preceding studies[13,14]. In the present work we used samples processed at a melt temperature $T_m = 145°C$ and a mould temperature of $T_c = 20°C$. In the HMW material a uniform high molecular orientation across the thickness of the samples, as revealed by birefringence measurements, is found. On the other hand, the LMW samples show 100–200 μm size regions of low orientation[13]. Shish fibrils are preferentially formed at zones near the centre of the mould. Therefore, the specimens investigated were about 1 mm thick cuts from the inner part of the bars where the regions with higher orientation are expected.

Techniques

The ultra-small angle X-ray scattering instrument (USAXS) in conjunction with the synchrotron source at DESY was used to obtain the SAXS patterns of the oriented PE samples. The changes in the SAXS pattern were followed at various temperatures, using a hot stage placed at the sample holder. The samples were positioned with the X-ray beam perpendicular to the injection direction. *Figure 1* illustrates the typical SAXS patterns obtained for the HMW samples at different temperatures. During the X-ray scattering experiments the specimens were wrapped with aluminium foil. This facilitated the heat exchange between the hot stage and the sample and prevented the flow of material at temperatures approaching the melting point. A sample–detector distance of 12 600 mm and a wavelength of 0.1337 nm were used. The beam path was kept in a vacuum of 10^{-6} mbar. A two-dimensional 512 × 512 multiwire detector with a spatial resolution of 0.361 mm per pixel was used.

The heating of the samples was carried out stepwise in the range between room temperature and the melting point at selected temperatures. A heating rate of 10 K min^{-1}, allowing the sample to reach the programmed temperatures in 1 min before the recording of the SAXS pattern, was used. Exposure times of 5 min were required. HASYLAB programs running in a 486 PC were used to perform meridional and azimuthal scans of the SAXS maxima.

Table 1 Name, molecular weight and density of the two polyethylene samples investigated

Sample	Trade name	$\bar{M}_w$	ρ(g cm^{-3})
HMW	Lupolen 5261z	478 000	0.958
LMW	Vestolen A6017	51 000	0.966

RESULTS

Axial long period

Figure 2 illustrates the profiles of meridional scattering intensity of the HMW sample obtained at different temperatures after background subtraction. It is quite interesting to follow the transition of the long periods from the starting two well resolved maxima $L_1 = 36.4$ nm and $L_2 = 65.7$ nm to the final value L_f as a function of temperature, as shown in *Figure 2*. With increasing temperature the scattered intensity of maxima is notably increased and a shift of the L_1 maximum towards the position of L_2, which remains nearly constant up to 125°C, is observed. Above 130°C the maxima L_1 and L_2 are not resolved any more and the 'single' maximum is shifted towards smaller scattering angles with increasing temperature. Concurrently, a conspicuous decrease of intensity in the meridional scattering is observed. For temperatures above 137°C (not shown in *Figure 2*), still below the macroscopic melting point, no meridional scattering was detected.

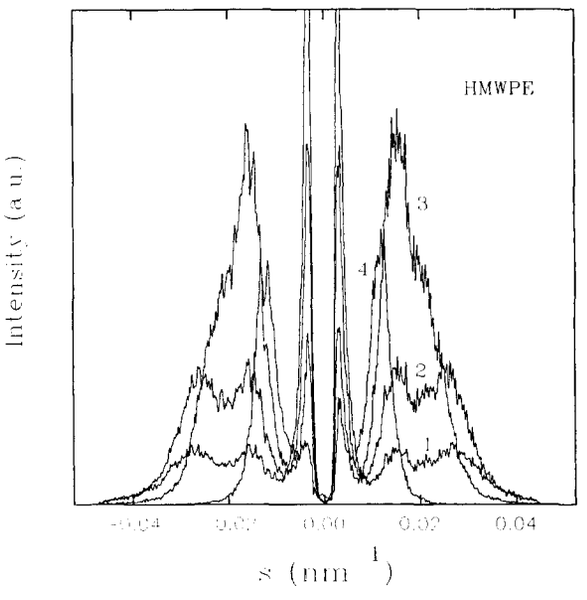

Figure 2 Meridional scans of the USAXS patterns of highly oriented HMWPE measured at different temperatures. (1) 25°C; (2) 110°C; (3) 125°C; (4) 133°C

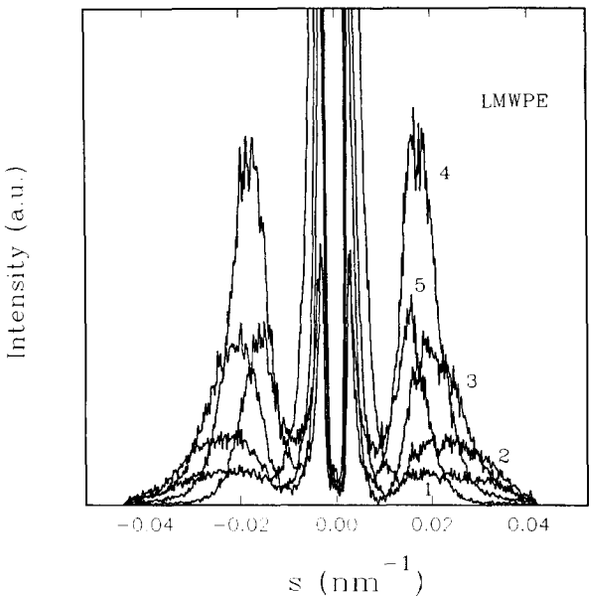

Figure 3 Meridional scans of the USAXS patterns of highly oriented LMWPE measured at different temperatures. (1) 25°C; (2) 100°C; (3) 120°C; (4) 127°C; (5) 133°C

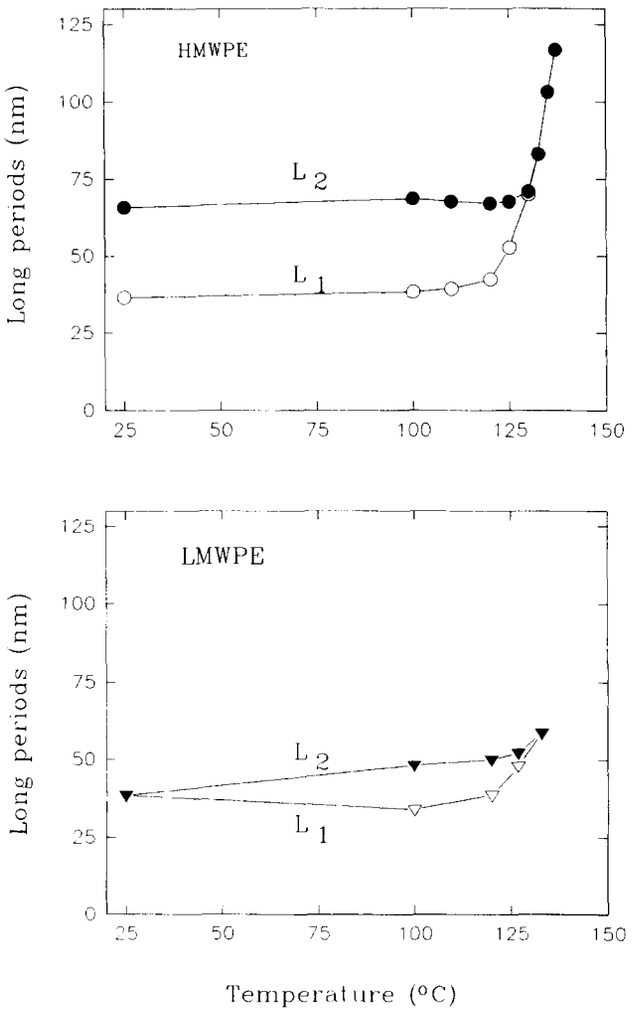

Figure 4 Meridional SAXS long periods for highly oriented HMWPE and LMWPE as a function of temperature

However, as will be shown below, the equatorial scattering continuously increases with temperature.

Figure 3 shows the meridional profiles for the LMW sample as a function of temperature after background subtraction. A first inspection of the profiles recorded at 25°C reveals the presence of a rather broad 'single' maximum. Upon heating, the scattering intensity also increases and the shape of the maximum becomes narrower. It is worth noting that the narrowing of this asymmetric maximum observed up to 120°C takes place from the outer side (higher scattering angle) of the maximum. For $T \geq 127$°C a nearly symmetric peak is observed which shifts towards smaller scattering angles with increasing temperature.

The long periods calculated from the position of the resolved peak maxima using Bragg's law for the HMW and the LMW samples are represented in *Figure 4*. Results show that, for both samples, the long period increase for the first maximum is independent from the spacing increase of the second maximum. Indeed, at room temperature the ratio L_2/L_1 is nearly equal to 1.8 for the HMW sample and it decreases gradually to a value of 1 for $T = 130$°C. For the LMW sample the scattering curve cannot be resolved in two maxima at 25°C. However, at 100°C, the ratio L_2/L_1 is only 1.4, i.e. much smaller than that observed for the HMW material at the same temperature. The variation of the ratio L_2/L_1 with temperature shows that the L_2 and L_1 values are not the first and second order reflection of the same periodicity. Above 137°C the intensity of the final maximum, L_f, vanishes for both PE samples, suggesting that the lamellae are molten at this temperature. After melting and subsequent quenching in liquid nitrogen of the HMW sample, a broad single meridional maximum with a value of $L = 38$ nm is obtained.

Most interesting is to follow the evolution of the long period upon cooling the sample from the molten state of the lamellae down to 25°C. By setting the temperature of the HMW sample at 132°C for 15 min a meridional scattering maximum at about 130 nm emerges (*Figure 5*).

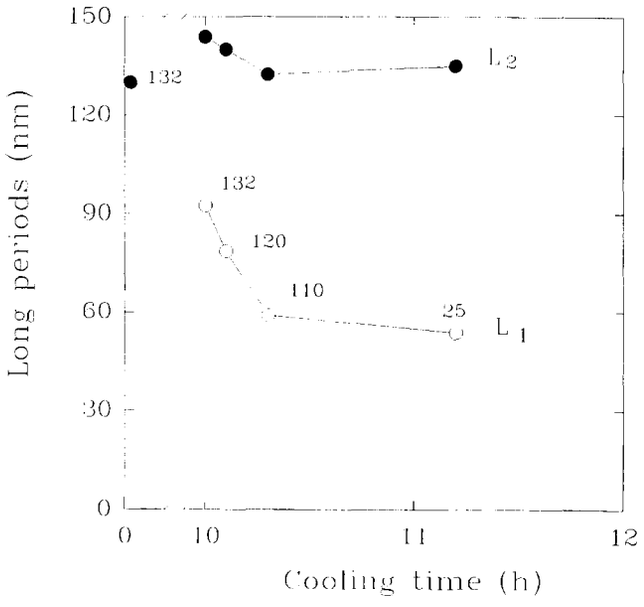

Figure 5 Variation of the long period of oriented HMWPE as a function of cooling time from the molten state, measured at different temperatures

After 10 h at the same temperature a second meridional maximum at 90 nm appears while the first one increases up to 145 nm. By cooling further the sample maxima shift to lower periodicities, it reaches limiting values of $L_2 = 130$ nm and $L_1 = 58$ nm which are totally different to the initial values ($L_2 = 71.8$ nm; $L_1 = 36.3$ nm).

Broadening analysis of the maxima

The meridional profiles of *Figures 2* and *3* were analysed by means of a peakfit program. The broadening of the SAXS reflections was measured to study the temperature dependence of the coherently diffracting domains in the chain direction. It is to be noted that in the case of the SAXS patterns of *Figure 3* the best fitting of profiles recorded at 100°C and 120°C requires two peak components for each asymmetric broad peak.

In Figure 6 we plot the temperature dependence of the coherence length along the fibre direction D_z as a function of temperature as calculated from the integral width $\delta\beta \sim 1/D_z$ of the two diffraction maxima (L_1 and L_2) for the two samples. This provides a minimum value for the coherently diffracting length corresponding to the lamellar stacks[15]. A similar D_z temperature dependence is observed for both samples. In both cases the value of D_z first increases slightly with temperature up to $T \approx 120$°C. Then it shows a rapid increase reaching a maximum of approximately 200 nm at a temperature of about 130°C, for which L_1 and L_2 match completely. At higher temperatures D_z falls to much lower values, similar to the initial ones. For the LMW material the maximum seems to occur at a temperature a few degrees lower than for the LMW sample. The D_z values for the HMW sample appear to be larger than for the LMW sample. In the case of the HMW sample, it is to be noted that D_z for the thinner lamellae is slightly larger than for the thicker ones at room temperature. For $T > 100$°C the coherence lengths for both lamellar stackings further increase with temperature. In this temperature range D_z for L_1 and L_2 shows similar values. At 130°C the existing single peak shows a maximum D_z value. For higher temperatures D_z gradually decreases.

Azimuthal scanning of SAXS profiles

Figures 7 and *8* illustrate the azimuthal profiles recorded for the L_2 SAXS maxima at different temperatures for both samples. The maxima appearing at 90° and 270° correspond to the equatorial scattering which is more intense for the HMW sample. (The maximum at 270°C is split due to the shadow of the beam stop.) We see here again that the intensity of the equatorial

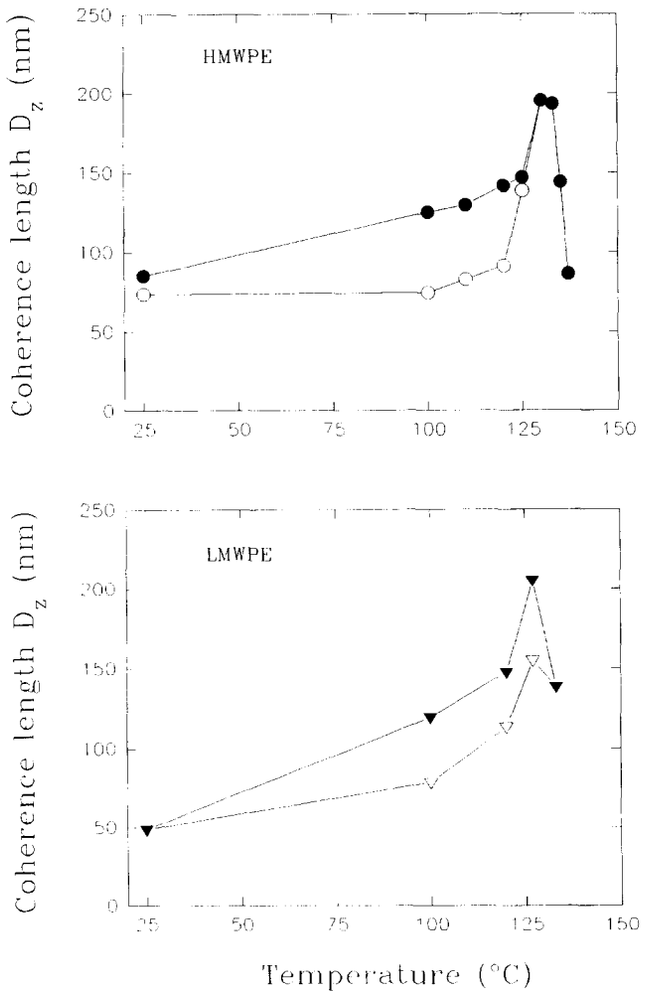

Figure 6 Coherence length D_z in the chain direction for highly oriented HMWPE and LMWPE as a function of temperature. Open and filled symbols correspond to L_1 and L_2, respectively

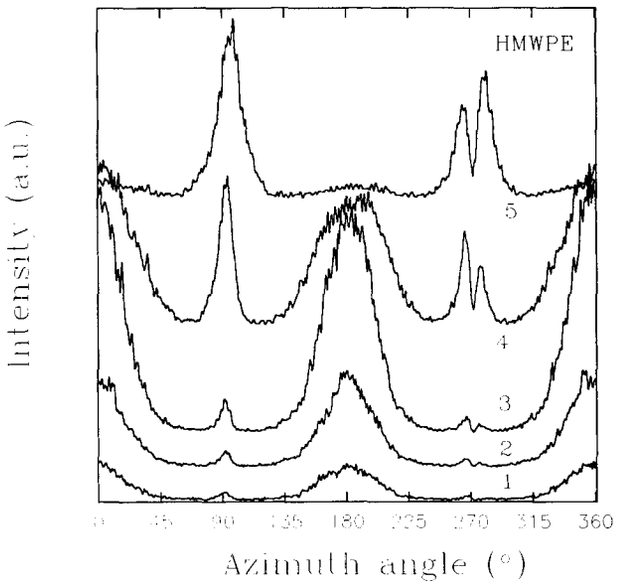

Figure 7 Azimuthal intensity profiles of the SAXS patterns corresponding to L_2 of highly oriented HMWPE: (1) 25°C; (2) 110°C; (3) 125°C; (4) 133°C; (5) 135°C

Table 2 Azimuthal half-peak breadths, $\delta\phi_1$ and $\delta\phi_2$ (degrees), of the two SAXS maxima (L_1 and L_2) observed at different temperatures for the two samples investigated

HMW sample				LMW sample			
T(°C)	$\delta\phi_1$(°)	$\delta\phi$(°)	$\delta\phi_2$(°)	T(°C)	$\delta\phi_1$(°)	$\delta\phi$(°)	$\delta\phi_2$(°)
25	37.5		46.4	25		50.2	
100	33.8		44.0	100	46.4		43.3
110	36.6		41.0				
120	37.0		42.3	120	46.9		40.2
125	42.2		41.4	127	44.7		41.9
130		38.8					
133		59.1		133		45.2	
135		71.4					
137		–					
25		49.5		25		180	

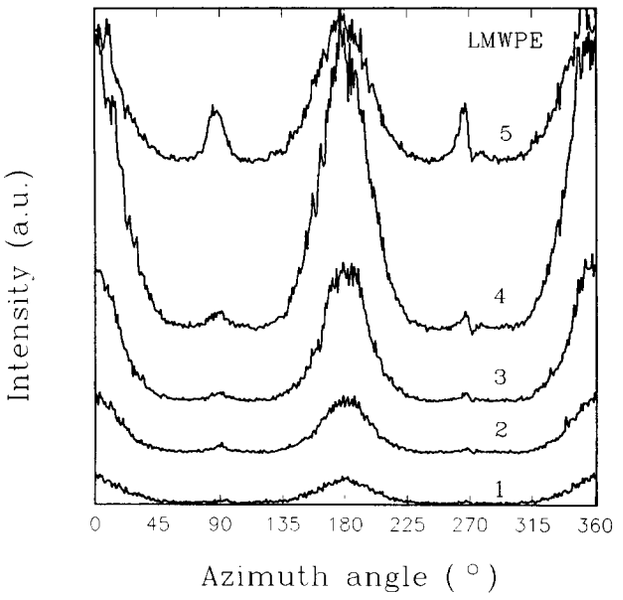

Figure 8 Azimuthal intensity profiles of the SAXS patterns corresponding to L_2 of highly oriented LMWPE: (1) 25°C; (2) 100°C; (3) 120°C; (4) 127°C; (5) 133°C

scattering increases continuously with increasing temperature up to the melting point. *Table 2* collects the azimuthal integral width $\delta\phi$ values observed for the $L_1(\delta\phi_1)$ and $L_2(\delta\phi_2)$ maxima at 180° for the two materials investigated. These values are related to the mean orientation of the lamellae with respect to the fibre direction. It turns out that $\delta\phi_1$ is smaller than $\delta\phi_2$ for the HMW sample while $\delta\phi_1$ is just a little larger than $\delta\phi_2$ for the LMW sample. In the case of the HMW sample $\delta\phi_1$ slightly decreases with temperature up to 120°C and then it increases again. On the contrary, the LMW sample shows decreasing $\delta\phi_1$ values with temperature. After heating above the melting point for a few minutes, and quenching in liquid nitrogen, the HMW sample shows a $\delta\phi_1$ value which is larger but not far from that of the original material. This indicates that the sample recovers, after cooling, nearly its original orientation. A prolonged heating treatment (1 h) at 150°C yields, after cooling the sample at 25°C, a final isotropic single SAXS maximum. On the other hand, after melting and recrystallization the LMW sample loses its orientation and the SAXS scattering appears to be totally isotropic.

DISCUSSION

The analysis of the azimuthal profiles reveals the widely different behaviour of the HMW and LMW polyethylene samples. In the first case the well-developed shish-kebab structure determines the thermal stability of the existing high molecular orientation. On the other hand, in the second case, the complete isotropic state found after melting the LMW material, suggests the absence of shish cores. Here the initial structure is one of highly-oriented lamellae, perpendicularly growing to the injection flow. A result which has been evidenced by EM observations[4]. In what follows, unless otherwise stated, we will concentrate mainly on the findings obtained with the HMW material.

From the data of *Figures 2* and *3* it is evident that the scattering intensity of the SAXS maxima increases with temperature in the 25–130°C range, suggesting that the quality of crystals improves during thermal treatment.

The healing of crystal lattice defects and the relaxation of the amorphous component is connected with longitudinal chain mobility in the crystal lattice. As soon as the temperature is raised, the mobility is high enough for pulling the chains through the thinner lamellae and the long period starts to grow because of the tendency to decrease the free energy; i.e. to reduce the surface to volume ratio of every lamellae. On the other hand, in the same temperature range, although the temperature is not sufficient to induce a thickening of the larger lamellae, it contributes to the observed increase of their coherence length.

Finally, for temperatures higher than 130°C the intensity of the single maximum decreases. This is probably due to a melting, or partial melting, of an increasing number of the lamellae within the shish-kebab structure.

Concerning the origin of the two long periods emerging in these oriented samples our results can be summarized as follows: while the larger long period L_2 remains constant with temperature up to 130°C the smaller long periodicity L_1 slightly increases at lower temperatures reaching finally, at about 130°C, the same value as L_2. In other words, at 130°C the maximum corresponding to L_1 merges into the maximum ascribed to L_2. From these results we may conclude that the oriented shish-kebab structure consists of two populations of lamellar stacks with the layer normals parallel to

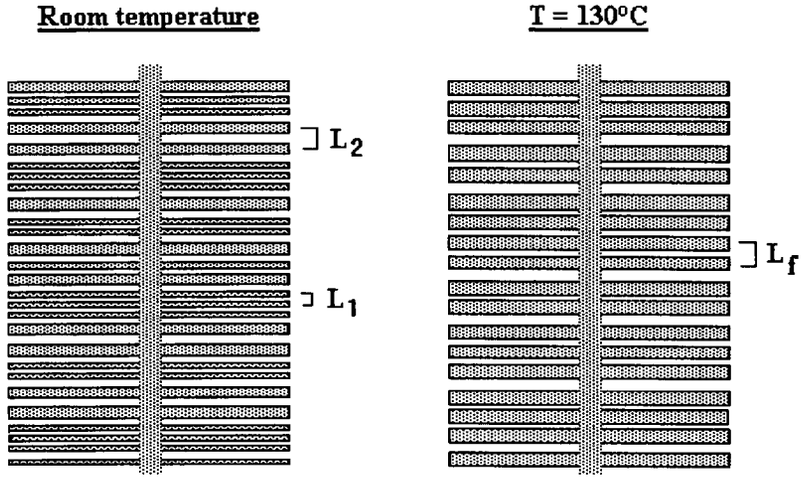

Figure 9 Schematics of the lamellar size distribution within a shish-kebab at room temperature and at 130°C

the injection direction: a population of presumably thicker crystals and a second population of thinner crystals giving rise to the L_2 and L_1 meridional periodicities, respectively (*Figure 9*). During injection moulding, under the influence of an elongational flow in the mould cavity, one may first expect the appearance of dominant thicker lamellae which nucleate statistically along the row structure which give rise to the L_2 maximum. Then, during the cooling process of the mould the subsidiary lamellae crystallize, filling-in the space available between the dominant lamellae, giving rise to stacks of better packed thinner lamellae which contribute to the long period L_1.

Upon heating the shish-kebab oriented samples only the thinner lamellae do thicken with temperature until they reach the size of the thicker ones. For temperatures higher than 130°C both populations of lamellae are indistinguishable from each other (*Figure 9*) and both families of crystals further thicken with temperature. It is to be noted that *Figure 9* does not intend to give a detailed molecular model but it just offers a schematic representation of the lamellar size distribution. Hence, particular details such as the tapering of lamellae allowing interlocking between adjacent shish-kebab are omitted[7,8].

At high temperatures ($T \geq 137$°C) the lamellae melt but the highly oriented shish fibrils are preserved for the HMW sample as shown by previous real time WAXS experiments[9]. Therefore, upon cooling the dominant lamellae emerge first and the subsidiary in-filling ones appear at lower temperatures giving rise to two meridional maxima which are different from the initial ones because the crystallization conditions are different from those of the injection moulding process. In the extreme case of quenching, the appearance of a broad single meridional maximum indicates that now only one population of coherently diffracting thinner lamellae is epitaxially formed on the oriented fibrils, while the formation of the thicker lamellae seems to be hindered.

From our intensity profile broadening measurements of the HMW sample at room temperature, it is concluded that the length of the coherently diffracting stacks is smaller for the thinner than for the thicker lamellae. Furthermore, it turns out that both coherently diffracting stacks, thinner and thicker, increase with temperature for both populations.

The azimuthal analysis of the SAXS profiles reveals that, on the whole, the mean orientation of the lamellae decreases with increasing temperature. To explain the decrease in orientation in the HMW sample one has to find some molecular mechanism which is not connected with the long period growth. Such a mechanism can be related to the relaxation of many interfibrillar tie molecules causing a certain misalignment of the highly-oriented microfibrils with respect to the fibre axis. The mismatching increase between adjacent fibrils produced by the temperature rise enhances, in addition, the microfibrilarity of the shish-kebab structure giving rise to an increase in the equatorial scattering of the SAXS pattern.

One also observes that the $\delta\phi_1$ values for the HMW samples are smaller than for the LMW ones.This means that the thinner lamellae are better oriented in the HMW sample because they are anchored in the shish fibrils. This result is, on the other hand, consistent with the stronger equatorial scattering which is observed in HMW samples in contrast to the LMW sample.

CONCLUSIONS

In conclusion, the two long periods L_1 and L_2 which appear in oriented shish-kebab structures correspond to two independent populations of lamellar stacks with the layer normals parallel to the injection direction.

The long period L_2 has been associated to the thicker dominant lamellae which nucleate during injection moulding along the row nuclei which are formed in the mould.

The long period L_1 is assigned to the stacks of thinner lamellae filling-in the free spaces between the dominant lamellae.

Annealing of the shish-kebab samples yields a gradual transformation from the initial two long periods, L_1 and L_2, at room temperature to the final single long period L_f at $T = 130$°C. At higher temperatures the lamellae melt and the scattering intensity of the two point diagram vanishes.

Since the oriented shish fibrils are preserved near and above the melting point, when slowly cooling the sample, the lamellae crystallize epitaxially and both stacking periodicities appear again.

In the case of the low molecular weight sample one long period, which corresponds to an oriented structure with a wide lamellar thickness distribution, appears at room temperature.

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