Epitaxial crystallization of monoclinic and orthorhombic polyethylene phases

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The crystallization of polyethylene (PE) on alkali halides and several organic substrates has been investigated by electron microscopy and electron diffraction in order to analyse the structural and dimensional requirements of polymer epitaxy. PE has a simple molecular shape and offers a wide range of interchain distances in its two phases: orthorhombic and monoclinic. Lattice matching requirements are found to be stringent enough to induce a given crystal phase and, within this phase, a given contact plane. Three different contact planes have been observed for both forms. The growth transition from monoclinic to orthorhombic phase appears to follow the so-called 'Mode I' described by Seto *et al.*

(Keywords: crystallization; polyethylene; electron microscopy; analysis)

INTRODUCTION AND BACKGROUND

Besides its well-known orthorhombic modification, polyethylene (PE) exists in a less common monoclinic phase, the cell geometry and structure of which have been determined by Seto *et al.*[1]. The monoclinic phase is metastable and is usually obtained from the orthorhombic one by application of stress. The orthorhombic to monoclinic phase transformation has been much investigated, for example by electron diffraction on deformed solution-grown PE single crystals[2] and by conformational energy analysis[3,4]. In their early work, Seto *et al.*[1]. suggested three different possible transformation pathways and favoured the mode denoted I which requires only small chain displacements, a view supported by later conformational energy analysis results[3].

The monoclinic phase of PE has also been obtained under two different growth conditions, i.e. in the absence of mechanical stress.

(1) Teare and Holmes[5] suggested that it can be produced by crystallization at low temperatures. More recently, Keller and co-workers[6] found traces of this phase in germ-free PE droplets crystallized at very high supercoolings, which are indeed known to induce unstable crystal forms in many systems.

(2) More relevant to the present work, Wellinghoff *et al.*[7] observed that epitaxial crystallization of PE from dilute solutions on alkali halide substrates may give rise to the monoclinic modification. However, growth of the monoclinic phase is only a transient phenomenon: a monoclinic to orthorhombic phase transformation takes place within a few nanometres from the substrate surface, and growth proceeds thereafter in the orthorhombic phase.

The present paper describes a structural investigation of thin films of polyethylene grown epitaxially on a range of substrates, including some of the alkali halides used by Wellinghoff *et al.* as well as a number of organic substrates. The paper addresses the possibility of forming the monoclinic crystal modification of PE merely by appropriate selection of the substrates on the basis of their chemical structure and cell geometry.For completeness and comparison, some earlier and newer results on epitaxy of the orthorhombic phase of PE are also either briefly recalled or presented. For each of the two crystalline phases three different orientations have been induced by epitaxy and the transformation from monoclinic to orthorhombic phase has been further investigated.

EXPERIMENTAL

Preparation of the substrate crystals

The alkali halide single crystals, NaCl and KBr (Harshaw Chemical Co.) were cleaved in air, quickly transferred to the vacuum bell jar and held under vacuum at room temperature for several hours before polymer deposition. The potassium or sodium salts of organic aromatic acids were produced by neutralization of the corresponding acids (Merck or Fluka). Crystals of the salts were grown on glass slides by slow evaporation of their ethanolic solutions, again followed by drying under vacuum at room temperature for several hours.

Single crystals of potassium benzyl penicillin were grown on glass slides by evaporation of a dilute chloroform/ethanol solution under mild heating. Whenever required (i.e. when composite diffraction patterns were to be recorded) the water soluble substrate crystals were grown directly on the carbon-coated grids.

Vapour deposition of the polyethylene thin films

According to Wellinghoff *et al.*[7] the monoclinic phase in epitaxially grown PE films is located at the NaCl interface as a layer a few nanometres thick. To increase significantly the proportion of monoclinic PE, deposition of a thin (about or less than 10 nm) and uniform film is required: this is achieved in the present study by vaporization under vacuum, condensation and subsequent crystallization of the polyolefin. The procedure is similar in its principle to that used in the polymer decoration technique[16]. A small PE chip (2–10 mg depending on the desired film thickness) is slowly

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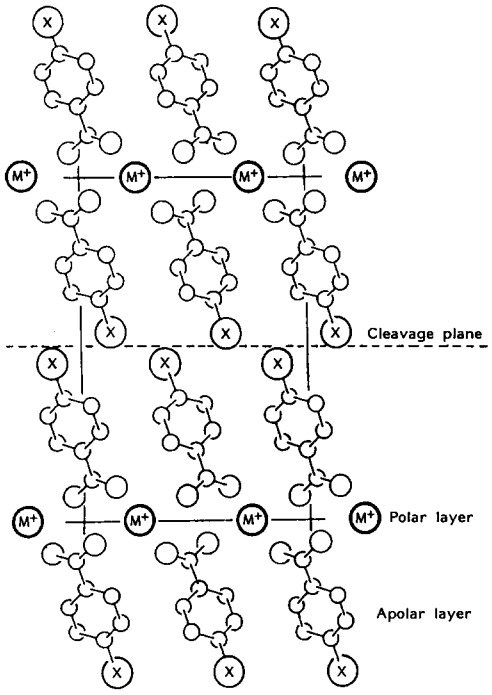

Figure 1 Crystallographic structure of *para*-substituted benzoic acid salts. This figure is adapted from the crystal structures discussed in reference 11

evaporated from a tungsten loop under normal incidence at about 10 cm above the substrate crystals. Care is taken to avoid sputtering of the molten polymer. The samples are shadowed with Pt/C, coated with a carbon film, floated off on water and mounted on electron microscope copper grids.

The polymer deposits or the polymer/substrate bicrystals are examined by transmission electron microscopy and electron diffraction using a Hitachi HU 11CS or a Philips CM12 microscope. Some diffraction patterns were internally calibrated with thin deposits of thallium chloride.

RESULTS

Chemical and crystallographic structure of the organic substrate crystals

The crystal structure of alkali halides is well known, and their action on PE crystallization documented by numerous works[7–9].

The crystal structures of a number of salts of aromatic acids have been determined by various authors[10,11]. These salts (and their corresponding organic acids) have important and characteristic features: a sandwich layered or sheet structure in which the anions (or the carboxylic groups for the acids) lie in a plane and the phenyl or *p*-substituted phenyl rings are arranged on both sides of this polar plane (*Figure 1*). In this highly anisotropic structure, each sheet has a strong cohesion provided by the ionic forces or hydrogen bonds of the inner polar part; successive sheets are linked only by relatively weak van der Waals forces between the substituted aromatic rings. As a consequence, large flat crystals or platelets are grown, the main faces of which are made of the aromatic part of the molecule. These apolar surfaces are of central importance in the present investigation since, as shown recently, polyethylene crystallizes epitaxially on this structured hydrocarbon part[12].

In the present context, one notes that:

(1) The surface atoms of the aromatic hydrocarbon plane and therefore its chemical nature can be changed by using substitution in *para* position. In the present investigation *p*-chloro and *p*-bromobenzoic acids or salts have been used.

(2) The aromatic hydrocarbon surface may retain the same structure irrespective of the chemical nature of the polar moiety. For example, *p*-chlorobenzoic acid (Cl–C_6H_4–COOH) and its salt potassium hydrogen *p*-chlorobenzoate (Cl–C_6H_4–COOH,Cl–C_6H_4–COOK), in which half of the acid functions are neutralized, are very nearly isomorphous. We observed also that the neutral salt (Cl–C_6H_4–COOK) has again *b* and *c* unit cell parameters very close to those of the two previous substrates.

(3) On the practical side, given the growth habit of the substrate, all diffraction patterns obtained in this study are taken normal to the exposed substrate surface, i.e. to the substrate and PE contact planes.

The above analysis helps explain our choice of potassium benzylpenicillin as a substrate for the oriented growth of polymer crystals. While this choice may at first sight appear surprising, it was in fact suggested by the most appropriate crystal structure of this benzylpenicillin derivative: the unit cell shown in *Figure 2* is orthorhombic, space group $P2_12_12_1$ with parameters $a=0.936$ nm, $b=0.637$ nm and $c=3.035$ nm. The crystal structure and molecular packing, like those of organic acid salts, point to the existence of layers with the methyl groups and the benzene rings on one side and the various oxygen atoms (of the carboxyl and amide groups and of the lactam rings) facing the polar layer with the potassium ions (*Figure 2*).

When prepared by evaporation of a hot chloroformic solution, potassium benzylpenicillin (KBP) forms irregular lath-shaped crystals elongated along the *b*-axis with well developed (001) basal planes parallel to the ionic and non-polar layers. As for organic acid salts, they correspond to easy cleavage planes between two adjacent non-polar planes.

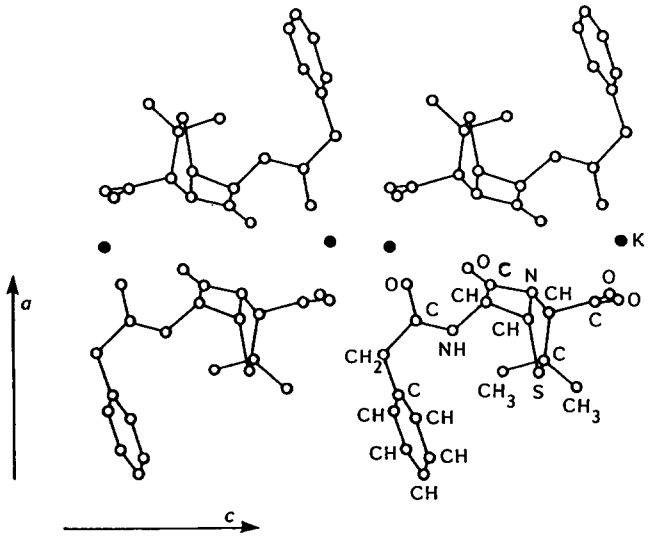

Figure 2 Part of the unit cell of potassium benzylpenicillin (KBP) as seen along the *b*-axis (redrawn after Reference 17). The view is down the axis of the 'furrows' on the contact surface (top or bottom planes) with a periodicity of 0.936 nm

Table 1

Substrate (1)	Contact phase of PE (2)	Substrate direction parallel to PE chain axis (3)	PE/substrate contact plane (4)	d(PE)/d(substrate)[a] (% disregistry)[a] (5)		Monoclinic → orthorhombic transition[b] Corresponding planes (6)	Mode I (7)	Mode III (8)
NaCl	Mono	⟨110⟩	$(010)_m/(100)$	4.04/3.98;	+1.53	$(010)_m \rightarrow (110)_o$ 4.04 → 4.458	5.9°	0.9°
KBr	Ortho	⟨110⟩	$(110)_o/(100)$	4.458/4.651;	−4.15	–	–	–
Anthracene	Ortho	⟨110⟩	$(100)_o/(001)$	4.946/4.93;	+0.32	–	–	–
p-Terphenyl	Ortho	⟨110⟩	$(110)_o/(001)$	4.458/4.60;	−3.09	–	–	–
Benzoic acid	Ortho	[100]	$(100)_o/(001)$	4.946/5.14;	−3.77	–	–	–
p-Br benzoic acid[c]	Mono	[001]	$(\bar{2}10)_m/(100)$	5.234/5.60;	−6.53	$(\bar{2}10)_m \rightarrow (100)_o$ 5.234 → 4.946	10.12°	64.0°
p-Phenyl benzoic acid	Ortho	?[d]	$(010)_o$ /?	?		–	–	–
K benzyl penicillin	Mono	[010]	$(\bar{4}10)_m/(001)$	9.182/9.36;	−1.9	$(\bar{4}10)_m \rightarrow (310)_o$ 9.18 → 8.29	6.12°	14.88°

[a] Epitaxial disregistry (percentage) calculated as: $100[d(\text{PE}) - d(\text{substrate})/d(\text{substrate})]$

[b] Column 6: planes of the monoclinic and, after phase transition, of the orthorhombic phases that are parallel to the substrate surface, and corresponding interchain distances
Columns 7 and 8: calculated angle between the orthorhombic and monoclinic planes indicated in column 6, assuming the monoclinic → orthorhombic transition modes I (7) and III (8)

[c] And related compounds: *p*-Cl and *p*-Br free acids, hemi-acids and alkaline salts. The disregistry has been calculated for the hemi-acid of *p*-Cl benzoic acid[11]

[d] Substrate lattice parameters and structure unknown to us

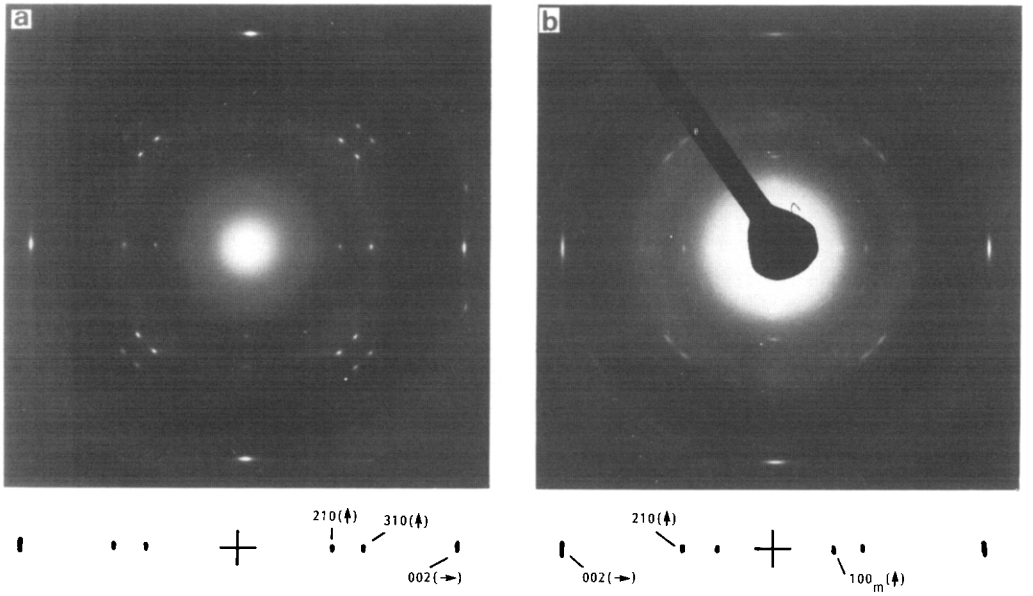

Figure 3 Selected area electron diffraction patterns (SAEDP) of thin PE films deposited on (a) a KBr (100) cleavage plane and (b) a (100) cleavage surface of NaCl. Indexing of the diffraction spots located on the equator of the pattern is given below the figure. As for similar figures, indexing of the orthorhombic phase is given without further qualification, while the monoclinic phase and the substrate are referred to by subscripts m and s, respectively. The arrows indicate the orientation of the chain axis in the population of crystals giving rise to the reflection

Epitaxial crystallization on the various substrates

The main results of our studies are summarized in *Table 1* and illustrated by *Figures 3–8*. Given the possibility of performing, in most cases, diffraction investigation on bi-crystals made of the substrate and the deposited polymer, the epitaxial relationships can be established unambiguously. A few comments are presented, concerning various polymer/substrate systems.

Ionic substrates. The present results are in agreement with the findings of Wellinghoff *et al.*[7]. KCl and KBr (*Figure 3a*) yield PE $(110)_{ortho}$ contact planes. The observation of a monoclinic phase in vapour-deposited films grown on NaCl (*Figure 3b*) is also in line with similar findings for solution grown epitaxial crystals. As evidenced by the presence of 210 and 310 orthorhombic reflections, a phase transition to the orthorhombic form takes place, following the scheme:

$$(010)_{mono} \| (100)_{NaCl} \xrightarrow{\text{phase trans.}} (110)_{ortho}$$

Again in line with previous findings, this transition takes place at some distance (several nanometres) from the substrate surface, since for very thin PE deposits the monoclinic reflections appear stronger.

Substituted aromatic acid salts. PE deposits on *p*-chloro and *p*-bromobenzoic acid salts have a unique

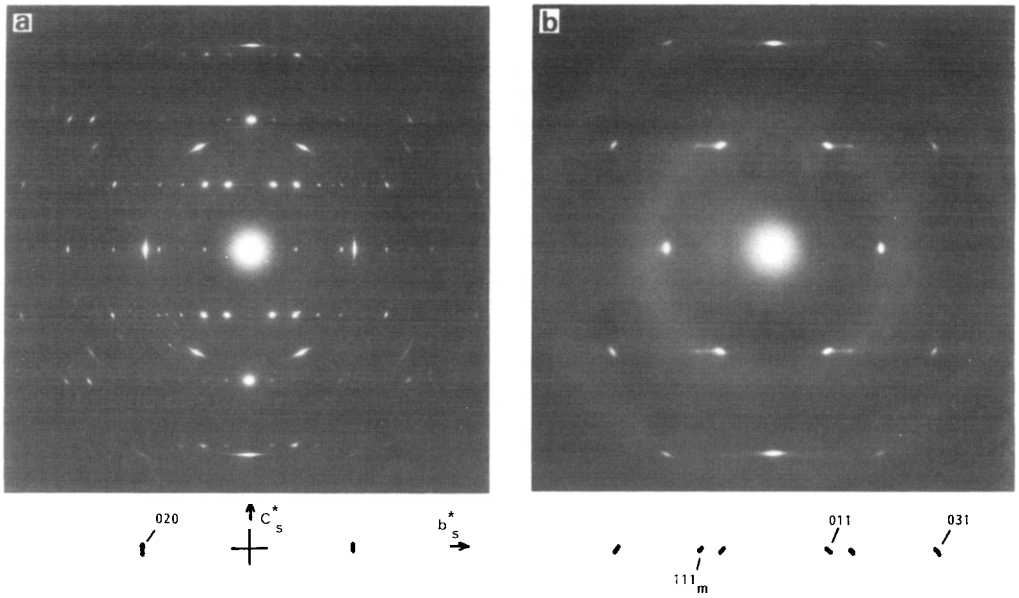

Figure 4 (a) Composite SAEDP of a thin film of PE and the substrate crystal of potassium salt of *p*-bromobenzoic acid. (b) Similar SAEDP of a thin vapour-deposited PE film after removal of the substrate crystal. Indexing of the reflections on the first layer line is shown below the figure. Note the characteristic 111_{mono} reflection (PE chain axis vertical)

chain axis orientation. They yield a set of 111 reflections of the monoclinic phase, indexed in *Figure 4(b)*, together with a clear streaking on the first layer line. All the other reflections of the pattern correspond to a (100) contact plane of orthorhrombic PE. Here again, a monoclinic layer is in contact with the substrate, with later transformation to the orthorhombic form following the scheme

$$(\bar{2}10)_{mono} \| (100)_{substrate} \xrightarrow{\text{phase trans.}} (100)_{ortho}$$

i.e. the phase transition results in a slightly more densely packed plane (interchain distances of 0.494 nm *versus* 0.524 nm, cf. *Figure 7*).

It should be mentioned that essentially the same pattern of epitaxy and phase transition is obtained when PE is co-crystallized from the melt with the corresponding free acids, which confirms first the structural similarity of the exposed contact planes of the aromatic acids, the hemiacids and the neutral salts, and secondly the fact that the observed epitaxies are not a result of the specific crystallization conditions linked with the vaporization and condensation of PE molecules.

Potassium benzylpenicillin. Potassium benzylpenicillin has been selected as a substrate for PE crystallization because its characteristic structure periodicity in the exposed face is larger than any interchain distances that exist in densely packed planes of monoclinic and orthorhombic phases of PE.

In the composite diffraction pattern obtained (shown in *Figure 5*), it was observed that the reflections associated with KBP crystals fade out more rapidly than PE ones, suggesting that KBP is even more sensitive to electron beam damage than PE. The diffraction patterns are characterized by the presence of strong equatorial 010_{mono} reflections superimposed on the 200 substrate reflections, together with 110_{ortho} and 220_{ortho}. In addition, the 002 reflections of polyethylene are located exactly on the fifth layer of the KBP pattern.

The epitaxy associates the (001) plane of KBP and the $(\bar{4}10)_{mono}$ plane of PE, with the *c*-axis parallel to $[010]_{KBP}$. The characteristic 0.936 nm inter-row periodicity of the substrate is matched by the 0.910 nm interchain distance in the $(\bar{4}10)_{mono}$ plane of polyethylene (mismatch: 1.9%). A second dimensional match is suggested along the PE chain axis between $c_{PE}/2$ and $b_{KBP}/5$, which are both equal to 0.127 nm.

The monoclinic to orthorhombic phase transition results in a change from $(\bar{4}10)_{mono}$ to $(310)_{ortho}$, i.e. in a contraction from an interchain distance of 0.918 nm to 0.829 nm as reported in *Table 1*, column 6, which summarizes the phase transitions from monoclinic to orthorhombic PE observed in the present investigation. As will be discussed later, these transitions can be accounted for in terms of a single relationship (and transformation mechanism) between the subcells of the two crystalline polymorphs.

Substrates yielding the orthorhombic phase of PE. Organic substrates that yield directly the orthorhombic phase of PE have been described on previous occasions[12,14]. In these investigations, cocrystallization of PE and the substrate (which acts as a solvent at high temperature) was made in the bulk.

Epitaxies so far observed include as substrates:

(1) Anthracene with matching of the 0.494 nm b_{PE} parameter and the 0.493 nm anthracene inter-row distance parallel to $\langle 110 \rangle$ [12].

(2) *p*-Terphenyl with an epitaxy very similar to that observed for anthracene, but with the significant difference that the PE contact plane is now a (110) plane; the shorter 0.46 nm inter-row distance in *p*-terphenyl is matched by the 0.445 nm interchain distance in the (110) plane of PE[12].

(3) Benzoic acid with a PE (100) contact plane as for KBr and anthracene, but with a single orientation of the PE chain and matching of the 0.494 nm PE interchain distance with the *b* parameter of benzoic acid (0.514 nm)[14].

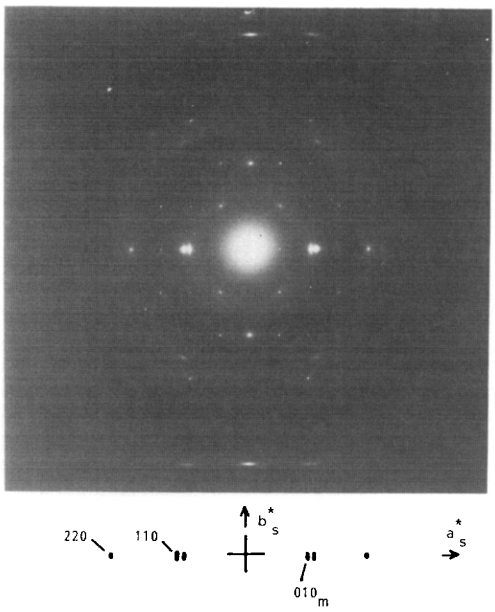

Figure 5 Composite SAEDP of a thin vapour-deposited PE film and the substrate crystal of potassium benzylpenicillin. This DP is the third of a series in which the diffraction spots of KBP have almost faded away, due to its high electron beam sensitivity. Indexing of the equator is shown below the figure (chain axis vertical)

During this investigation, two orientations of orthorhombic PE were observed with the potassium salt of *p*-phenyl benzoic acid. One of them is original in that it involves the (010) plane of PE, i.e. implies an interchain distance of 0.742 nm (*Figure 7*). The crystal structure of this substrate is however not known to us, which precludes any detailed analysis of the underlying epitaxy.

All the above experimental results are summarized in *Figure 6*, which represents the orthorhombic and monoclinic crystal modifications of polyethylene as seen along the chain axis, and indicates the observed contact planes.

In summary, three distinct contact planes of the monoclinic modification of PE have been obtained. This unstable modification exists only as a thin (several nanometres) layer near the contact surface and transforms on further growth into the stable orthorhombic form. Three different contact planes of the orthorhombic form have also been observed for epitaxies which do not involve a transient growth in the monoclinic form. Finally, the range of interchain distances in the two forms and the observed epitaxies are summarized on a linear scale in *Figure 7* and the monoclinic to orthorhombic phase transformations indicated in *Table 1* are sketched in *Figure 8*.

DISCUSSION

Structural and dimensional requirements for polymer epitaxy

The results on epitaxial crystallization obtained in the present investigation extend earlier results[12-15] to a range of organic substrates with substrate contact surfaces of different chemical natures and a large variety of substrate periodicities. They provide a basis for analysing in some detail the structural and dimensional requirements of polymer epitaxy, as studied through the specific example of polyethylene. This polyolefin appears to be quite appropriate when dealing with these issues: its molecular shape is simple, and thus avoids possible complications observed with helical polymers[15]; the molecular conformation remains unchanged in the orthorhombic and monoclinic modifications; these two modifications are of comparable energy and it is known that the unstable form can be induced by epitaxy; finally, PE offers a wide range of interchain distances in its two crystal forms.

The choice of the substrates was dictated mainly by two requirements: reasonable compatibility with PE and homogeneity in the structure of the contact plane. Apart from the alkali halides, all substrates used have exposed faces that contain phenyl rings in a number of different forms: simple (benzoic acid), condensed (anthracene), multiple (*p*-terphenyl, *p*-phenyl benzoic acid), substituted (*p*-chloro or *p*-bromobenzoic acid) or, finally, as a pending group of a bulkier molecule (penicillin). Phenyl or substituted phenyl-bearing substrates were shown to produce favourable interactions with polyolefins and in particular with polyethylene[12,14,15]. Phenyl rings are present in the molecular architecture of many well-known nucleating agents of these crystalline polymers, as best illustrated by sodium benzoate.

Lattice matching in polymer epitaxy is a controversial and unsettled issue. The early investigations on polyethylene/alkali halide epitaxies yielded somewhat contradictory results. While lattice matching was recognized as an important feature in the formation of the monoclinic phase of PE on NaCl, epitaxies were also observed with other alkali halides for which no clear-cut lattice matching could be detected. It was therefore concluded[9] that 'lattice matching is an unimportant criterion in polymer epitaxy'.

This view has been challenged by the results of epitaxial crystallization of polyethylene on aromatic hydrocarbon substrates mentioned above: anthracene and *p*-terphenyl have structurally very similar contact faces but with (110) lattice periodicities of nearly 0.49 nm and 0.46 nm that are matched by the 0.494 nm and 0.445 nm interchain distances in the (100) and (110) PE contact planes, respectively[12]. This change in contact plane can only be linked to lattice matching requirements. The present results add further strength to this argument. They

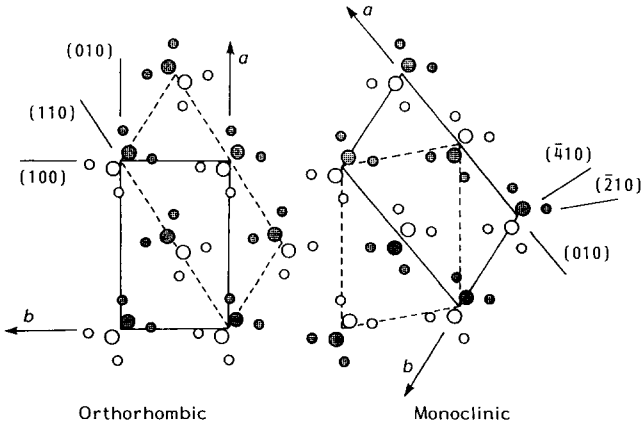

Figure 6 Orthorhombic (o) and monoclinic (m) unit cells of PE and the various contact planes observed in the present investigation (adapted from Reference 18). The indicated contact planes are observed with the following substrates: $(110)_o$, *p*-terphenyl, KBr; $(010)_o$, *p*-phenyl benzoic acid (and its salts); $(010)_m$, NaCl; $(\bar{2}10)_m$, *p*-Cl and *p*-Br benzoic acids and related salts and hemiacids; $(\bar{4}10)_m$, potassium benzyl penicillin

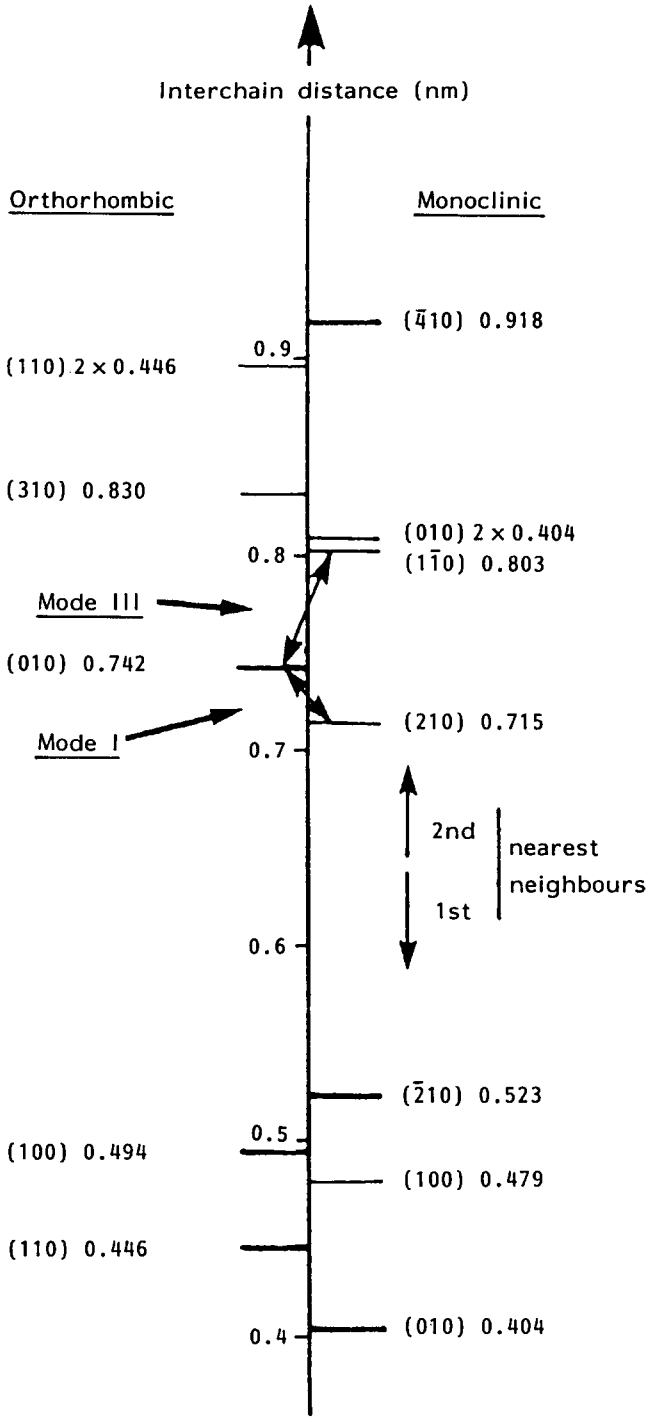

Figure 7 Linear scale of interchain distances in the low index planes of orthorhombic (left) and monoclinic (right) PE unit cells. The observed contact planes are indicated by heavy lines. Note the wide gap between planes with first and second nearest neighbour chains. Two orthorhombic ↔ monoclinic transition modes are indicated. Current evidence suggests that Mode I is operative (see text)

provide several examples of organic substrates that induce the monoclinic phase of PE, and demonstrate that lattice matching requirements may impose a specific crystal modification and, within this modification, a specific contact plane.

In the discussion of the present data, it is convenient to scan the interchain distance scale shown in *Figure 7*. This scale indicates that, in PE, first nearest neighbour chains are at a distance of 0.404, 0.479 and 0.523 nm in the monoclinic phase and at 0.446 and 0.494 nm in the orthorhombic phase. Second nearest neighbours cover a broader distance scale ranging from 0.742 nm in the $(010)_{ortho}$ plane to 0.918 nm in $(4\bar{1}0)_{mono}$, with a significant gap between the two families of planes.

The observed epitaxies involve mostly densely packed contact planes with first nearest neighbour PE chains. The densest of these, $(010)_{mono}$, with chains 0.404 nm apart, becomes the contact plane only for very short substrate repeat distances; it was observed here only with NaCl substrates, but was also found in the polyethylene decoration of polyoxymethylene single crystals (characteristic distance of 0.38 nm)[16].

For intermediate repeat distances, only the orthorhombic form is observed: given the usual tolerance ($\pm 10\%$) in epitaxial disregistries, the 0.446 and 0.494 nm interchain distances can be accommodated on a variety of substrates. It must be noted that out of five densely packed planes in orthorhombic and monoclinic PE, only the $(100)_{mono}$ has not been observed as a contact plane. Its interchain distance of 0.479 nm is intermediate between those of orthorhombic form ones (0.445 and 0.494 nm); it therefore falls in an 'orthorhombic domain' where this more stable form is preferred. On the 'larger' side of this domain the monoclinic phase is again observed: the $(\bar{2}10)_{mono}$ contact plane ($d = 0.523$ nm) is selected on *p*-chlorobenzoic acid salts, matching with a substrate periodicity of 0.56 nm ($b/2$). In all cases, formation of the monoclinic phase appears to result from a delicate energy balance, the better epitaxial fit of the monoclinic phase superseding the gain of energy resulting from the growth of the orthorhombic phase.

Epitaxies which involve PE contact planes with second nearest neighbours are *a priori* less favourable than those involving more densely packed planes. In fact they would not be expected under 'normal' crystallization conditions, i.e. from solution or from the melt. In the present investigation, advantage was taken of the vaporization technique and the unusual crystallization conditions to,

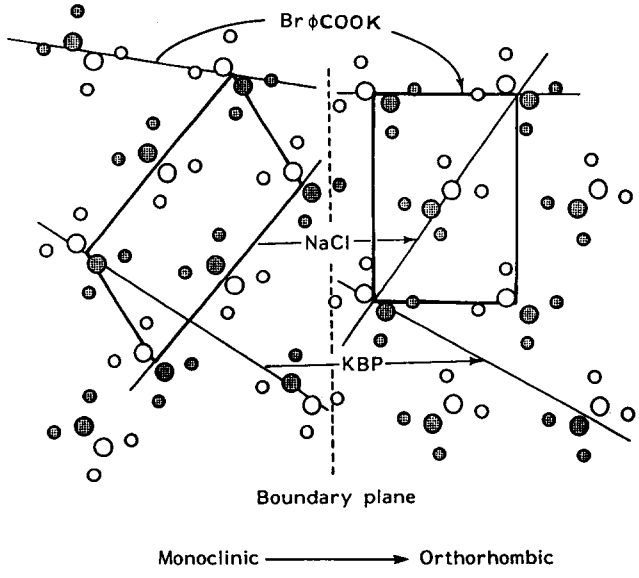

Figure 8 Filiation of the monoclinic and orthorhombic PE phases following transformation Mode I[1]. The boundary plane associates $(010)_o$ and $(210)_m$ crystallographic planes. The three monoclinic contact planes in epitaxial crystallization are indicated, as well as the corresponding orthorhombic planes after phase transformation. The small departures from coplanarity are reported in *Table 1*, column 7, and are compatible with experimental results (column 6)

in some way, 'force' these less likely epitaxies. The best documented example among them is that of the $(\bar{4}10)_{mono}$ PE contact plane on the benzylpenicillin salt. It should again be stressed that selection of this substrate for epitaxial growth of PE was by no means fortuitous. Based on its known crystal structure, the compatibility with PE was anticipated and, moreover, the observed contact plane was foreseen. Similar experiments would be possible with other unorthodox substrates that fulfil both requirements of compatibility and lattice matching. Beyond the scientific game, the present results illustrate profusely the importance of the lattice matching criterion in polymer epitaxy, much more so than previously admitted on the basis of the limited experience with alkali halide substrates.

The monoclinic to orthorhombic phase transition

The mechanically induced phase transformation from the orthorhombic to the monoclinic phase of PE is well documented. A detailed study has dealt with deformation of single crystals, which are ideally suited for such investigations since the chains are seen along their molecular axis[2]. It appears that these transformations involve planes with second nearest neighbour chains in the two crystal forms and are brought about by rotations of chains on their axis. The two major pathways result in transformations of the $(010)_{ortho}$ plane into the $(210)_{mono}$ and $(\bar{1}10)_{mono}$, respectively. They are named Modes I and III, and are characterized by lattice mismatches in the boundary planes of -3.66 and 7.69% (*Figure 7*).

Phase transitions during crystal growth from the epitaxially induced monoclinic to the more stable orthorhombic form take place systematically within a few nanometres of the substrate surface, in agreement with the earlier observations of Wellinghoff *et al.*[7]. Direct observation of the transition planes (which are of *hk*0 type) is precluded in the present case by the molecular orientation, normal to the electron beam. However, as discussed now, analysis of the relative orientations of the orthorhombic and parent monoclinic lattices makes it possible to establish the relationship between the two phases.

As shown in *Table 1*, column 6, the phase transitions may be characterized by planes of the monoclinic and orthorhombic phases that are parallel, or nearly so, to the substrate surface. If these planes were considered as boundary planes, no simple relationship between the two phases would exist. A rationale appears, nevertheless, when considering the above mentioned transformation modes suggested by the studies on mechanically deformed PE. For this purpose, the orientation of the orthorhombic plane known to be nearly parallel to the substrate contact plane is determined from the known orientation of the monoclinic lattice, assuming transition modes I or III. As seen in columns 7 and 8 of *Table 1*, the transitions in films grown on NaCl and KBP could be accounted for by either Mode I or Mode III. However, a similar analysis applied to thin films grown on *p*-Cl benzoic acid clearly favours Mode I, which brings the $(100)_{ortho}$ plane nearly parallel to the substrate surface, in agreement with experimental results; by contrast, with Mode III, the plane would be 64° away from its actual orientation.

Mode I, which accounts in a unified way for all our experimental results (*Figure 8*), therefore appears highly favoured: the 'structural correspondence' between orthorhombic and monoclinic PE lattices illustrated in *Figures 6* and *8* prevails under the present experimental conditions. This analysis is clearly in line with the early conclusions of Seto *et al.*[1] It suggests that the monoclinic to orthorhombic transition follows preferentially a single pathway both in mechanical deformation and during crystal growth.

CONCLUSION

Epitaxial crystallization of condensed polyethylene vapours (produced by thermal degradation under vacuum) has been achieved on two alkali halide substrates, a variety of organic aromatic acid salt crystals and a penicillin derivative.

Depending on the substrate, the stable orthorhombic and the unstable monoclinic phases of PE are obtained, the latter merely as a thin layer (a few nanometres thick) in direct contact with the substrate surface. On further growth, the monoclinic phase transforms into the orthorhombic one, following the transformation Mode I described by Seto *et al.*[1], which associates $(010)_{ortho}$ and $(210)_{mono}$ as the boundary planes between the two phases.

The issue of lattice matching has been investigated in some detail, by taking advantage of the range of interchain distances available in the orthorhombic and monoclinic unit cells of PE, and by using a variety of substrates with very similar contact surfaces (made of simple or substituted aromatic rings) but with widely different characteristic periodicities. Six different contact planes have been observed (three in each crystal form), involving four planes with nearest neighbour chains (two in each form) and two planes with second nearest neighbours. For first nearest neighbours, substrates with periodicities ranging from about 0.44 to 0.52 nm induce the orthorhombic form with either (110) or (100) contact planes. On the shorter and wider sides of this range, the monoclinic form is initiated with (010) or $(\bar{2}10)$ contact planes, respectively. Furthermore, a most unusual epitaxy has been predicted and actually achieved between the $(\bar{4}10)$ monoclinic plane (0.930 nm interchain spacing) and a benzyl penicillin salt.

Based on the above results, it appears that lattice matching between the polymer interchain distance and the substrate periodicity is an essential feature of polymer epitaxy. Two-dimensional lattice matching (i.e. also with matching along the polymer chain axis) may be an added feature, but appears less critical. As clearly demonstrated, lattice matching criteria control not only the crystal modification (orthorhombic or monoclinic) but also the contact plane in each form. It offers a simple geometric rationale for explaining a wide body of experimental results that have accumulated in recent years. With the proper adjustments required by their more complicated molecular conformation, these lattice matching criteria were also found to apply to helical polymers[15].

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