Epitaxial crystallization and crystalline polymorphism of poly(1-butene): form I′

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The hexagonal form I′ of poly(1-butene) is epitaxially crystallized on 4-bromo and 4-chlorobenzoic acids, on the potassium salts of these acids, and on the hemiacid, potassium hydrogen 4-chlorobenzoate. The contact plane in all cases is (11.0). In form I′, the successive (11.0) planes contain, alternately, only left-hand or only right-hand helices. The observed epitaxies can therefore be differentiated according to the chirality of the helices in interaction with the substrate. Epitaxies are governed by a one-dimensional match which involves the interturn distance, i.e. the distance between successive outer helical paths. For less specific interactions, appropriate tilts of the helix axis helps achieve matching with the substrate lattice periodicities.

(Keywords: poly(1-butene); crystal polymorphism; epitaxy)

INTRODUCTION

In this paper we consider the epitaxial crystallization of isotactic poly(1-butene) (PBu1), form I′ (forms II and III are discussed in a companion paper[1]). The structure of this phase, and of the related form I, was established by Natta and co-workers some years ago[2]. Forms I and I′ are characterized by 3_1 and 3_2 helical conformation and a hexagonal (trigonal) unit cell with the parameters, $a = b = 1.77$ nm, $c = 0.65$ nm, and the space group R3c or R$\bar{3}$c. Form I is obtained by a solid-state transformation of form II; it is often referred to as a 'twinned' form, following single crystal investigations by Holland and Miller[3].

As pointed out by Natta *et al.*[2], the form I′ crystal structure bears close analogies with the most common, monoclinic α-form of isotactic polypropylene (iPP), having a similar 3_1 helix conformation. Specifically, it consists of bilayers made up of helices of opposite chirality (cf. *Figure 1*, adapted from the paper of Natta *et al.*[2]). Any bilayer parallel to the (11.0) plane is made of deeply interdigitated helices, with each face of the bilayer containing helices of only one hand. As a result, the structure is polar: when examined from opposite directions, the two faces of the bilayer are related by a mirror symmetry (crystallographic glide plane parallel to (11.0)). Recognition of this polar character is a key feature in this present analysis of form I′ epitaxies.

In addition, most substrates used in this study are characterized by their lack of symmetry. The mutual orientation of polymers and substrates of low symmetry helps to set the rules for helix chirality selection and makes it possible to gain an unmatched insight into epitaxy of helical polymers.

EXPERIMENTAL

Materials, experimental procedures and investigational techniques are as described in the companion paper[1]. Substrates are limited to 4-chlorobenzoic acid, potassium hydrogen 4-chlorobenzoate, and to the salts of 4-chloro and 4-bromobenzoic acid. Potassium hydrogen 4-chlorobenzoate and the salts were prepared in the laboratory by reaction with stoichiometric (for the hemiacid) or excess amounts of dilute solutions of potassium hydroxide. As the hemiacids and salts are stable in the vacuum of an electron microscope, several composite electron diffraction patterns of substrate and polymer have been recorded, which facilitates the structural analysis of the epitaxies.

Many of the diffraction patterns presented in this paper were purposely taken on the electron microscope using a conventional daylight photographic emulsion (Agfapan 100). This type of emulsion has significant advantages in the present context: strong reflections are not overexposed, whereas weaker ones (notably on upper layer lines) come out fairly prominently.

RESULTS

Form I′ is obtained by epitaxial crystallization on 4-substituted benzoic acid, various salts and the hemiacid. The PBu1 interacts with an ordered array of chlorine or bromine atoms which line the contact (cleavage) plane of the substrate. Subtle differences in structure, characteristic periodicities, etc., of these arrays induce different epitaxies which can be analysed in some detail. We examine first the epitaxy of PBu1 on 4-chlorobenzoic acid (4ClBzAc) which, like its 4-bromo analogue (4BrBzAc)[1], induces epitaxy of both forms I′ and II, but with form I′ now dominant; next we examine the epitaxy on the hemiacid and the salts, which induce form I′ only.

Epitaxy of form I′ and II on 4ClBzAc

Structure of 4-chlorobenzoic acid. The unit cell of 4ClBzAc is triclinic[4] (space group P$\bar{1}$) with the following parameters: $a = 1.4392$, $b = 0.6227$, and $c = 0.3861$ nm; $\alpha = 88.68$, $\beta = 100.12$, and $\gamma = 93.31°$. 4ClBzAc, as with all

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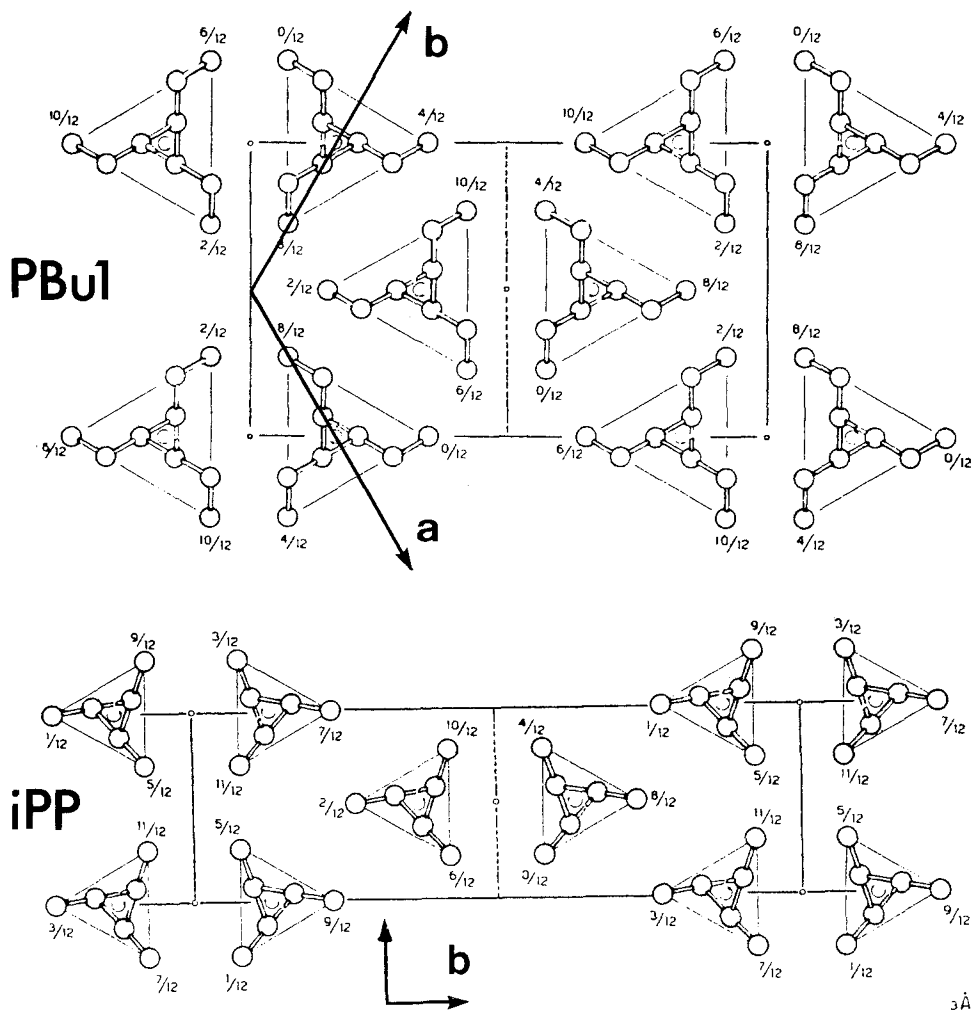


Figure 1 Illustration of the similarity between the crystal structures of PBu1 (forms I and I') and the α-phase of iPP (adapted from Natta *et al.*[2])

of the acids and salts examined in this series, has a polar–apolar sandwich structure, based on dimers of the acid linked by hydrogen bonds. The structure of the contact surface (*bc* plane) is a near-rectangular (since $\alpha = 88.68° \sim 90°$) array of chlorine atoms, 0.623 and 0.386 nm apart. The latter distance almost corresponds to the atomic contact of the chlorine atoms (van der Waals radius = 0.18 nm): nearly continuous rows of chlorine atoms parallel to *c* are strong features of the contact surface. In addition, neighbour hydrogen atoms in position 3 of the benzene ring (which is nearly parallel to the (110) plane), are located on the ⟨110⟩ diagonal (*Figure 2*). This surface has strong structural similarities with that of 4BrBzAc which also contains rectangular arrays of bromine atoms with dimensions in this case of 0.615 × 0.398 nm[1].

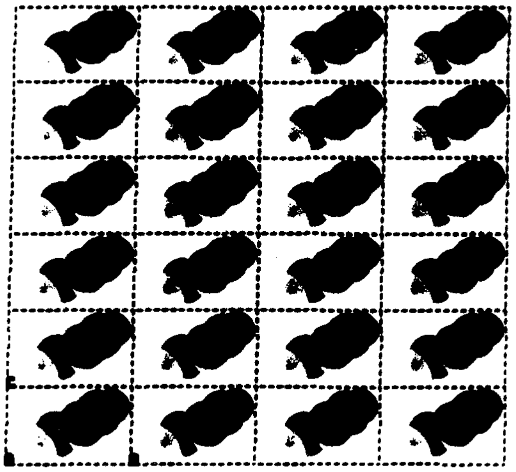


Figure 2 Computer generated molecular model of the 4ClBzAc surface structure (*bc* plane) which is in contact with the polymer. (All molecular models, plus *Figure 3b*, are generated using a Cerius molecular modelling software package obtained from Molecular Simulations Inc.)

Diffraction and morphology evidence. *Figure 3a* is a selected-area electron diffraction (SAED) pattern of a PBu1 film grown on 4ClBzAc. (Since the acid sublimes in the electron microscope column, it has been dissolved in ethanol prior to examination.) This illustrates, in the clearest fashion, the major features of the epitaxial crystallization of PBu1, form I' on this acid. In particular, the following should be noted: (i) a single chain orientation is observed, as indicated by the set of layer lines; (ii) the measured chain axis repeat distance of 0.65 nm is characteristic of form I'; (iii) on the equator, only 300 reflections (spacing $0.511\ \mathrm{nm}^{-1}$) (cf. *Figure 3b*) and their higher orders are observed. The contact plane is therefore (11.0) (long, horizontal diagonal in *Figure 3c*); (iv) *diffraction on the layer lines is asymmetric.* This asymmetry is in sharp contrast to the symmetry that would characterize classical biorientation induced by

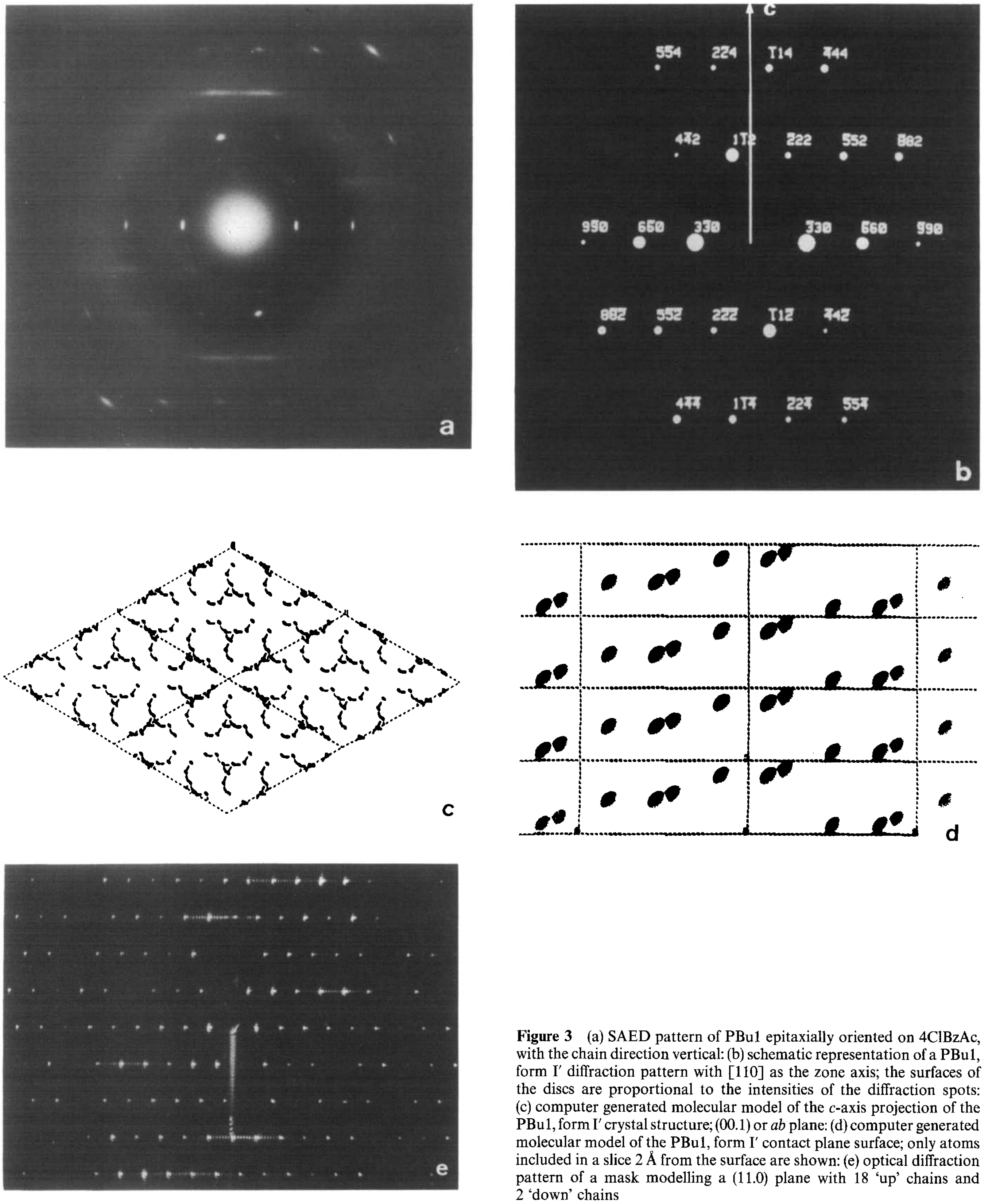


Figure 3 (a) SAED pattern of PBu1 epitaxially oriented on 4ClBzAc, with the chain direction vertical: (b) schematic representation of a PBu1, form I' diffraction pattern with [110] as the zone axis; the surfaces of the discs are proportional to the intensities of the diffraction spots: (c) computer generated molecular model of the *c*-axis projection of the PBu1, form I' crystal structure; (00.1) or *ab* plane: (d) computer generated molecular model of the PBu1, form I' contact plane surface; only atoms included in a slice 2 Å from the surface are shown: (e) optical diffraction pattern of a mask modelling a (11.0) plane with 18 'up' chains and 2 'down' chains

mechanical means, as well as transformation of epitaxially crystallized form II (cf. ref. 1, Figure 6a). The whole pattern is that of a 'single crystal' of form I' of PBu1, in spite of the multilamellar structure of the area selected (cf. later, *Figure 5*), and; (v) the odd layer lines of the pattern are significantly streaked, again in an asymmetric way (cf. first layer line) whereas reflections on the even layer lines are much sharper (cf. fourth layer line).

The two latter features of the diffraction pattern can be analysed in structural terms in the following way:

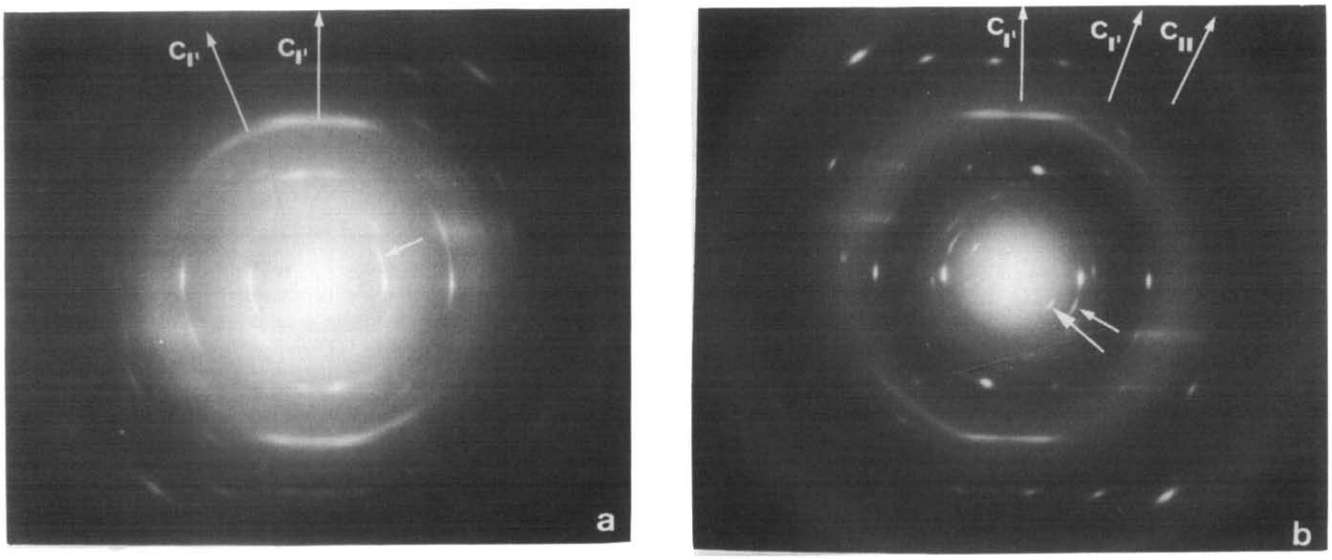
1. The *asymmetry* reflects the polar character of the structure of form I', discussed in the Introduction. *It makes it possible to determine the hand of helices in the contact surfaces of the area selected for diffraction.* In *c*-axis projection, the threefold helices may be shown

schematically by triangles. The contact surface can be composed of helices with either the bases or the tips of the triangles exposed. When the surface is seen from the substrate side, and if it is made of helices with exposed bases (cf. *c*-axis projection of *Figure 3c*, (11.0) plane or long horizontal diagonal of the figure), *the strong 01.2 (or* $1\bar{1}.2$*) reflection on the second layer line corresponds to crystallographic planes parallel to the helical path of exposed helices in the contact planes.* As a consequence, the diffraction pattern of *Figure 3a* corresponds to exposed *right-handed helices.* Alternatively, an easy rule-of-thumb considers the stronger intensities on the upper, fourth layer line: in *Figure 3a*, strong reflections are on the *right* of the meridian; and the exposed helices are *right*-handed. The corresponding exposed face is illustrated in *Figure 3d.*

2. The *streaking* on the odd layer lines results from a statistical arrangement of ‘up’ or ‘down’ helices in the structure. Replacement of one helix by its anticlinic counterpart on any site in the crystal lattice was considered earlier by Natta and Corradini for both iPP[5] and PBu1[2], forms I and I′: provided that the helix sense is maintained, this replacement is nearly isosteric. It produces, however, a characteristic streaking (shown in *Figure 3e*). This optical transform of a mask featuring 20 PBu1 chains with two inversions of chain sense reproduces indeed the main characteristics of the streaks seen in *Figure 3a*, i.e. layer lines and asymmetry[6]. It should be noted that *all of the following discussion does not discriminate between syncline or anticline helices: it is only concerned with the helical hand.*

Figure 4a illustrates a more frequently occurring diffraction pattern. Besides the main epitaxy (based here on right-handed helices in the contact plane), a small additional epitaxial component, also in form I′, shows up through an additional 300 reflection located 24° apart (anticlockwise) from the main 300 equatorial reflection (reflection marked by a small straight arrow).

Figure 4b illustrates in a more prominent fashion the coexistence of two orientations. The main epitaxy involves left-handed helices in the contact plane (in mirror symmetry with *Figures 3a* and *4a*) and the additional component is turned 24° clockwise (shown by a small straight arrow). The patterns of the two orientations are related by a *mirror symmetry and the*



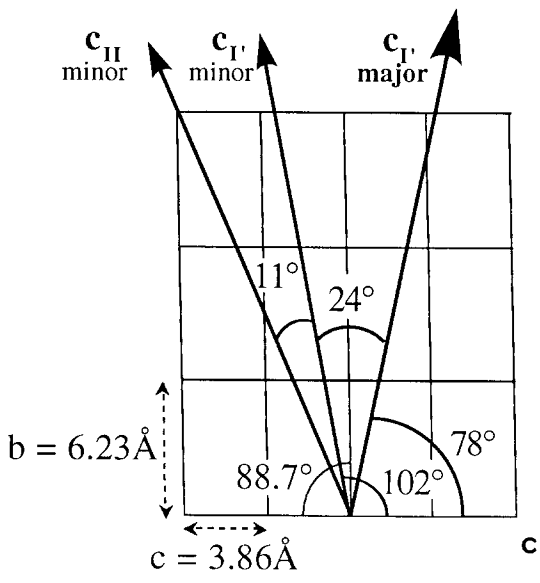


Figure 4 (a) SAED pattern of PBu1 epitaxially oriented on 4ClBzAc with two form I′ chain orientations 24° apart; note the difference in intensity of corresponding reflections for the two chain orientations, indicating a major and a minor component: (b) SAED pattern of PBu1 epitaxially oriented on 4ClBzAc with two PBu1, form I′ chain orientations 24° apart and one PBu1, form II chain orientation at 11° and 34° from the minor and major chain directions, respectively: (c) schematic representation of the relative orientations of the PBu1 chains on the 4ClBzAc contact surface

mirror plane passes almost through the 10.2 reflections, which are thus common. This feature is essential in the discussion of the polymer–substrate interactions.

The second feature of *Figure 4b* is the existence of a small component of form II (inner 200 reflection, long arrow). The corresponding equator is tilted clockwise by 35° relative to the main equator of form I′. Note that the tilts of the (minor) form I′ and form II are in the same sense; this is a general feature, systematically observed in all of the diffraction patterns.

To sum up the experimental observations, epitaxy of PBu1 on 4ClBzAc leads to three populations of crystals:

(i) *a major component* in form I′;
(ii) *a minor component* in form I′, with its helix axis tilted 24° and its structure related by mirror symmetry to the major component in form I′, and;
(iii) *a minor component* in form II, with its helix axis tilted 35° relative to the major form I′ and in the same direction as the minor form I′. This form II transforms over a period of time to form I.

Figure 4c represents schematically these relative orientations and includes the underlying substrate orientation, which wll be justified in the later discussion. This figure will be used as a guideline for structural analysis of the various epitaxies, after a short comment here on the lamellar structure.

Figure 5 illustrates the multilamellar structure of the films, as revealed by gold decoration. Lamellar morphology displays significant 'waviness' with the orientation of various portions of the lamellae differing by up to ~30°, which, however, is difficult to correlate with the presence of populations of forms I and II having chain orientations at ~24, or ~35°. Note also that forms I′ and II cannot be distinguished by their different lamellar thicknesses, as was the case with benzoic acid as the substrate[1]; low-angle electron diffraction (inset) reveals only one peak, in spite of the waviness of the lamellae structure. The lamellar thickness thus determined is in the 10 nm range.

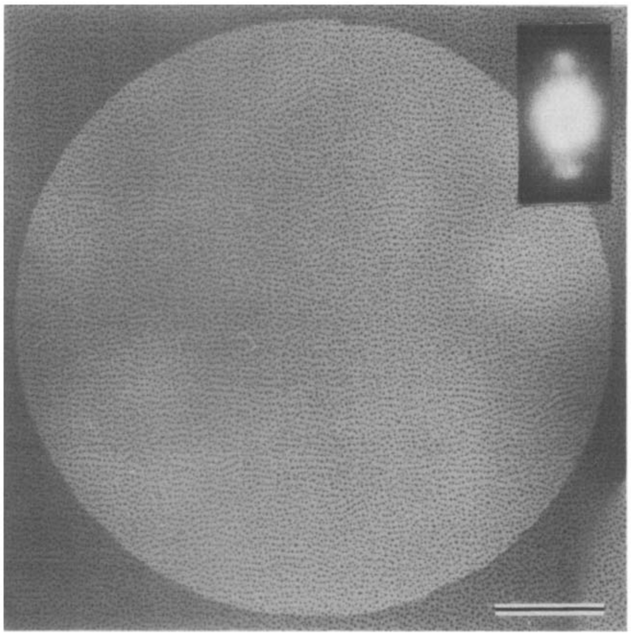


Figure 5 Electron micrograph of gold decorated lamellae of PBu1, form I′ oriented on 4ClBzAc with scale bar = 0.2 μm: note the waviness of the lamellae. Inset shows a low-angle diffraction pattern of a similar area

In conclusion, lamellar morphology and low-angle electron diffraction are rather uninformative: they do not allow discrimination between the three populations of epitaxially crystallized forms. Wide-angle electron diffraction evidence is much clearer, and might conceivably help morphological studies via selective dark field imaging of the various populations of forms.

Epitaxial relationships of PBu1 on 4ClBzAc. Given the complexity of the epitaxies, a composite polymer–substrate diffraction pattern would be of considerable help. Even in the absence of such a pattern, the epitaxial relationships can be worked out, thanks to the existence of different polymer forms and polymer orientations and to a comparison with the related epitaxies observed on 4BrBzAc, for which form II is dominant[1]. The analysis must account for the following:

(i) existence of two form I′ orientations at 24° to each other;
(ii) predominance of one of these two orientations, and;
(iii) existence of a form II, oriented at 35° to the major form I′.

(a) Existence of two form I′ orientations at 24° to each other

As is usual, epitaxy is characterized by the contact planes, and by the relative orientations of the lattices. Contact planes are easily defined: they are the (100) cleavage plane of 4ClBzAc and, from diffraction evidence, the (11.0) plane of PBu1, form I′. Thus:

$$(11.0)_{\mathrm{PBu,I'}} \| (100)_{\mathrm{4ClBzAc}}$$

Relative orientations of the lattices are derived more indirectly. The key feature appears to be the existence of two form I′ orientations, at an angle of 24° to each other. If these orientations play a nearly symmetrical role relative to the substrate, then the *bisector* of these two orientations must be a special feature of that substrate. If the outside bisector corresponds to the *c*-axis, i.e. to the rows of chlorine atoms of 4ClBzAc, a wholly consistent picture of the epitaxy emerges.

Having set one element of the relative polymer and substrate orientations, one notes that the axes of the polymer chains are at an angle (78°) which does not correspond to any specific crystallographic direction of the substrate. It is preferable, and more precise, to use the angular relationship, thus:

$$[00.1]_{\mathrm{PBu,I'}} \Lambda [001]_{\mathrm{4ClBzAc}} = 78° \textbf{ and } 102°$$

Once the mutual epitaxies of form I′ and substrate are established it becomes possible to define the orientation of form II which, as indicated in *Figure 4c*, is at 35° to the main form I′ and in the same sense as the minor form I′. Thus:

$$(10.0)_{\mathrm{PBu,II}} \| (100)_{\mathrm{4ClBzAc}}$$

$$[00.1]_{\mathrm{PBu,II}} \Lambda [001]_{\mathrm{4ClBzAc}} = 67° \textbf{ or } 113°$$

The above epitaxial relationships can be explained on a molecular basis by the parallel alignment of helical paths (ethyl and methyl rows) with the rows of chlorine atoms in the *c*-axis substrate direction. Since the helical path is oblique to the chain axis direction, this alignment implies symmetrical tilts in opposite directions for left- and right-handed helices. This symmetrical tilt also implies that the substrate direction of the rows (*c*-axis) is a bisector of the angle defined by the two helix axis orientations (cf. *Figure 4c*).

The *c*-axis direction of the substrate parallels the (10.2) plane trace in this (11.0) plane. The relation can therefore be alternatively written as:

$$(10.2)_{\mathrm{PBu,I'}} \| (001)_{\mathrm{4ClBzAc}}$$

The molecular interactions described above appear highly favourable since any (11.0) contact plane of PBu1, form I' is made of isochiral helices, and also the exposed ethyl–methyl rows of neighbouring helices are well aligned (cf. *Figure 3d*).

In addition, the distance between these rows is 0.65 nm × sin 102° = 0.635 nm. This matches the 0.625 nm distance between the rows of chlorine atoms in the (100) 4ClBzAc substrate contact plane. The dimensional mismatch is therefore +1.7%.

(b) Preferred chirality of helices in the contact plane

The above discussion does not account for the marked preference for one particular orientation, as illustrated in *Figures 3a*, *4a* and *4b*, because it considers only the ethyl and methyl groups of the PBu1 chain, and the rows of chlorine atoms on the substrate. However, the polymer chain has a lower symmetry when considering backbone atoms. Furthermore, a significant substrate asymmetry arises from the presence of hydrogen atoms in position 3 (cf. *Figure 2*). These elements must also affect the energy balance of the epitaxy and favour one helix chirality over the other since our experimental patterns indicate a definite preference for *one* orientation. *Figure 6* illustrates schematically the substrate and polymer asymmetries involved. Indications for (or against) the energetic preference for any orientation is not readily apparent from this figure: both orientations seem to have steric conflicts. The preferred orientation should be obtained by docking experiments via molecular modelling and energy analysis. The ultimate check will rest on composite PBu1 polymer–4ClBzAc substrate diffraction patterns which, for reasons already indicated, are not available at the present time.

(c) Existence of a form II, oriented at 35° to the form I' major component

Since the minor form II component has its chain axis tilted 35° away from the major form I' population and 11° away from the minor one, it follows that it is at an angle of 23° to their bisector, i.e. to the substrate *c*-axis. This same angle is observed for form II epitaxy on the closely related 4BrBzAc[1].

The existence of only one form II orientation must be related to the low symmetry, triclinic unit cell of the substrate. Orientation of the helix axis parallel to both [032] and $[0\bar{3}2]$ 4ClBzAc directions provides correct orientation (angle calculated with the *b* axis: 22.3 and 22.6°, respectively) and dimensional match with the *c* axis repeat of form II (21.05 nm): when considering three substrate cells, distances along [032] and $[0\bar{3}2]$ are 2.04 and 2.0 nm, respectively. The dimensional differences between the two orientations [032] and $[0\bar{3}2]$ are small, but appear to correspond to important structural differences of the substrate structure. Whereas [032] is nearly parallel to the plane of the benzene ring, $[0\bar{3}2]$ is at a significant angle to it: selection of one orientation probably rests on differences in interaction energies linked to this structural difference, rather than on differences in the dimensional match.

To summarize, therefore, analysis of epitaxial crystallization of PBu1 on a low symmetry substrate makes it possible to discriminate the preferred helical hand of the depositing helices. The direct correlation of this hand and the substrate structure is not yet possible due to the lack of composite electron diffraction patterns. Surprisingly, it is also observed that the asymmetric substrate induces preferential orientation of form II, in spite of its contact face being composed of both right- and left-handed helices.

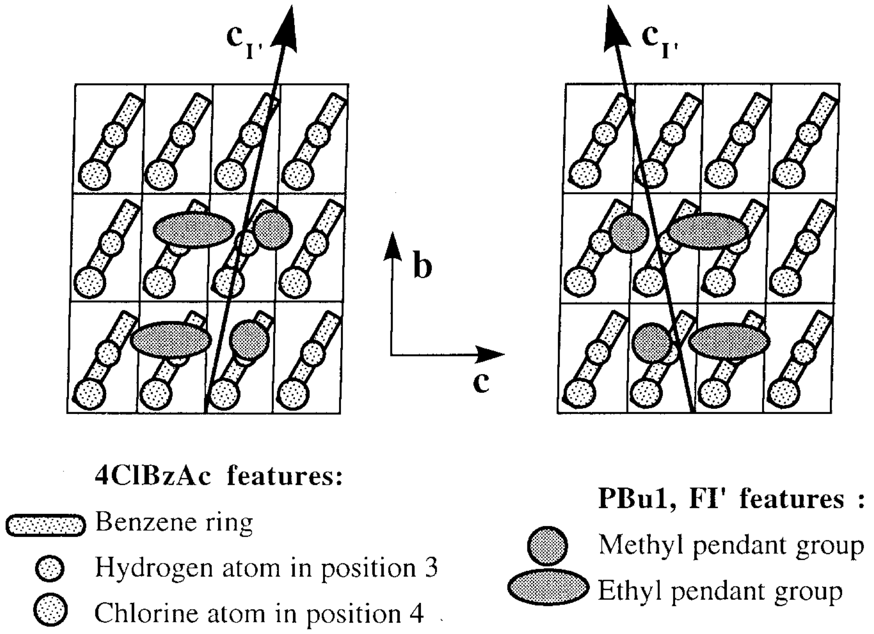


Figure 6 Two possible schematic orientations of the PBu1 chains on the 4ClBzAc contact face. A possible preference for parallelism of the chain axis with benzene ring orientation (i.e. right part of the scheme) is suggested as being the most likely situation

Epitaxy of form I' on potassium hydrogen 4-chlorobenzoate and potassium 4-chloro and 4-bromobenzoates

Structures of potassium hydrogen 4-chlorobenzoate and the potassium salts of 4-chloro and 4-bromobenzoic acid. Potassium hydrogen 4-chlorobenzoate and the potassium salts are nearly isostructural; furthermore, the 4-bromo and 4-chloro derivatives also have a very similar structure. A representative example is potassium hydrogen 4-chlorobenzoate: its structure is the familiar polar–apolar bilayer with apolar, halogen-containing contact faces. The unit cell is monoclinic (nearly orthorhombic) with the following parameters[7]: $a=3.31$, $b=0.3846$, and $c=1.121$ nm; $\beta=89.91°$; space group = C2/c. Note that the surface structure differs significantly from that of the 4-Cl and 4-Br acids (*Figure 7*). In particular, the pattern of chlorine atoms is less regular than for the acids since one chlorine atom is shifted from the geometrical centre of the unit cell.

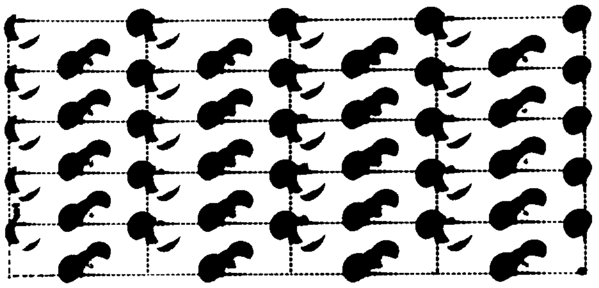


Figure 7 Computer generated molecular model of the contact plane surface of potassium hydrogen 4-chlorobenzoate

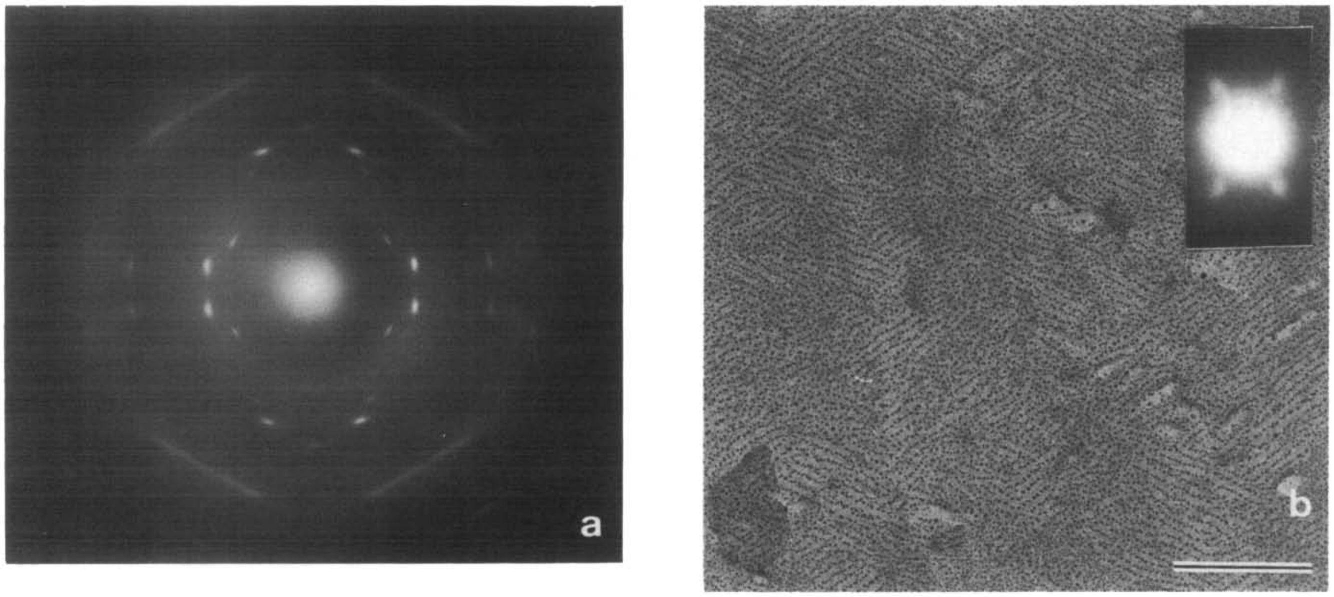
Epitaxy of PBu1, form I'. Similar epitaxial relationships are observed when PBu1 crystallizes on potassium hydrogen 4-chlorobenzoate and other potassium salts. *Figures 8a* and *8b* display, respectively, the diffraction pattern (after dissolution of the substrate) and the lamellar morphology of the epitaxially crystallized films (as revealed by gold decoration). Two chain and lamellar orientations are apparent. *Figure 8b* is characterized by the small size of domains with identical lamellar orientation: most domains comprise less than about ten lamellae.

The structural relationship between polymer and substrate, shown schematically in *Figure 8c*, must again be defined by the contact planes and angular relationships, thus:

$$(11.0)_{\mathrm{PBu,I'}} \| (100)_{\mathrm{substrate}}$$

$$c_{\mathrm{PBu,I'}} \Lambda b_{\mathrm{substrate}} = \pm 30°$$

Form I' has a (11.0) contact plane (cf. *Figure 3a*), as indicated by its, by now, familiar diffraction pattern. However, the angle between the two chain orientations is significantly larger than for 4ClBzAc (60° as opposed to 24°), although the asymmetry of the diffraction pattern



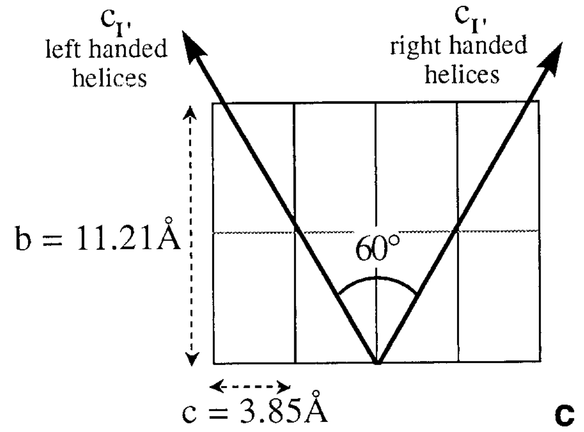


Figure 8 Features of PBu1 oriented on the potassium salts and the hemiacid: (a) SAED pattern of PBu1, form I' epitaxially oriented on the hemiacid; (b) lamellar morphology of PBu1, epitaxially oriented on the hemiacid, as revealed by gold decoration with scale bar = 0.2 μm. Inset shows a low-angle diffraction pattern of such an area, and; (c) schematic representation of the PBu1–salt/hemiacid epitaxial relationships

for any one chain orientation (similar to *Figures 3a* and *4a*) *indicates again a selection of helices in the contact plane according to their chirality.*

Comparing the structure of polymer and substrate contact planes does not provide any straightforward clue to the observed epitaxy. In particular, no significant crystal periodicity or surface feature exists on the hydrogen 4-chlorobenzoate or salt surfaces at 30° to the *b*-axis: *this epitaxy cannot be analysed in classical terms by a two-dimensional lattice match.* It is therefore necessary to take a more global view of the possible interactions.

In its most elementary acceptance, epitaxy of a polymer chain on a substrate must be defined as a *one-dimensional epitaxy*, which involves only one important parameter, namely the helical turn periodicity. In the present case, this periodicity is 0.65 nm and must match a much shorter substrate periodicity, i.e. 0.56 nm.

The only possible means to achieve such matching is through an appropriate tilt of the chain, by an angle equal to:

$$\arccos(5.6/6.5) = 30.5^\circ$$

When the substrate periodicity corresponds to rows (in this case, of chlorine or bromine atoms), and the polymer surface is made of isochiral helices (as in the case of PBu1, form I′), *the preferred sense of tilt is that which tends to align the helical path* (*oblique to the chain axis*) *and the substrate rows* (*Figure 9*). This simple steric requirement appears to be at the root of *selection of helix chirality in the contact plane.*

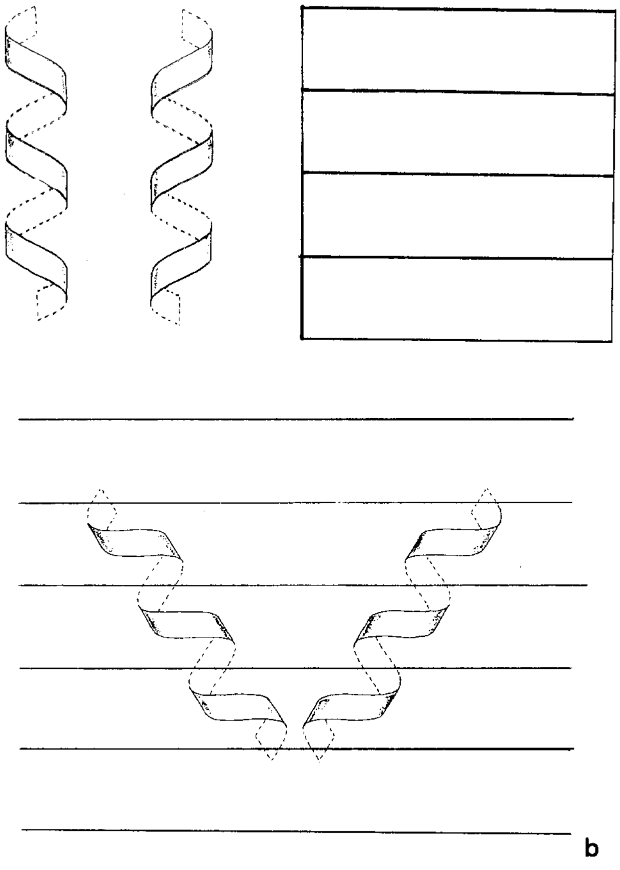


Figure 9 Schematic representation of epitaxial interactions of PBu1 individual right- and left-handed helices: (a) left, left and right helices of PBu1 with 0.65 nm chain axis repeat distance. Right, substrate with horizontal rows (of chlorine or bromine atoms) 0.56 nm apart; (b) deposition of the PBu1 helices on the substrate. To fit the substrate periodicity, tilts of 30° to the right (for the right-handed helices) and to the left (for the left-handed helices) are required

The observed epitaxy of PBu1, form I′ on the hemiacid and the potassium salts is wholly consistent with these simple and very general rules, and steric requirements: this epitaxy rests on the barest and most elementary epitaxial interactions conceivable for a helical polymer, which amount to considering (a) a one-dimensional match which involves the helical turn periodicity and (b) the helical path, oblique to the chain axis, which may set the stage for helix chirality selection.

The interaction mechanism thus described emphasizes molecular (helical) interactions, as opposed to lattice interactions. As a consequence, nucleation (local interactions) appears to play a key role in the epitaxy, as opposed to growth (long-range propagation linked to lattice matching of favourable local interactions). This inference is corroborated by the unusually high nucleation density (or, alternately, the unusually low impact of growth processes) evident from the lamellar organization which can be seen in *Figure 8b*.

DISCUSSION

Epitaxial crystallization of form I′ of poly(1-butene) on chlorine or bromine 4-substituted benzoic acid is of special interest in analysing the epitaxy of helical polymers for three major reasons:

1. The substrate surfaces, although consisting of the same species (chlorine or bromine atoms, and neighbouring hydrogen atoms) offer a *range of related structures, differing only in their finer, but nevertheless crucial, details of symmetry and dimensions.* In particular, 4ClBzAc has a triclinic structure which alleviates any possible ambiguities in interpretation linked with substrate symmetry.
2. The organization of ethyl side chains in the (11.0) contact plane of PBu1, form I′, determines a physically clear-cut *helical path.* This path is unaffected by helix reversal (anticline or isocline helices). Furthermore, the helical path is *not* parallel to a low index crystallographic direction: as such its structural role can be distinguished from that of 'conventional' lattice matching (involving crystallographic planes or lattice periodicities) in the analysis of epitaxy. This situation thus contrasts markedly, for example, with that of α-isotactic polypropylene, in which the helical path is parallel to [101] in the *ac* plane[8].
3. The (11.0) face of PBu1, form I′ is built of *isochiral helices.* As already observed for the homoepitaxy and epitaxy of isotactic polypropylene (α-phase[8]), which has a related structure (cf. *Figure 1*), selection of helix chirality becomes a crucial issue in the epitaxy. This selection takes place in the first layer, i.e. the contact plane. Of course, subsequent growth on that layer follows the crystallographically required alternation of antichiral helices but, in doing so, *keeps the memory of the first layer helix chirality*; as a result, *the whole epitaxially crystallized thin film is an indicator of helix chirality of the first layer in contact with the substrate*, and provides an unmatched insight into the local interactions taking place at the polymer–substrate interface.

The epitaxy on potassium hydrogen 4-chlorobenzoate and the other potassium salts, which *do not* provide any crystallographic match for the depositing lattice, results in a high nucleation density, and diffraction evidence indicates a clear-cut relative polymer–substrate interaction. This orientational relationship must be analysed in terms of the least specific, and therefore most general, helical polymer–substrate interaction, which involves two features:

(i) an appropriate tilt of the chain axis to match the (shorter) substrate periodicity, and;

(ii) within the constraints defined by the above tilt, selection of chirality to align the helical path and the most prominent substrate features, as exemplified here by rows of chlorine atoms. If the tilt angle is equal to the so-called pitch angle (in projection, the angle between the helical path and normal to the helix axis), helical path and substrate features are parallel (as in *Figure 9b*). However, this ideal situation need not necessarily be realized: in the present case, for example, the tilt angle is 30°, whereas the pitch angle is 11°.

As a whole, therefore, epitaxy of form I' on the potassium hydrogen 4-chlorobenzoate and the other salts must be described by a one-dimensional match, the unique direction being the helix axis, with the most prominent dimension in the interturn distance. This analysis 'blurs' the more frequent notions and/or requirements of lattice matching (preferably two-dimensional) but does not, however, eliminate it. Indeed, when the helix tilt is close to creating a 'conventional' epitaxy, this epitaxy is realized, as illustrated for 4ClBzAc: the calculated tilt is 16°, whereas a 12° tilt is preferred, as this corresponds to the low index (10.2) planes.

Finally, epitaxy on 4ClBzAc, with its triclinic unit cell, illustrates a further degree of helix chirality selection: when substrates with low symmetry of the contact plane are involved, deposition of one helical hand may be significantly preferred, as illustrated by 'major' and 'minor' form I' and unique 'minor' form II epitaxy on this substrate.

CONCLUSIONS

Epitaxy of PBu1 in its form I' has been achieved on 4-chlorobenzoic acid, and on hemiacids and salts. Analysis of the epitaxies and interactions indicates that (a) subtle variations in substrate structure and dimensions influence formation and orientation of the various forms, (b) helix chirality of PBu1 in the contact surface can be defined from straightforward diffraction evidence, and (c) low symmetry of the 4ClBzAc substrate discriminates a preferred chirality of interacting helices.

The epitaxies underline the major role of the helical path in the contact surface, as is best illustrated for PBu1, form I'. All epitaxies result in near parallelism of this helical path with rows of chlorine or bromine atoms of the substrate. Since the helical path is oblique to the helix axis, this results in symmetrical tilts for helices of opposite hand, thus providing an *enantioselective feature sensitive to helix conformation*, as opposed to molecular configuration.

In the process, a lattice match between polymer and substrate may be realized and is preferred when compatible with the dimensions involved. However, some epitaxies of form I' must be analysed in terms of a one-dimensional match with the helix axis as the only clearly definable direction in the epitaxy.

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