PROBLEMS RELATING TO LONG PERIOD DETERMINATION IN POLYETHYLENE SHISH-KEBAB STRUCTURES

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Abstract

The X-ray long periods from high molecular weight injection molded polyethylene (PE) with a shish-kebab structure have been compared with values derived from electron micrographs. It is shown that while the small angle X-ray scattering (SAXS) presents two long periods, the direct measurements from transmission electron microscopy (TEM) furnish only the lower SAXS periodicity. In an attempt to clarify this discrepancy of results, laser light diffraction and Fourier transformation of electron micrographs has been undertaken. Using this method two long periods are found in all regions investigated. Results are discussed in terms of the role played by the structured or "weakly crystalline" interlamellar parts, containing a lower electron density, which are neglected by the small angle scattering of X-rays and which give rise in particular regions to larger scattering periodicities.

1 Introduction

In a previous study we have investigated the influence of molecular weight of injection molded polyethylene on the arrangement and the thickness distribution of the oriented lamellae [1]. Two of the techniques used were small angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). If the molecular weight is sufficiently high (above $\overline{M}_w \sim 100 \times 10^3$) the SAXS patterns reveal the presence of a double long period (L_1 and L_2) [2]. On the other hand, TEM investigations of the same samples show up typical shish-kebab structures with relatively broad lamellar thicknesses and long period distributions. A quantitative measure of the spacings between adjacent lamellae on the electron micrographs shows a frequency distribution of long periods with only one maximum value (L_1). This value was shown to correlate with the smaller long period as determined by SAXS [1]. The changes of the two long periods as a function of temperature have been followed by ultra-small angle X-ray scattering (USAXS) using synchrotron radiation [3]. The temperature variation of the long period L_1 is shown to be independent from the changes of the L_2 periodicity. This result leads to the conclusion that the structure is composed of two types of stacks of lamellae. A view which is also supported by the two independent melting points which shows the material [4].

The aim of the present study is to discuss the difference between the results obtained from SAXS and TEM and to clarify the structural reasons for the scattering experiments in both cases. Specifically the long periods determined from electron micrographs have been compared with values derived from scattering techniques. In particular, results of laser-light diffraction of electron micrographs are compared with SAXS results.

2 Experimental

Highly oriented injection molded samples of linear PE with an average molecular weight of about 478,000 and an injection temperature of the melt of $T_m = 144^\circ\text{C}$, i.e. very close to the melting point of the polymer, were investigated. The moldings were produced following a method that enhances axial elongation flow during the filling stage [5,6]. In the present study the oriented injection molded materials had a square cross section of $4 \times 4 \text{ mm}^2$. Surface regions 0.5 mm from the outer face of the moldings were investigated. Data corresponding to an inner region, at 0.5 mm from the long axis, are also mentioned. Additional details of the samples are described in references [1-4].

SAXS patterns were obtained at room temperature using a Kiessig camera with Ni-filtered Cu K_α radiation from a Rigaku rotating anode X-ray generator. A sample-film distance of 500 mm was used. For electron microscopy, small samples of the injection molded piece were taken from the region of interest and prepared by the technique of selective staining by chlorosulfonic acid and osmium tetroxide. Ultra-thin layers were cut in a cryo-ultramicrotome, mounted on copper grids and finally investigated under the TEM.

Quantitative determination of the thickness, the thickness distribution and the long period of the lamellae stacking were determined by direct measurement on the electron micrographs and by using the contrast distribution between lamellae and interlamellar amorphous regions measured in a micro-densitometer [7]. To determine the long period, laser light diffraction on the negatives of electron micrographs has been used as a third method. As a modification of the latter, fast Fourier transformation (FFT) of negatives shows directly the long periods.

3 Results

3.1 Morphology

The injection molded material shows, near the surface of the molding (outer region), a well defined orientation of lamellae belonging to a conspicuous shish-kebab morphology (Figure 1). The lamellae, sharply limited by amorphous regions, are perpendicularly grown to the shish fibrils with shish widths of a few tenths of μm and lengths of several μm . Lamellar thicknesses vary between 4 and 15 nm, with an average value of about 9 nm (Figure 2). In the inner region a well pronounced parallel arrangement of lamellae forming shish-kebab structures can be also observed, though in some areas a weaker and not so clear orientation appears [1].

3.2 Long period determination

SAXS investigations of the material show two meridional maxima, corresponding to two long periods L_1 and L_2 . The L_2 value corresponds to the intensity maximum appearing at lower diffraction angles. In the inner region the maxima are at 35 and 62 nm, respectively. In the outer region maxima appear at 31 and 56 nm, respectively (see Table 1). In [1] it has been shown that below a certain critical molecular weight of $\overline{M}_c \sim 10^5$, the long periods L_1 and L_2 slowly increase with molecular weight (proportional to: $1/2 (\overline{M}_w + \overline{M}_n)^{1/2}$). As a general rule, the long periods measured in the inner region are always larger than the corresponding ones in the outer region.

In the outer region, containing shish-kebab structures, the long periods can also be determined on the electron micrographs. The long periods have been measured in five different areas using two different methods (Table 1):

- (i) Direct measurement on electron micrographs with high magnification under light optical control. We have also measured the contrast distribution using

a micro-densitometer. From the contrast distribution curves the long periods can be measured as illustrated in the scheme of Figure 3. The long period is the sum of lamellar thickness l_c , the thicknesses g of lamellar boundaries, and the thickness l_a of the amorphous interlamellar region:

$$L = l_c + 2g + l_a \quad (1)$$

- (ii) From negatives of electron micrographs (at lower magnifications than in case i) laser light diffraction patterns were taken, showing maxima, which allow to calculate the long period. As an example, Figure 4 shows an electron micrograph of area 3 with a typical shish-kebab structure and the corresponding laser light diffraction pattern from a small well-ordered part of this area. Fig. 4c shows the densitometer curve of the diffraction pattern with the maxima, giving two long periods L_1 and L_2 . The corresponding contrast distribution curve determined from Fourier transformation of the whole area 3 is shown in Fig. 5, giving main maxima for the long periods L_1 and L_2 . There are also some small secondary maxima, corresponding to a smallest long period of about 15 nm and a largest one of about 80 nm.

Using method (i), only the adjacent lamellae are taken into account, yielding relatively small values of long period. The long periods show a variation in every area and also from one area to the next one. The results are summarized in Table 1. The long periods from all the 5 different areas vary in the range from 9 to 31 nm with a frequency maximum of about 18 nm. Using method (ii), two long periods were found in each area with a small variation from area to area. These values are also presented in Table 1.

4 Discussion

It is rather surprising that the direct determination of long periods on electron micrographs (method (i)) yields a frequency distribution with only one maximum L , whereas application of laser light diffraction to the same micrographs reveals the occurrence of two maxima which practically coincide with the SAXS data. The largest long periods derived from direct measurement on the micrographs (about 30 nm) correspond to the smaller maximum L_1 from the laser light diffraction. The scattering maximum L_1 from laser light diffraction and SAXS data corresponds to the upper limit of frequency distribution of long periods directly measured on electron micrographs. The long periods directly measured on micrographs vary in a range from about 9 to 31 nm, correlating with a variation of lamellar thicknesses l_c from 4 to 14 nm (see Fig. 2). Thin lamellae contain the highest amount of crystalline defects in form of chain ends or branchings [8,9]. During cooling from the melt, these thinnest lamellae are produced at a late stage between the earlier crystallized thick lamellae, i.e., they are produced in a melt with a higher content of defects and a greater hindrance of molecular mobility [10,11]. Therefore, the difference in electron density between thin lamellae and amorphous zones can be strongly reduced, not contributing, or only in a reduced manner, in some areas to scattering. Thus, the smallest long periods, which are directly measurable on electron micrographs, are not detectable by the techniques of SAXS and laser light diffraction.

The second difference is the appearance of the second scattering maximum L_2 in SAXS and laser light diffraction. Larger periodicities than 30 nm are observed directly on micrographs. However, in such cases the interlamellar regions are not homogeneously stained, showing small brighter zones or spots, resembling to very tiny lamellae or small crystalline blocks. These regions seem to contain not only "regular" amorphous material, but also parts with a certain higher ordering or with a somewhat worse crystalline orientation. This situation is shown in the very high

magnification of Figure 6. Similar microdomains within interlamellar regions have been described in [12]. If one neglects these structures contained in the interlamellar regions, long periods between the well pronounced lamellae of up to 80 nm can be detected directly on micrographs (see Figure 7). These larger values are in the range of the second SAXS maxima L_2 (see Table 1). On the other hand, laser light diffraction patterns show a total variation of long period between approximately 15 nm and 80 nm, in very good agreement with the direct measurement on electron micrographs.

From the foregoing it can be concluded that small angle scattering of X-rays, as well as light scattering of electron micrographs, clearly detect the electron density difference between separated well defined lamellae. However, X-ray scattering and light scattering of electron micrographs neglect the lower electron density contrast from small and "weakly crystalline" parts. On the other hand, electron micrographs of selectively stained ultra-thin sections reveal such "weakly crystalline" interlamellar structures. Since only adjacent lamellae are used for the measurement of the long period directly on electron micrographs, in this case, only the smaller distances contribute to the L_1 value.

At this point it arises the question as to what must be the "quality" of macromolecular orientation to count either to the amorphous or to the crystalline part. Besides the "regular" lamellae, detectable by all the techniques, there are very thin lamellae containing defects, which are better detectable by direct TEM investigation. In a similar way, there are some better ordered microdomains in the "regular" amorphous interlamellar regions which are detectable only directly on the electron micrographs (see Fig. 6). Scattering techniques are obviously not the appropriate ones to detect these "weakly crystalline" structures.

The above findings can be explained in the light of the oriented lamellar structure formed during the axial elongational flow process which arises upon injection

moulding. During cooling from the melt, at first, long and relatively thick dominant lamellae with nearly no crystalline defects appear. These sequences of lamellae give rise to the largest L_2 periodicity. In the free spacings between these well-oriented lamellae, more and more additional thinner secondary lamellae crystallize (in accordance to step-wise or insertion crystallization views discussed by Basset [13] and Strobl [10,11]). If the thicknesses of the interlamellar amorphous regions reach a minimum size (depending on molecular weight, branching degree, cooling rate and others [9,11]), crystallization stops, yielding long periods in the range of the first maximum L_1 . However, there are also many larger spacings between lamellae, due to the presence of, either, interlamellar material containing a high degree of non-crystallizable components (such as defects, chain ends, branching...) or tie molecules which reduce the mobility of macromolecular segments. Here, "regular" lamellae cannot crystallize, but microdomains with a somewhat better ordered macromolecular segments can appear. This is schematically drawn in Fig. 8. These microdomains possess small density differences with respect to the surrounding, which are, however, large enough to yield density differences by the staining procedure and, therefore, to be observable under the electron microscope. However, the density differences are too small to give sufficient contrast to be detected by SAXS or by laser light diffraction. Therefore, these regions contribute only to the larger second scattering maxima L_2 .

5 Conclusions

In conclusion, a direct visualization of electron micrographs of oriented shish-kebab structures yields apparently smaller spacings between non-stained areas (lamellae and other crystalline parts) and gives rise to smaller long periods. Furthermore, the "weakly crystalline" parts containing a lower electron density between adjacent lamellae are neglected by the small angle scattering of X-rays. These given regions of the material yield larger long periods.

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Figure Captions

- Fig. 1 Electron micrograph from the outer region of HDPE, showing a well defined orientation of lamellae in the form of shish-kebabs (selectively stained ultra-thin section, TEM).
- Fig. 2 Frequency distribution of lamellar thickness l_c measured on electron micrographs.
- Fig. 3 Schematic representation of contrast distribution determination between lamellae and interlamellar amorphous regions, using a micro-densitometer and directly yielding the long period.
- Fig. 4 a) Electron micrograph of a shish-kebab structure from the outer region.
b) Corresponding laser light diffraction pattern of a).
c) Micro-densitometer curve of b).
- Fig. 5 Contrast distribution curve of a Fourier transformation of an electron micrograph of the same area as in Fig. 4.
- Fig. 6 High magnification electron-micrograph showing oriented lamellae and interlamellar regions in shish-kebabs of HDPE. The chemical staining in the interlamellar regions is not homogeneous, revealing an internal structure.
- Fig. 7 Frequency distribution of long periods between well pronounced ("regular") lamellae, neglecting the "weakly crystalline" microdomains within interlamellar regions. Measurements were directly carried out on electron micrographs.
- Fig. 8 Scheme showing the arrangement of well-defined lamellae and amorphous layers, giving rise to smaller long periods L_1 . Larger long periods L_2 are due to the presence of "weakly crystalline" microdomains (denoted by circles).

Table 1: Comparison of long period determination using different techniques.

	Direct optical measurement on micrographs		Laser light diffraction		Fourier transformation			SAXS	
area	range	maximum of frequency distribution	1.Max.	2.Max.	range	1.Max.	2.Max.	L_1	L_2
1	14-25	19		63.5	20-90	40	50	31	56
2	14-31	19	30.0	51.3	13-80	37	60	"	"
3	9.5-22	17	30.0	53.6	15-80	36	60	"	"
4	11-22	17	32.3	58.0	12-80	35	64	"	"
5	12-21	17	33.4		12-75	36	64	"	"
total	9-31	18	31.4	56.6	15-80	36.8	59.6	31	56

Fig. 1

Fig. 2.

thin section

electron micrograph

contrast curve

a)

l_c = thickness of lamella

l_g = total thickness of lamella

l_m = average thickness of lamella

g = thickness of surface layers (interface)

l_a = thickness of amorphous interlamellar layer

L = long period

b)

Fig. 4

Fig. 6

(*)

fig. 7

4

Fig. 8