

Subsidiary WAXS maxima and morphology of aliphatic polyester crystals obtained by crystallization from solution

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The wide angle X-ray scattering pattern of mats of filtration of single crystals of poly(ethylene sebacate) and poly(ethylene sebacate) presents subsidiary (non-Bragg) diffraction spots. The occurrence of such extra maxima is related to the extremely low number of repeat units in the crystalline part of the lamellae. The experimental intensity along the c^* direction has been compared with structure factor determinations and WAXS simulations to determine the nature of the fold in single crystals of poly(ethylene sebacate). It has been found that the folds are made of the octamethylene groups contained in the sebacate parts of the macromolecules. The crystalline length l_c obtained from the simulations is in good agreement with the experimental value of the long period when the description of the fold and of the interlamellar gap are taken into account. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The structure of aliphatic polyesters was among the first macromolecules studied by X-ray diffraction techniques¹, after their historical synthesis by Carothers². One of the main results is that the chain conformations depart from the all trans planar configuration in contradistinction with the cases of polyethylene and aliphatic polyamides. The morphology of single crystals of all these three mentioned polymers have been studied at different degree to obtain various informations like crystal habits, thickness, orientation.

In the cases of polyamides, the nature of the fold was investigated from a combined analysis of both wide-angle and small-angle X-ray scattering (WAXS and SAXS) data³⁻⁵, using the existence of subsidiary (non-Bragg) maxima for very thin lamellar crystals having only a few repeat units in their thickness. Both Atkins *et al.*⁴ and Magill *et al.*⁵ conclude that there is a strong preference for acid units within the fold portions. As it was pointed out by Keller⁶, this way also allows to assess unambiguously and independently the coherently diffracting core thickness of the crystals together with the long period associated to the stack of the lamellae.

Coming back to aliphatic polyesters, we present in this paper the study of mats of filtration of poly(ethylene sebacate) single crystals. This polymer, numbered 2-10 polyester, is depicted in *Figure 1*. In the planar zigzag conformation, the length is calculated to be 1.713 nm. In fact, the chain shortening in the crystal phase due to the presence of kinks is of the order of 0.035 nm, as it is attested by the monoclinic unit cell information^{1,7,8} ($a = 0.552$ nm, $b = 0.730$ nm, $c = 1.680$ nm and $\beta = 115^\circ$). A previous investigation of single crystals and crystal mats⁸ has shown that they are well defined lozenge shaped single crystals and has also revealed that the fold surfaces are parallel to (001)

crystallographic planes. By a closer examination of the WAXD pattern of sedimented mats of polyester crystals precipitated from isoamylacetate, taken with the beam parallel to the mat surface, Kanamoto⁹ has found that weak meridional diffraction arcs were present between the (001) and (002) reflections and between the (002) and (003) reflections. Crystals precipitated at 25°C from isoamylacetate have a long spacing of 7.6 nm and gave two subsidiary maxima (1.11 and 0.94 nm) between (001) and (002) reflections and two (0.66 and 0.57 nm) between the (002) and (003) reflections. The spread of orientation of the subsidiary maxima is the same as the (001) reflection. Using the existence of such subsidiary maxima, we want, in this work to elucidate the nature of the folds, considering that they can be made either by the ethylene glycol group, either by a part of the sequence of methylene groups.

EXPERIMENTAL

Materials and single crystal mats preparation

Poly(ethylene sebacate) (PES) was synthesized by an ester-exchange technique¹⁰. PES was dissolved in boiling methanol under nitrogen atmosphere to obtain a dilute solution (0.01 wt%). The solution was kept at the crystallization temperature T_c (25°C) during 24 h and afterwards slowly filtrated with a Buchner glass funnel (porosity 4). The funnel was kept at room temperature under vacuum to remove the last traces of solvent. Well oriented sedimented mats of filtration were obtained with such a procedure.

X-ray diffraction

Wide- and small-angle X-ray (WAXS and SAXS) scattering techniques were used to investigate the structure of mats of filtration of PES. X-ray patterns were recorded with the incident beam oriented along the plane of the mat of filtration. The diffraction patterns were recorded with an image plate detector. SAXS and WAXS measurements were

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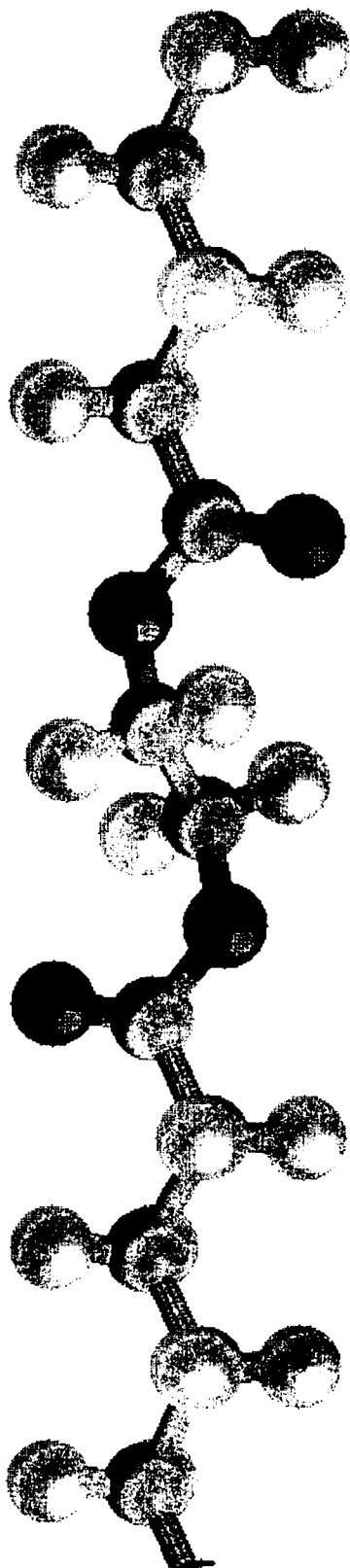


Figure 1 Representation of the poly(ethylene sebacate) unit

conducted at the D43 beam line of the LURE-DCI synchrotron radiation facility (Orsay, France). The wavelength λ and the distance between the sample and the detector were 0.1266 nm and 211.5 mm, respectively.

Raman L.A.M. measurement

The recording of the Raman LAM (longitudinal acoustic mode) spectrum has been performed using a Dilor

spectrometer. The spectrum presents a clear maximum at a wavenumber 28 cm^{-1} . This measurement is just mentioned here as a reminder, because the crystal length cannot be obtained, since the elastic modulus of the chain has not been found in the literature.

RESULTS

Figure 2 shows the X-ray diffraction pattern of a poly(ethylene sebacate) mat of filtration obtained at 25°C . In part *b* of the figure, the intensities are modified in order to emphasize the three subsidiary maxima which are clearly visible between the (002) and (003) spots. Other weak non-Bragg diffractions can be detected between (001) and (002) spots. To specifically analyse these extra-diffractions, we have made an integration of the intensities in a sector of 30° aperture angle centred on the meridional line. The intensity curve so obtained is presented in Figure 3. In the SAXS part, the second-order of the long spacing of the lamellar crystals at $s = 0.232\text{ nm}^{-1}$, which corresponds to a long period $l_p = 8.6\text{ nm}$, is easily identified. The wide-angle X-ray diffraction part is composed of the main meridional reflections: the (001) peak is particularly important compare to the (002) and (003) peaks. Three subsidiary maxima, labelled s_1 , s_2 and s_3 , are observed between the (002) and

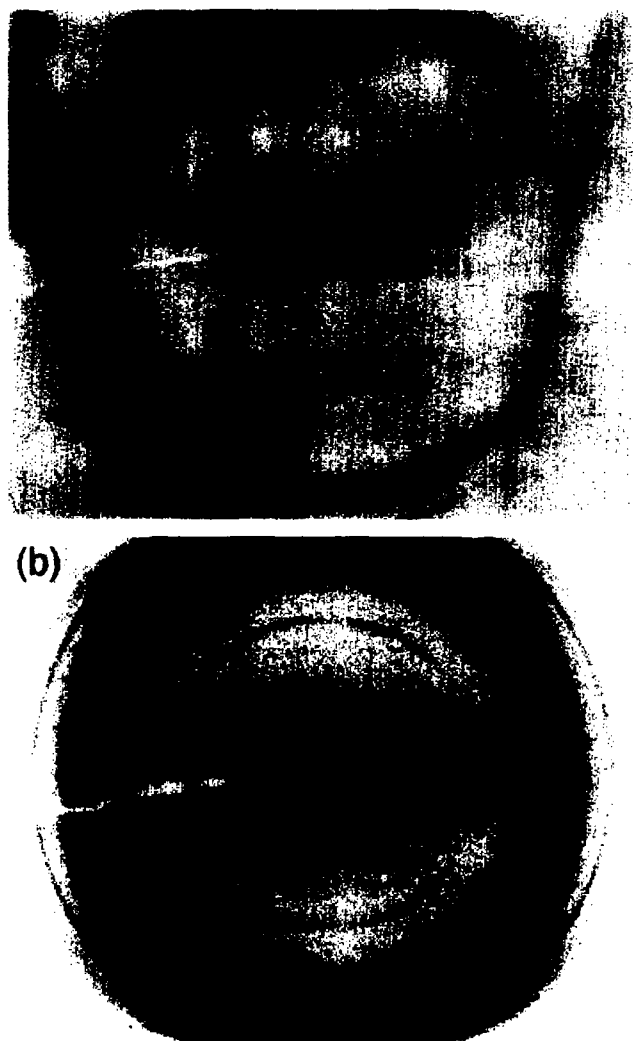


Figure 2 (a) X-ray diffraction pattern of single crystal mats of Poly(ethylene sebacate); (b) The same diffraction pattern, but with modified grey levels in order to emphasize the subsidiary maxima on the meridional line

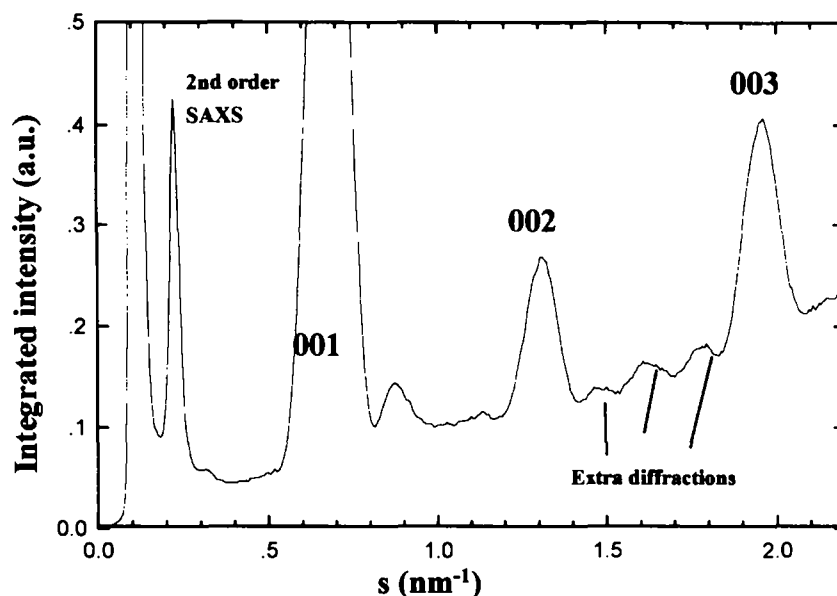


Figure 3 Integrated profile in a 30° sector of the diffraction pattern presented in Figure 2

Table 1 Numerical deconvolution using Gaussian shapes for the peaks of the experimental profile shown in Figure 2

Indexation	Bragg spacing (nm)	s/c	Intensity (a.u.)	Width-H M (nm ⁻¹)	Integrated area (a.u.)
001	1.471	1.035	6.81	0.110	0.7945
r_1	1.126	1.35	0.46	0.148	0.0732
002	0.765	1.99	1	0.120	0.1276
s_1	0.6798	2.24	0.17	0.077	0.0138
s_2	0.620	2.46	0.22	0.141	0.0328
s_3	0.564	2.70	0.19	0.078	0.0161
003	0.511	2.98	1.32	0.119	0.1669

(003) spots. Between (001) and (002) diffractions, only one clear subsidiary maximum can be attributed (and labelled r_1). Others, if present have intensities of the order of the noise. Table 1 presents the results of a numerical fit using Gaussian peak shapes to characterize the seven maxima (001), r_1 , (002), s_1 , s_2 , s_3 and (003). The data are not corrected from instrumental and sample corrections, but are considered to be valid for a further comparison with simulations, on a semiquantitative basis. These global pattern can be qualitatively compared to the profile obtained from mats of filtration of nylon-6,6 single crystals⁵, which also presents three subsidiary maxima. The fundamental explanation of the existence of such maxima is contained in the analysis of the Laue function for a small crystal (see for example Guinier¹¹ or Kakudo and Kasai¹²). For a one-dimensional crystal of N scattering points separated by a distance d , the diffraction intensity is proportional to the Laue function $\sin^2(N\pi sd)/\sin^2(\pi sd)$, where s is the norm of the reciprocal vector. The enlargement of this function has been used in the Scherrer theory to estimate the crystallite size, but the peaks centred on each nodes of the reciprocal lattice are separated by $N - 2$ secondary maxima at positions $1.5/Nd, 2.5/Nd, 3.5/Nd, \dots$. From this analysis and taking into account the existence of the three subsidiary maxima, the number of repeat units in the crystal core along a direction perpendicular to the basal plane of the lamellae is 5. However, this value needs to be properly stated using a more detailed model, which is also intended to determine the chemical nature of the fold, or the relative placements of ester groups in the lamellae.

STRUCTURE FACTOR CALCULATIONS

The first step is to correctly describe the crystalline structure of the poly(ethylene sebacate). The unit cell, as previously mentioned, has been determined by different authors (and has been checked on our samples in the present study). Structural studies on poly(ethylene adipate) and poly(ethylene sebacate), the 2-6 and 2-8 aliphatic polyesters, have been performed by X-ray diffraction (Turner-Jones and Bunn¹³) and by energy minimization (Liau and Boyd¹⁴). Both unit cells are monoclinic with two chains (and monomers) per cell; space group is P21/a (non-standard orientation of the y -axis unique (2nd setting) group P21/c), the two chains being related by a glide of $a/2$ in the plane perpendicular to b at $b/4$. The sets of internal coordinates that both papers propose can be extended in the case of poly(ethylene sebacate), and yields to c -values respectively equal to 1.689 nm and 1.644 nm. Thus, the first internal coordinates set proposed by Turner-Jones and Bunn¹³ has been accepted, in order to accommodate the mean experimental unit cell: $a = 0.552 \pm 0.003$ nm; $b = 0.730 \pm 0.005$ nm; $c = 1.680 \pm 0.010$ nm; $\beta = 115 \pm 0.5^\circ$.

In order to investigate the single crystal morphology and simulate the diffraction spectra, we make the following hypotheses

Hypothesis 1. Across their thickness, the crystals are symmetric, the central part being occupied either by a 'sebacate' ($-\text{OCO}-(\text{CH}_2)_8-\text{COO}-$) or a 'glycol' ($-\text{O}-(\text{CH}_2)_2-\text{O}-$) part. The variation of the thickness allows thus to simulate single crystals with folds made of different

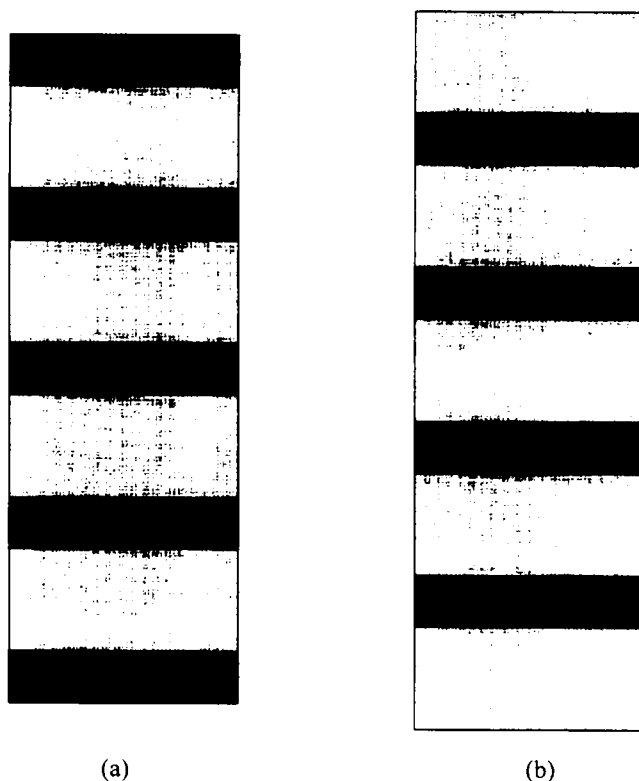


Figure 4 Schematic view of the two possible models of the lamellae: (a) with a symmetry about a sebacate group; (b) with a symmetry about a glycol group. The sebacate and glycol groups are respectively presented as light and dark grey rectangles

chemical groups since we in fact impose the nature of the stem ends. This is equivalent to the technique used by Atkins *at al.*⁴ in the case of the nylon-6,6, for which either amine or acid folds were considered. *Figure 4* schematically represents sebacate and glycol models, with the positions of the carbonyl oxygen planes, at the distances 0.338 and 0.662 in fractional unit. Indeed the contribution of these planes in the structure factor calculation should be the most important, due to the electron density fluctuation they produce.

Hypothesis 2. There is no coherent interference between members of the assembly of crystals (a relevant hypothesis as discussed by Keller⁶). The fact that we observe the 2nd order SAXS peak indicates a quite good degree of order in the mats of filtration. Dreyfuss *at al.* have also shown that for nylon-6,6, it is possible to improve the lamellar packing by heat treatment. After this annealing, the diffraction pattern between (001) and (002) was not strongly modified. We consider thus that, at least in a semi-quantitative way, the apparent (or approximative) relative intensities of the subsidiary peaks can be used to infer the chemical nature of the fold.

The procedure to obtain simulated diffraction profiles is the following: the cartesian coordinates have been computed from the internal coordinates derived from the Turner-Jones' set, with the repeat length $c = 1.689$ nm. The planar hydrocarbon chain lies at a mean angle of 40° to the ac -plane. Knowing this angle, the fractional coordinates of all atoms in the unit cell have been calculated. It is easy to 'build' any lamellar with a thickness ranging between 3 and 6 unit cells and, assuming the symmetry of the crystal about a central 'sebacate' or 'glycol' group (see Hypothesis 1). Instead of speaking about the classical denomination of the

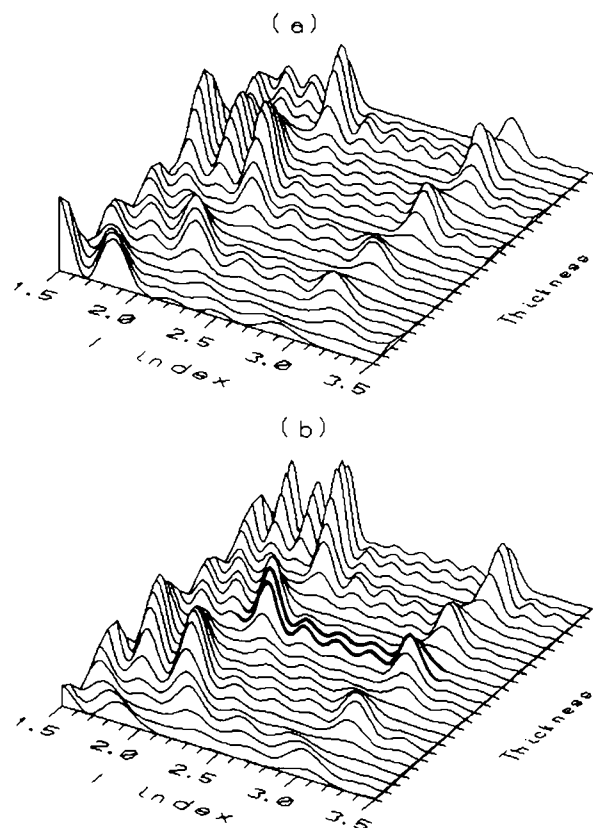


Figure 5 Simulated WAXS maps. Two maps (for 'sebacate' (a) and 'glycol' (b) cases) showing the successive simulated intensities with s/c^* (or the continuous Miller index 'l') varying between 1.5 and 2.5, and unit-cell thicknesses varying from 3 to 6

structure factor F_{hkl} , we use the expression of the crystal intensity I_{cr} depending on the reciprocal vector s . Since we are specially interested by the diffraction along the meridional line, the corresponding structure factor amplitude $A_{cr}(s)$ along the 00l direction will be used:

$$A_{cr}(s) = \sum_j f_j(s) \exp(2\pi i s z_j)$$

where s is the reciprocal vector norm, j the indices of atoms in the crystal, f_j the corresponding atomic structure factor and z_j their fractional coordinates along the c 'unit cell' vector. A single chain is taken for the evaluation of $A_{cr}(s)$, since neighbouring chains have the same z_j sets. The various instrumental corrections are then applied: polarisation, Lorentz, absorption, Debye-Waller (using an estimated value for $B \gg 0.01$ nm²). The corrected intensity profiles are presented in *Figure 5*. Under the form of two maps (for 'sebacate' (a) and 'glycol' (b) cases) showing the successive simulated intensities with s/c^* (or the continuous Miller index 'l') varying between 1.5 and 2.5, and unit-cell thicknesses varying from 3 to 6.

DISCUSSION

Two profiles in the 'glycol' case, corresponding to the thicknesses $4.38/c^*$ and $4.45/c^*$, are highlighted for the purpose of comparing to the experimental profile of *Figure 2*. Indeed, the results of the deconvolution of simulated profiles given in *Table 2* shows that they can be favourably related to the data of *Table 1* if we consider their approximative positions, relative intensities and width, in contradistinction to all other simulated profiles. The comparison with

Table 2 Numerical deconvolution of simulated profiles assuming 'glycol' symmetry (see text)

Crystal thickness	Peak	slc^* centre	Intensity (a.u.)	Width-HM $\times c^*$ (nm ⁻¹)	Integrated area (a.u.)
$l = 4.38/c^*$	002	2.09	1	0.090	0.0957
	s_1	2.34	0.28	0.064	0.0189
	s_2	2.56	0.14	0.062	0.0090
	s_3	2.75	0.09	0.049	0.0048
	003	2.98	1.15	0.102	0.1237
$l = 4.45/c^*$	002	2.06	1	0.084	0.0888
	s_1	2.30	0.31	0.063	0.0207
	s_2	2.52	0.21	0.064	0.0143
	s_3	2.73	0.20	0.059	0.0123
	003	2.98	0.80	0.094	0.07963

experiments yields to a measurement of the length of the crystalline part of the lamellae $l_c \gg 4.4/c^* = 6.7$ nm. As already mentioned, the long period of the lamellar stack is $l_p = 8.6$ nm.

The difference ($l_p - l_c$) $\gg 1.9$ nm can be mainly explained by two unavoidable contributions:

(i) The minimum fold size: for the mentioned l_c value, and assuming that the central part of the lamellae is occupied by a glycol sequence, the crystalline stems are terminated just after carboxylic groups (in fact $-\text{O}-\text{CO}-\text{CH}_2-$). Consequently, if we assume regular configurations of sharp folds with adjacent re-entry, they are made by the alkyl groups contained in the sebacate part of the polyester and the minimum size of the folds must follow the conformation of the six remaining methylenes. The estimated contribution for the folds of both faces of the lamellae is about 2×0.4 nm.

(ii) The necessary interlamellar contact, due to Van der Waals forces, is of the order of 0.4 nm if we consider for example the Dreiding generic force field¹⁵.

The remainder (about 0.7 nm) can be attributed to various causes, the most important of which being imperfection and amorphicity in the fold surface including well known concepts like loose loops, non-adjacent re-entries, cilia, physically adsorbed macromolecules, ... Also the disorder and misorientations in the stack of lamellae could contribute to increase the long period compare to the crystal core thickness. Finally, a small part can be attributed to some extent to the accuracy of the measurements.

Another way to obtain the crystalline length is to examine the broadening of the diffraction peaks, using what is classically known as the Scherrer formula. We should want to point out that it is dangerous to systematically applied this formula without careful examination of its hypothesis. Indeed, the experimental data (see Table 1) yields a mean width at half maximum WHM = $.116 \text{ nm}^{-1}$ which in turn indicates a minimum size of 7.7 nm ($0.888/0.116$) for the crystallites if we consider that all instrumental corrections tend to increase the widths of the peaks. Even if we use the integral breadth which does not introduce the factor 0.888, the minimum size is found to be 8.1 nm (the mean value of $6.81/0.7945$, $1/0.1276$ and $1.32/1.669$). In fact, as clearly explained by Guinier¹¹, the Scherrer formula has been established from the analysis of the Laue Function, but when the crystallites are very small, consisting of only a few unit cells, the principal maxima of the Laue function exhibit considerable broadening (see also Kakudo¹²). If $|F^2|$ (of the

unit cell) varies at all rapidly with diffraction angle in the region of these maxima, the shape of the diffraction changes. The effect of the change is such that the position and the width of the principal maxima of I_{cr} are strongly modified. Kusanagi *et al.*¹⁶ have reached a similar conclusion from the study of poly(ethylene terephthalate) and nylon 66 crystallites. Therefore, the Scherrer's formula must be applied with care. Indeed, taking the mean value of the width for the simulation (Table 2), it is observed that its reciprocal value ($1/0.0925 \text{ nm}^{-1} = 10.8$ nm) has almost nothing to do with the imposed thickness (6.7 nm). However, the comparison between experimental and simulated breadth is compatible with a 25% ($0.116/0.0925$) broadening of the peaks due to the experimental setup.

CONCLUSION

The present work confirms the usefulness of Bragg subsidiary maxima to study the morphology of small crystallites like polymer single crystals. Our measurements on poly(ethylene sebacate) have shown that in single crystal mats of this polymer, the folds are constituted by $(-\text{CH}_2-)_6$ segments of the sebacate parts, the esters groups remaining in the crystal. The crystalline length obtained from the comparison with WAXS simulated profiles agrees well with the independently measured long period when we take into account the description of the inter-lamellar zones (fold, Van der Waals contact, amorphicity and disorder).

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