



Organisation, structure and morphology of organic thin films via electron microscopy

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Abstract

Recently, molecular materials have emerged as challenger to inorganic materials for the active layers in opto-electronic devices. However, if they require comparatively low operating voltages, it is still difficult and a major challenge to grow organic macroscopic single crystals. Therefore, these molecular materials are incorporated in the devices as ordered thin films rather than as single crystals. Different procedures, among which epitaxial growth, are used to elaborate “single-crystal like” thin films as perfect as possible. The macroscopic performances of these films rely strongly on their quality. Therefore, both their morphology and their structure have to be carefully characterised and understood.

Among the various ex-situ techniques commonly available to control thin films, electron microscopy (EM) that can examine both the real and the reciprocal space is most appropriate. Combining the various EM modes one can visualise the crystal habits and morphology down to a few nanometres, the sizes, number and shapes of micro-defects or grain boundaries at the heart of the crystallites. The potentiality of EM as a versatile tool to characterise the fine structure of thin films is illustrated via the description of some distinctive cases of epitaxially grown thin films. We first recall the geometrical matching rules for usual epitaxy and then describe two cases of specific selection rules: a topographic selection for some polyolefins, a molecular selection for some diacetylenes. Finally, the morphology, structure and quality of ordered thin films for opto-electronic will be reported.

Though very diverse at first sight, the four chosen examples illustrate the process of understanding step by step the epitaxial growth of organic thin films on orienting substrates. These examples demonstrate that the origin of the orientation of a crystal onto another crystal can be very diverse. The major and ultimate goal is to yield large well-oriented thin films based on polymer or molecular crystals. This can only be achieved by a careful selection of the deposit-substrate pair. Such films will optimise the opto-electronic response of organic materials at the macroscopic scale, a prerequisite for future development.

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1. Introduction

These last decades have seen the progressive emergence of molecular materials as challenger to inorganic materials [1–3]. Different types of devices (field effect transistors, light emitting diodes) based on electroactive organic materials, were recently reported. One main advantage of organic materials, compared to inorganic polycrystalline semiconductors, is that they require comparatively low operating voltages. Some devices were built on freestanding single crystals. They take advantage of the basic characteristics of molecular single crystals: high purity, low trap concentrations, high electron mobility and few structural defects. The unique physical properties of the molecular single crystals are directly linked to the favourable alignment of the active molecules, mainly aromatic or heterocyclic conjugated molecules, in the crystal itself. However, the growth of organic single crystals is still a challenging task and the brittleness of these crystals will hamper the development of devices at an industrial scale. The required characteristics of single crystals (directional orientation of the molecules, low density of defects) can be preserved in ordered thin films. For the best cases, these polycrystalline films maintain the unique orientation of the molecules present in the native single crystal. Therefore, the molecular design of ordered thin films is a pivotal challenge for practical applications.

Mastering the elaboration of “single-crystal like” thin films is feasible with appropriate procedures. Different means can be considered to order molecules in thin films. Rubbing [4], a method commonly used for liquid-crystals, produces mostly thin films with a unique orientation in the plane of the film, the molecules are laid down along the rubbing direction but with little control of the organisation in the two other directions. On the contrary, Langmuir–Blodgett technique [5] brings in a unique orientation of the molecules orthogonal to the plane of the film, but again, with little control in the two other directions; moreover, the technique is limited to amphiphilic molecules. Though more restrictive and more demanding than the two previously mentioned methods, epitaxial growth [6–10] allows a three dimensional

control of the relative orientations of the deposit on the substrate. Epitaxial growth is an appropriate tool to control and master the elaboration of highly crystalline ordered films. Traditionally, epitaxy is associated with a 2-D linear dimensional matching between the interacting species in the contact planes, although a 15% dimensional mismatch is still compatible with epitaxy. Yet, depending on the symmetry of the 2-D arrangement of the molecules in the contact planes of the deposit and of the substrate, epitaxy may result in the desired “single-crystal like” organisation of the deposited film, or may, unfortunately give rise to two (or more) equivalent orientations that are of course not favourable for macroscopic properties. Therefore, both the morphology and the structure of the films oriented via epitaxial growth have to be examined in details.

Various ex-situ techniques are commonly used for the characterisation of thin films. Optical microscopy and near-field microscopies observe at different scales the morphology and the overall orientation in the real space, whereas X-ray, neutron or electron diffraction explore the reciprocal space to establish the positions and relative orientations of the unit-cells and of the molecules. Electron microscopy (EM) is the only means that can examine on a given location of a film both the real space and the reciprocal space, allowing thus morphology and crystallography features to be correlated. In particular, EM uses various modes, which carry different information. Bright field imaging (BFI), the most commonly used mode, selects the forward scattered electrons to provide images that display morphological markers and crystal habits down to a few nanometres. Dark field imaging (DFI) exploits only some selected diffracted electron beams; it provides images with a weaker intensity but a higher contrast. Selecting a priori some of the diffracted electrons yields specific markers of the selected diffracting planes, hence, DFI authorises a detail analysis of orientations in the corresponding planes, reveals the size, the number and the shape of defects of microdomains or of grain boundaries in the heart of the crystallites [11,12]. Moreover, when high resolution imaging (HREM) is achieved, direct imaging of rows of atoms can be achieved [13,14]. In

addition, when substrate/deposit bilayers can be examined in EM, the determination of the relative orientations of the two components is straightforward.

Rather than trying to make an exhaustive review on EM, four selected examples are presented hereafter to demonstrate the potential interest of EM as a versatile tool to characterise, post-mortem, the order and the quality of polycrystalline organic thin films.

The first example deals with two original observations of epitaxial growth of polyolefins on molecular crystals: namely isotactic polypropylene (iPP) and syndiotactic polypropylene (sPP) on 2-bromo benzoic acid (2BrBzAc) and 2-quinoxalinol (2-Quin), respectively. The selection of the contact plane for the polymer overgrowth does not obey the best dimensional matching; in both cases a *topographic matching* prevails over the usual dimensional matching. The second example concerns the epitaxial overgrowth of two carbazoyl substituted polydiacetylenes (pDA), one symmetrically and one non-symmetrically substituted on potassium acid-phthalate (KAP). The symmetrically substituted derivative is the poly[1,6-bis(9-carbazoyl)-2,4hexadiyne] (pDCH), the non-symmetrical one is poly[9-(9-carbazoyl)-5,7 nonadiyn-1-ol ethylurethane] (pCNEU). The oriented growth of DCH reveals a novel “*molecular epitaxy*”, whereas the evolution with temperature of the oriented growth of the CNEU shows an amazing competition between “*molecular and geometrical epitaxy*”. For, the third example, the *quasi-epitaxial overgrowth* of *para*-sexiphenyl (PSP) on mica (001), is examined in detail to get informations on both the orientations and the quality of the crystallites. Finally, we describe some recent observations on the growth of two thiophenes: quaterthiophene (4T) and α,ω -dihexyl quaterthiophene (α,ω -DH4T) thin films on KAP single crystals.

In these works, KAP single crystals have often been selected due to some interesting characteristics. Its easy cleavage plane, that will be the contact plane, is molecularly flat, thus the nucleation of crystal growth at the wedges of the steps is prevented. This plane is lined up with well-defined rows of aromatic rings that play a key role in

epitaxial growth. Finally, large single crystals are commercially available. Then physical characteristics can be easily measured and their uniformity checked.

2. Experimental procedures

Both iPP and sPP used for the present work have a high degree of tacticity. Following well established procedures, the polyolefin films (<40 nm) are solution cast onto a glass plate from a dilute ($\approx 1\%$) *p*-xylene solution. 2BrBzAc and 2-Quin are laid down on iPP and sPP, respectively, both systems are co-melted prior to re-crystallisation. Next, the single crystals of low molecular weight compounds are removed by dissolution in hot ethanol, leaving a thin polymer film with the imprint of the substrate crystals.

The pDA's undergo a topotactic polymerisation [15]. Thus the films are prepared via epipolymerisation (short for epitaxial growth followed by polymerisation). The monomers are vacuum sublimated ($P = 10^{-7}$ mbar, $T_{\text{source}} = 180\text{--}240$ °C) on freshly cleaved KAP single crystals, maintained at fixed temperatures in the range of -196 to 100 °C with sublimation rates between 0.02 nm/min and 0.5 nm/s. The nominal film thickness controlled by a quartz balance varies from 2 to 50 nm. DCH is polymerised at 150 °C for 24 h, whereas CNEU is UV polymerised at 254 nm at 25 °C for 10 min.

The PSP films were prepared using two slightly different methods. On GaAs, the films were prepared by molecular beam epitaxy (MBE) in an As atmosphere of 1×10^{-4} Pa, $T_{\text{source}} = 230$ °C, the substrate is maintained at temperatures ranging from 90 to 150 °C. On freshly cleaved mica (001) the films were prepared by Hot wall Epitaxy [16] ($P = 6 \times 10^{-6}$ mbar, $T_{\text{source}} = 240$ °C maintained at 90 °C, the average thicknesses range from 1 to 20 nm.

The 4T or α,ω -DH4T films, 10 nm thick, were grown by organic Molecular Beam Deposition [17] ($P = 8 \times 10^{-10}$ mbar, $T_{\text{source}} = 190$ °C) on silica or on freshly cleaved KAP maintained at 25 °C.

For requirements of EM observation, the films are backed with a carbon film, after Pt-carbon

shadowing or gold-decoration (when needed), and removed from the substrate. PSP and Poly(olefins) are removed with the help of a poly(acrylic acid) backing, subsequently floated on water. KAP crystals are dissolved in water. These carbon backed films floating on water are transferred on copper electron microscopy grids. All the EM observations were performed with a Philips CM12 microscope operated at 120 KV equipped with a rotating stage. Indexation of the experimental diffraction patterns and modelling of DH4T organisation were carried out with the Cerius 2 Software by ACCELRYs.

3. Results and discussion

3.1. Some historical rules for epitaxy

As already mentioned, we choose to illustrate the advantages of EM to characterise the organisation and quality of organic thin films with examples of epitaxially grown films. Therefore, we recall the basic rules established long ago for minerals (lattice matching) or more recently for organics (dimensional optimisation between prominent groups). Then some appealing exception will be described, namely *topographical adaptation and molecular epitaxy*.

3.1.1. General rules

For epitaxial growth, the contact planes are frequently dense crystallographic planes that are also natural growth faces. A long accepted rule of thumb is that oriented overgrowth requires a mismatch between corresponding dimensions of the deposit $\mathbf{d}_{\text{depos}}$ and the substrate \mathbf{d}_{subs} smaller than 15%.

$$\text{Mismatch (in \%)} = 100[(\mathbf{d}_{\text{depos}} - \mathbf{d}_{\text{subs}})]/\mathbf{d}_{\text{subs}}$$

For the very first experiments of overgrowth of minerals on minerals, the distances taken into account to estimate the mismatch were the lattice parameters of both partners, since the deposit and the substrate usually crystallise in the same crystallographic system. However, molecular crystals are basically different from minerals. First, organic

compounds crystallise in various crystallographic systems, therefore, the symmetry of the deposit and of the substrate may not be identical. Second, the atoms are covalently linked within the molecule, therefore, adaptation via some small relative motions of the atoms is impossible.

The above-mentioned features impose a distinctive geometry in the contact planes. For many organic crystals, rows of molecules or prominent groups (in case of polymer with helical chain) line up the contact planes and delimit well-defined grooves. This succession of valleys (grooves) and mounts is the key feature that controls the orientation of the deposit on the substrate. This is well established for polyolefins as only weak van der Waals interactions are expected.

3.1.2. Dimensional matching rules: the case of polyethylene

Interchain distances govern the epitaxy of polyethylene (PE), the first member of the polyolefins family. At atmospheric pressure, PE crystallises in a zig-zag conformation; the chains are featureless cylinders which pack in two different polymorphs: an orthorhombic stable one and a monoclinic metastable one. Both polymorphs orient on alkali halides going from LiF to KI with cell parameters ranging from 0.401 to 0.705 nm and with $d_{(110)}$ ranging from 0.284 to 0.499 nm. When necessary for best geometrical fitting, the first layers of PE in the vicinity of the substrate crystallise in the metastable monoclinic form as for instance on NaCl [18]; further away from the substrate, the film crystallises in the bulk stable orthorhombic form which implies a solid phase transformation. A recent systematic investigation of the deposition of PE on alkali halides and on molecular crystals reports the corresponding selection rule [19]. The selected polymorph and selected contact plane correspond to the best geometrical fit between the substrate and the nearest inter-chain distances or exceptionally second nearest neighbours. This dimensional selection rule is very critical; when two potential PE planes fit the 15% rule of thumb for a given substrate only the best-adapted plane (in term of inter-chain distances) is selected.

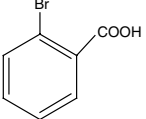
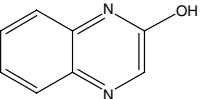
3.2. Topographical adaptation

3.2.1. Isotactic polypropylene

The second member of the polyolefins family, polypropylene, in its isotactic form (iPP) crystallises in three different forms based on different packing of the same 3_1 helix [20]. The more frequent forms are the α monoclinic form and the β trigonal one. The α unit cell is based on alternating isochiral layers of left or right helices while the β unit cell is built on isochiral helices. Though some work has just been published on the epitaxial growth of the β phase [21], we will focus our attention on the epitaxial growth of the stable α phase. One key feature for the epitaxial growth of the α polymorph is the organisation of the prominent methyl (Me) groups in (0 1 0) plane. They are ordered in a lozenge pattern that is at the origin of the specific quadrite morphology of iPP via homoeptaxy [22]. The Me rows line up the (0 1 0)_{iPP} plane with three characteristic distances 0.425, 0.505 and 0.65 nm parallel to the long diagonal, the short diagonal and along $c(=a)$ axis, respectively. A thorough examination of epitaxial growth of iPP on a number of different alkali halides and organic single crystals [23] showed that the dimensional adaptation is the general rule on both type of crystals, ionic or molecular crystals. However, one interesting exception was observed

on 2BrBzAc (the experimental conditions are summarised in Table 1). The bright field image (Fig. 1) shows a quadrite morphology that implies, as confirmed by electron diffraction a (0 1 0)_{iPP} contact plane (Fig. 1(b)). The quadrite morphology is nevertheless uncommon, one set of lamellae is more developed than the other one. 2BrBzAc crystallises in a monoclinic unit cell with parameters $a = 1.482$ nm, $b = 0.41$ nm, $c = 2.59$ nm, $\beta = 118^\circ$. As a result of hydrogen bonding between acid moieties, the 2BrBzAc crystal is built of dimers aligned along (1 0 1) while the benzene rings emerge in the (0 0 1) cleavage plane in rows 0.741 nm apart along a and 0.41 nm apart along b . The latter periodicity is a little smaller than the 0.425 nm distance between the Me rows parallel to the long diagonal of iPP (-3.66%). Yet, the (0 1 0)_{iPP} is not deposited on 2BrBzAc with the short diagonal parallel to $b_{2BrBzAc}$; the lozenge is turned by 18° (see Fig. 4(c) in Ref. [23]). Therefore, the Me rows of iPP lay down parallel to the linear grating formed by the prominent benzene rings along the (1 1 0)_{2BrBzAc} plane, though the corresponding inter-row distance (0.391 nm) leads to a less favourable dimensional matching of -8.7% . Thus, the orientation of α_{iPP} is directed by the best topographical adaptation (deposition) of the array of Me groups in the grooves delimited in the contact plane by the benzene "mounts".

Table 1
Substrates, polymers and experimental conditions used for epitaxially grown films of polyolefins

Substrate	Deposit	Deposition method
2-Bromo-benzoic acid	Isotactic polypropylene	Solution casting and co-crystallisation ^a
		
2-Quinoxalinol	Syndiotactic polypropylene	Solution casting and co-crystallisation ^a
		

^a The thin films of polymer are cast on a glass cover-slide from a dilute solution (1% in *p*-xylene.). The film is sprinkled with the substrate. Polymer and substrate are co-melted before crystallisation at a fixed temperature. The substrate is removed prior to the ME observation by dissolution in ethanol.

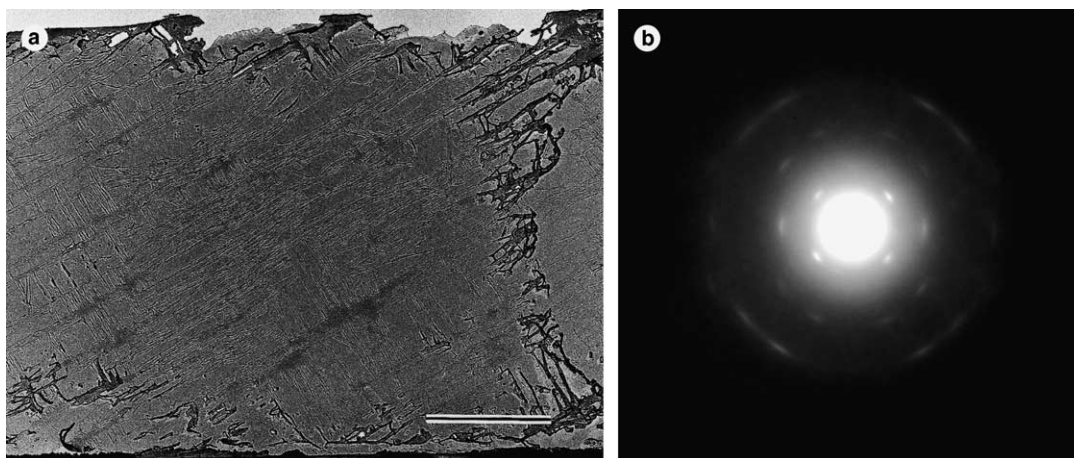


Fig. 1. Transmission electron micrograph of an iPP film grown on 2BrBzAc crystal, Pt/C shadowing. (a) Bright field image. Note the quadrite morphology, the quadrite axis is tilted relative to edges of the crystal of 2-bromobenzoic acid. Scale bar: 2 μm . (b) Electron diffraction pattern indicating that the ac plane is the contact plane.

3.2.2. Syndiotactic polypropylene

The syndiotactic form of this same polypropylene (sPP) provides another appealing case of topographic adaptation [24]. sPP exhibits a complex crystalline polymorphism based on both different chain conformations and different packings [25]. We will consider here the orthorhombic form I and form II based on the same stable chain conformation t_2g_2 . The stable chiral form I has a four chains unit cell ($a = 1.43$ nm, $b = 1.12$ nm, $c = 0.74$ nm) with a perfect alternation of left and right-handed helices along a and b . The less stable form II has a two chains unit cell ($a = 1.45$ nm, $b = 0.56$ nm, $c = 0.74$ nm) with isochiral helices. Due to the different space group symmetries, the chains in form II are located at the same height along c axis, whereas the chains in form I are shifted along c by $c/2$. Form II was found so far under specific conditions in stretched fibres or at elevated pressures; it results from a solid state transformation of extended chains to the stable t_2g_2 helical chains. In our experiments sPP was crystallised on 2-Quin at different temperatures (the experimental conditions are summarised in Table 1). 2-Quin crystallises in an orthorhombic cell ($a = 0.435$ nm, $b = 0.734$ nm, $c = 2.132$ nm). Once more, as a result of hydrogen bonding between the alcohol moiety and an hydrogen of the

opposite benzene ring, the 2-Quin crystal is built on dimers aligned along $(10\bar{4})$ and (104) and the benzene rings emerge in the (001) cleavage plane forming a 2-D rectangular grating arranged in rows 0.435 nm apart along a and 0.734 nm apart along b (Fig. 2(c) I). Two different behaviours are observed when sPP is isothermally crystallised on 2-Quin. At high temperature there is no preferential orientation when at low temperatures, below 110 $^{\circ}\text{C}$, the lamellae of sPP are perfectly oriented on single crystalline 2-Quin (Fig. 2(a)). sPP is crystallised in form II, the contact plane is $(110)_{\text{sPP}}$ with $b_{2\text{-Quin}}/c_{\text{sPP}}$. The prevalence of form II of sPP does not correspond to the best minimum dimensional matching but is understandable when looking at the topography of the contact planes (Fig. 2(c)). In the two sPP forms the (110) planes have some similarities, they are lined up by Me rows 0.74 nm apart along the chain (same helix), 0.916 nm apart and 0.778 nm apart in the direction orthogonal to the chain for forms I and II, respectively. Thus, the matching along the chain direction is not discriminative, the mismatch in the direction parallel to $a_{2\text{-Quin}}$ ($2a = 0.87$ nm) and the inter-chain distances are +5.3% and -10.6% for forms I and II, respectively. Hence, on the basis of pure dimensional matching the former stable form I should be favoured. *The decisive influence of*

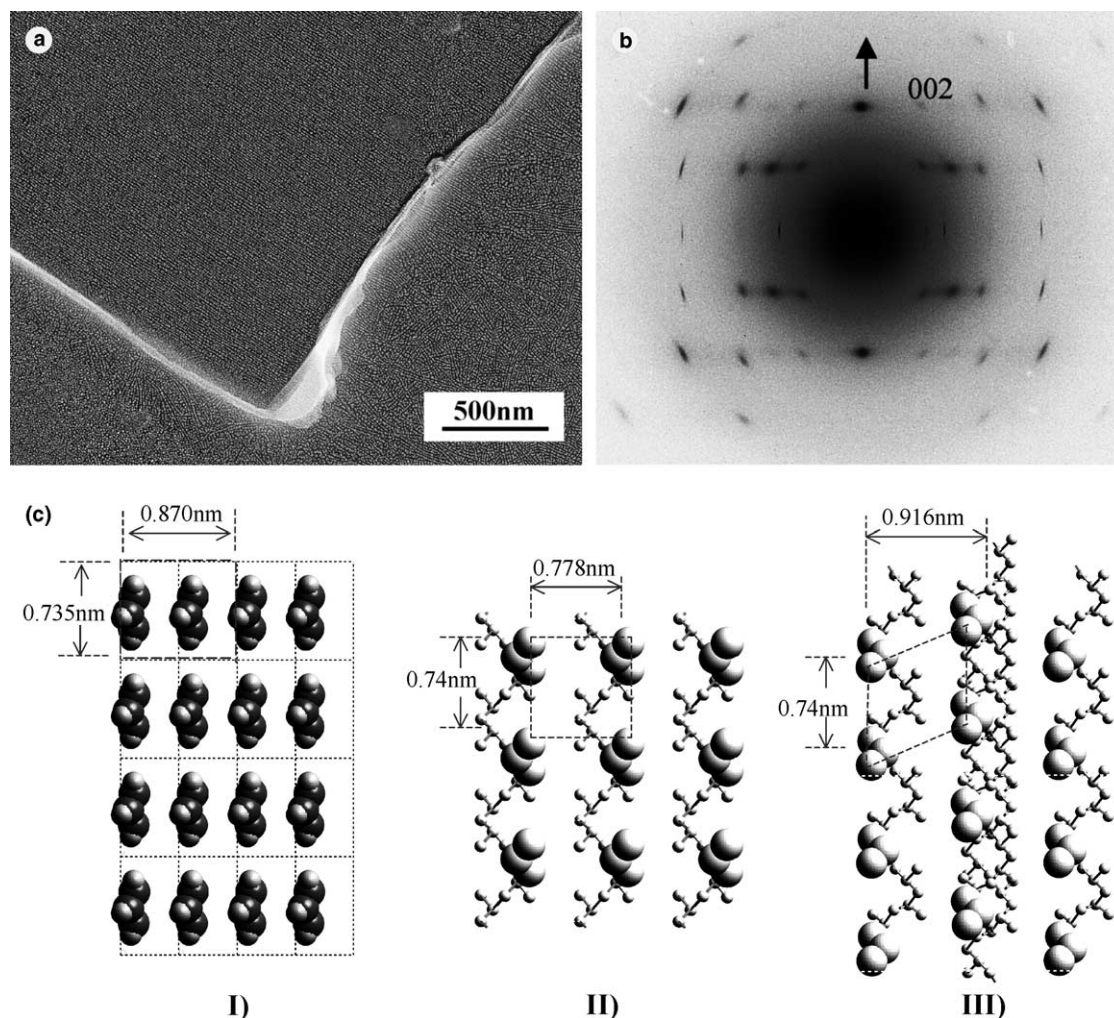


Fig. 2. Transmission electron micrograph of an sPP film grown on 2-Quin, gold decorated and after dissolution of the on 2-Quin substrate. (a) Bright field image, the gold decoration reveals the orientation of the lamellae. The lamellae are well aligned on the upper left part corresponding to a corner of a 2-Quin single crystal, chain axis at one o'clock/normal to the lamellae orientation. (b) Electron diffraction pattern of the sPP film chain axis vertical. (c) Molecular models of the organisation of the prominent groups in the cleavage plane of 2-Quin (cI) and in the (110) planes of the sPP form II (cII) and sPP form I (cIII). Note the rectangular symmetry of the surface topography for both 2-Quin and sPP form II which explains the prevalence of form II of sPP in the epitaxial growth on 2-Quin. (Fig. 2 is part of the figures of Ref. [24].)

topography is proved by two experimental observations: (i) at low temperatures the metastable form with its 2-D rectangular grating is favoured while the stable form with its 2-D oblique grating is rejected (Fig. 2(c) III); (ii) at high temperatures, for which the thermal stability forces the crystallisation of sPP in the stable form, the orientation of sPP on 2-Quin is not observed.

3.3. Molecular epitaxy versus dimensional epitaxy

3.3.1. Molecular epitaxy of a symmetric diacetylene

A most important exception to the geometrical rule has been observed on pDA. pDA are valuable for optical devices because of their large non-resonant third order susceptibilities, their rapid response time and their high damage threshold to

intense light flux [26]. pDCH, the pDA symmetrically substituted with carbazol, is also resistant to heat and oxidation. However, the crystals of the monomer (DCH) and the polymer (pDCH) are long and extremely thin needles. This morphology is detrimental for use in non-linear optic (NLO) and integrated devices, which require a uniform film with a controllable thickness. Epipolymerisation (EP) [the orientation of a monomer onto a substrate followed by polymerisation] is one way to overcome this drawback. EP is a valuable tool for controlling molecular engineering of polymeric, fold-free, single crystal-like films with few defects.

DCH films grown by rapid sublimation on KBr kept at room temperature and then converted to pDCH by heating show a crosshatched bi-oriented texture. This texture derives from a 1-D epitaxial growth of DCH on the cubic substrate KBr with a $(20\bar{3})_{\text{pDCH}}$ contact plane [27]. $(20\bar{3})_{\text{pDCH}}$ comes from the original $(10\bar{2})_{\text{DCH}}$ natural growth face of the monomer. Bi-orientation attained on cubic crystals is not fully adequate for optical devices. Our approach has been to choose as substrate an organic crystal with a lower degree of symmetry. DCH was vaporised on the easy cleavage plane of KAP crystals (the experimental conditions are summarised in Table 2) [28]. EM bright field indicate a fine polycrystalline texture made of needles and rectangular platelets oriented in a unique direction again with $(20\bar{3})_{\text{pDCH}}$ as contact plane (Fig. 3(a),(b)). Taking into account the

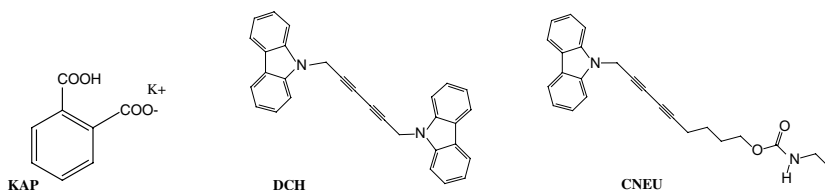
modification involved during phase transformation of DCH to pDCH, the relations derived from the composite diffraction pattern for the initial orientation of DCH monomer on KAP are $(\bar{1}02)_{\text{DCH}}//(\bar{0}10)_{\text{KAP}}$ and $b_{\text{DCH}}//c_{\text{KAP}}$. These relations correspond to mismatches well above the accepted dimensional limits [30% along c_{KAP} and 38% along a_{KAP}].

This orientation of DCH on KAP can be reproduced. In addition, increasing the temperature of the substrate and decreasing the vaporisation rates improve the quality of the films. For a 32 nm thick film grown at 0.3 nm/min on KAP kept at 100 °C the diffraction spots are perfect points. So, we believe that the orientation of DCH on KAP is driven by the molecular insertion of the carbazolyl group between the KAP phenyl rings, the more so that the angle between the phenyl planes and the contact planes are not very different 41.8° and 32.8° for DCH and KAP, respectively. The spacing between the two carbazols of DCH is very close to that of twice the distance between the parallel rows of aromatic rings along a_{KAP} . The diacetylenic rigid core of DCH is thinner than the carbazolyl substituent; therefore, there is no steric hindrance with the other row of phenyl groups intercalated on the cleavage plane of KAP (Fig. 4(a)). The position of the first DCH molecule is stabilised through π - π interactions between the phenyl group of deposit and substrate. We thus call this mechanism *molecular epitaxy*.

Table 2

Model compounds, experimental conditions and growth mode for diacetylene thin films deposited on KAP

Substrate	Deposit	Deposition method	Growth mode
KAP	DCH	Epipolymerisation ^a	Volmer–Weber
KAP	CNEU	Epipolymerisation ^a	Volmer–Weber



^a Epipolymerisation: a thin film of monomer (DCH or CNEU) is evaporated under vacuum at a controlled rate on a freshly cleaved single crystal of KAP. The monomer is converted into a polymer by thermal or UV topotactic polymerisation for DCH and CNEU, respectively. The optimal condition for DCH conversion is 150 °C for 24 h under inert atmosphere. CNEU is UV irradiated at 254 nm after a thermal treatment at 100 °C.

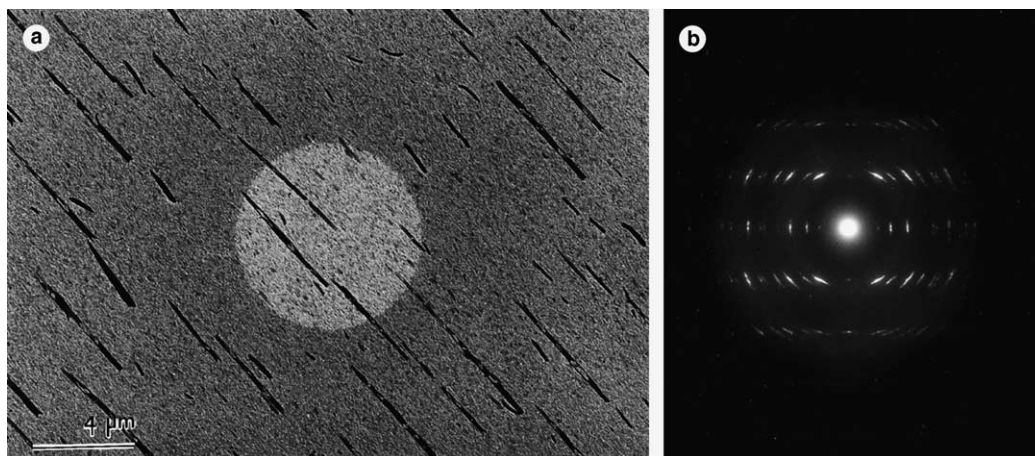


Fig. 3. Transmission electron micrograph of a 30 nm DCH film grown on KAP at room temperature after dissolution of KAP, the sample is Pt/C shadowed. (a) Bright field image, the b axis of pDCH (= polymer axis) is vertical. (b) Electron diffraction in correct relative orientation showing different layers corresponding to 0.49 nm spacing along b_{pDCH} .

3.3.2. Epitaxy of a non-symmetric diacetylene

To ascertain the molecular interaction of DCH with KAP, we have worked with an asymmetrical DA with only one carbazolyl group, the pCNEU. The second substituent consists of a urethane group ended by an alkyl moiety [29]. When CNEU is deposited on KAP at room temperature (the experimental conditions are summarised in Table 2), the crystalline needles are elongated along three directions: parallel to c_{KAP} , to $[101]_{\text{KAP}}$ and to $[10\bar{1}]_{\text{KAP}}$ (Fig. 4(c)). The two latter are a minority; since they do not appear in the EM diffraction pattern, we can estimate that they represent less than 5% of the film. Once more, increasing the substrate temperature and reducing the evaporation rate improves the quality of the film in terms of orientation and intrinsic defects. In particular, the two minor orientations are no longer observed for the optimal conditions. The main orientation, which is unique at high temperature corresponds to that of DCH/KAP with $(b_{\text{CNEU}}//c_{\text{KAP}})$ (Fig. 4(b)).

Thus, a single carbazolyl group is enough for the specific molecular interaction between the DA monomer and the rows of benzene of the phthalate surface to occur. Of course, it induces a weaker epitaxy than in the presence of two groups. However, the other substituent, the alkyl urethane, is also able to interact with KAP, in a way that is

similar to the geometrical epitaxy of PE on KAP [30]. It gives rise to two orientations at 67° to one another as demonstrated for the PE chains lying down in the valley along $\langle 101 \rangle$ directions of KAP (Fig. 4(c)). The sophisticated epitaxy of CNEU on KAP that changes with the temperature of the substrate is the result of the competition between the π - π interactions of the molecular epitaxy and the geometrical interactions. We thus confirm the previous results on DCH deposited on KAP and demonstrate that several mechanisms of interactions may regulate the epitaxial overgrowth of molecular crystals.

3.4. Characterisation of thin films for opto-electronics

In view of future applications in electronics and photonics, it is crucial to control the quality of oriented thin films of emerging molecular materials. The macroscopic properties of the active layers of the devices are strongly dependant on the quality of the films via the orientation of the molecules and via the density of defects in the crystals. We have examined with EM the films of three model compounds: PSP, 4T and DH4T deposited on various substrates. The type of interactions leading to epitaxial orientation, the mode of growth and the quality of the crystallites are examined with the

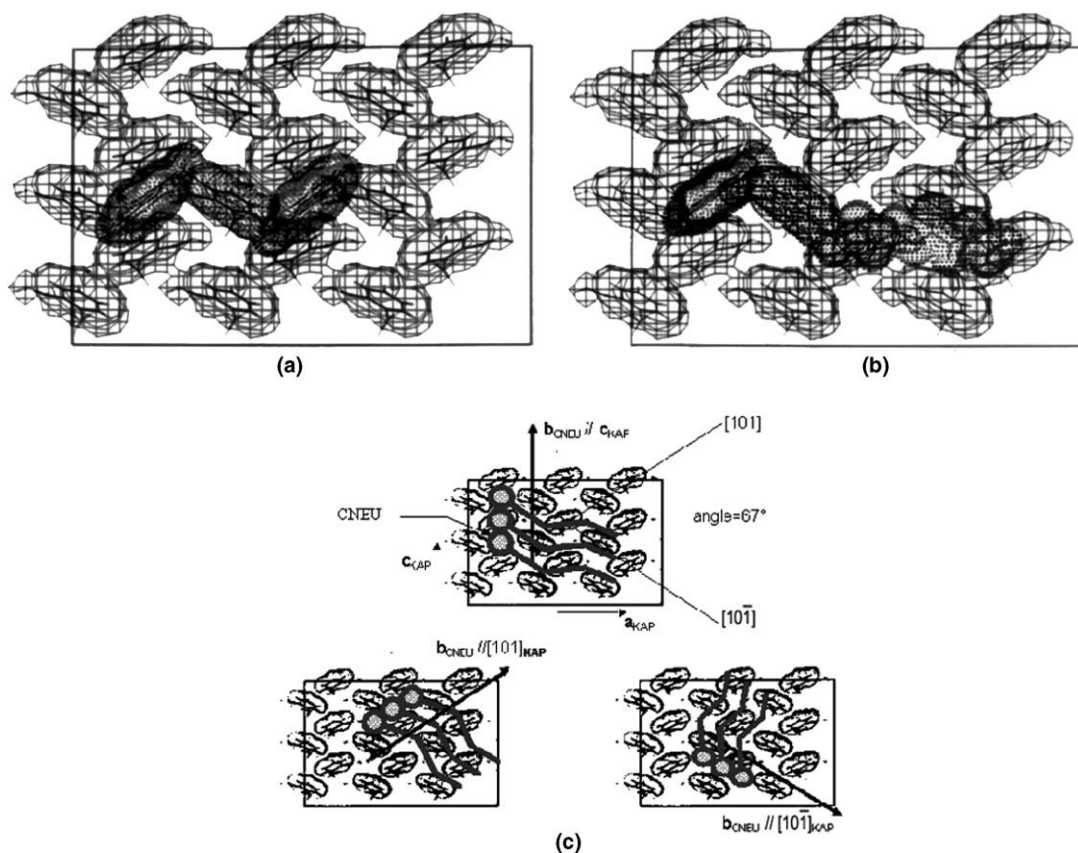


Fig. 4. Molecular model showing the insertion of a DCH monomer and a CNEU on the rows of KAP, c_{KAP} is vertical. (a) DCH on KAP. (b) CNEU on KAP for the unique orientation observed at high temperature stabilised by π - π interactions. (c) Three possible orientations at room temperature indicating competition between molecular and geometrical interactions. (This figure is a redrawing of Fig. 9 from Ref. [29].)

combined use of bright field, diffraction and dark field modes.

3.4.1. Para-sexiphenyl

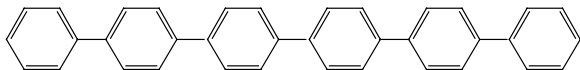
PSP, the six rings oligomer of *para*-phenylene, is very attractive; its photoluminescence in the blue range combined with reasonable charge carrier and good mobility characteristics makes PSP an appropriate material for opto-electronic devices [31].

Thin films of PSP were prepared by MBE on GaAs (001) or GaAs (111) at temperatures ranging from 90 to 170 °C (the experimental conditions are summarised in Table 3) [32,33]. PSP crystallises in its β monoclinic form, space group $P2_1/c$ with ($a = 2.62$ nm, $b = 0.557$ nm, $c = 0.809$

nm and $\beta = 98.2^\circ$). In the bulk, the long PSP molecules adopt the typical herringbone structure, the long axes are parallel to each other and adjacent molecular planes are tilted by 66° . The PSP polycrystalline films grown on both GaAs (001) and GaAs (111) are oriented and they grow with a 3D Volmer–Weber mode. Growth on GaAs (001) has been analysed in detail. The needle-like islands, elongated along b_{PSP} , are oriented along $\langle 100 \rangle_{\text{GaAs}}$ in two orthogonal directions. The corresponding spacing of the atoms on GaAs ($a_{\text{GaAs}} = 0.565$ nm) fits the b axis of PSP ($b_{\text{PSP}} = 0.557$ nm) within 1.5%, well under the accepted limit of 15%. This 1-D epitaxy gives rise to two different contact planes identified by electron diffraction as $(1001)_{\text{PSP}}$ and $(110\bar{2})_{\text{PSP}}$. As a result

Table 3
Substrates, experimental conditions and growth mode for the para-sexiphenyl ordered films

Substrate	Deposit	Deposition method	Growth mode
GaAs (001)	PSP	MBE ^a	“Volmer–Weber”-like ^b
GaAs (111)	PSP	MBE ^a	“Volmer–Weber”-like ^b
Muscovite (001)	PSP	HWE ^c	“Volmer–Weber”-like ^b



PSP:

^a The GaAs surface is thermally deoxidised at 650 °C prior to the molecular beam epitaxy process. During the deposition experiment, the vacuum is 10^{−6} mbar, the PSP source is at 230 °C and the substrate at 150 °C.

^b “Volmer–Weber”-like growth mode refers to the fact that no monomolecular continuous layer is observed on the grown films. The Frank–Van der Merve and Stranski–Krastranov growth modes can, therefore, be ruled out.

^c The muscovite single crystals are freshly cleaved prior to the evaporation of PSP by hot wall epitaxy [16]. During the deposition experiment, the vacuum is 6 × 10^{−6} mbar, the PSP source is at 240 °C and the substrate at 90 °C.

of this crystal growth, the molecular axes of PSP molecules are oriented at 90° and 40° to the substrate surface, respectively. The observed contact planes are not natural growth planes; they intersect the PSP molecules. For the observed (1001)_{PSP} contact plane, the results have been explained assuming a (100)_{PSP} contact plane associated with a micro twinning with a (30 $\bar{2}$) twin plane. For the observed (1102)_{PSP} contact plane, the results have been explained by assuming a rotation twin relative to the previous described orientation with (010)_{PSP} as twinning plane and a rotation twin parallel to *a*. This rotation twin implies a favourable strong overlapping of the phenyl rings in the contact plane of the twin. Rotation twins are well known in the field of polymers, and the overlapping of phenyl rings may again stabilise the observed orientation via π – π interactions.

The oriented growth of PSP films on freshly cleaved muscovite (001), a polytype of mica, is very complex (the experimental conditions are summarised in Table 3) [34–36]. To be properly described, the films have to be examined using different investigations techniques and at different growth stages. The films were investigated by X-ray diffraction, atomic force microscopy (AFM) and EM. The 20 nm thick PSP films are made of perfectly aligned PSP nano-needles on a given mica terrace; but for the different terraces only two orientations at 120° out of the three expected ones (mica has a hexagonal symmetry) were observed. AFM, X-ray and EM diffraction reveal for these

thick films on a given terrace, a well ordered highly crystalline film. Three different types of contact planes and orientations of the needles denoted (a), (b) and (c) with the following epitaxial relationships were found (11 $\bar{1}$)_{PSP} || (001)_{mica}; [1 $\bar{2}$ $\bar{1}$]_{PSP} || [−340]_{mica} (a) (−1 $\bar{1}$ 1)_{PSP} || (001)_{mica}; [−110]_{PSP} || [−340]_{mica} (b) (11 $\bar{2}$)_{PSP} || (001)_{mica}; [−20 $\bar{1}$]_{PSP} || [−310]_{mica} (c). (Note that in this part of the work the PSP unit cell has been taken as follows: space group *P*2₁/*a* with *a* = 0.809 nm, *b* = 0.557 nm, *c* = 2.62 nm and β = 98.2°.) Though the overgrowth of PSP on mica is clearly oriented, the 2-D lattices of PSP and mica in the contact planes are incommensurate. In fact, the three observed orientations correspond to nearly equivalent tilt of the long axis of PSP molecules: they are tilted by 5° with respect to the mica surface. This corroborates previous optical results [37].

Bright field imaging illustrates clearly the situation (Fig. 5(a)) it shows needles oriented in a quite unique direction, the needles are 800 nm wide and 100 μ m long on average for a 20 nm thick film. But the diffraction taken from a group of needles does not indicate a unique orientation with an ideal “single-crystal like” texture (Fig. 5(a)). Typical diffraction patterns of these PSP films have two specific features. The meridional spots are found in three neighbouring directions corresponding to the orientations denoted above (a), (b) and (c). If the direction of orientation (a) is considered as the reference one, the two other meridians are tilted by

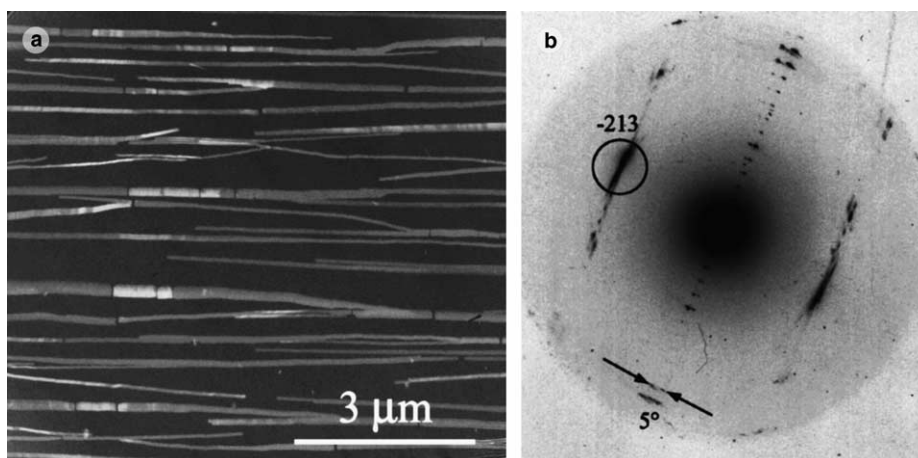


Fig. 5. Transmission electron micrograph of a 20 nm thick PSP film grown on mica (001). (a) Bright field image. (b) Electron diffraction from a zone where orientations *a* and *b* coexist.

5° and 16° for (b) and (c), respectively. Thus intense diffraction spots, such as $\bar{2}13$, are smeared out due to overlapping of the strong diffraction spots. As an example, Fig. 5(b) shows a case where *a* and *b* orientations coexist.

Fundamental questions come up from these complex results. Do the different orientations coexist in a given needle? Do these orientations exist at the very first stage of growth or are they developed during the bulk growth of the “thicker films”? DFI of two different growth needles of a 20 nm thick film are shown in (Fig. 6(a)). These DFI are taken using the smeared $\bar{2}13$ diffraction spots; they indicate that the needles are not single crystalline. The borders between the domains are either parallel or orthogonal to the needles axis and can be explained in terms of non-perfect twinning between (a) and (b) and (b) and (c), respectively. An extensive investigation of the needles by both SAED and DFI reveals that two or even sometimes all three orientations are present in a single needle. At the very first growth stages, the characteristic morphology of a 1 nm thick film shows the occurrence of rectangular needles 60 nm long and 30 nm wide (Fig. 6(b)). A systematic investigation of these rectangular needles by SAED, not illustrated here, shows the co-existence of the different orientations in a given needle. Thus, the different orientations exist already at the very beginning of the film growth.

The dispersion of the orientation of the observed contact planes for this *quasiepitaxial* growth of PSP on mica has to be understood in terms of a competition between strong interactions of PSP molecules in the bulk and weaker Coulombian interactions of PSP molecules with mica [36].

3.4.2. Quater-thiophenes

Oligothiophenes show extremely promising characteristics for applications in electronics and photonics [38]. The role of crystal size in these thiophene films was investigated for OFET's based on octathiophene and sexithiophene as active layers [39]. Therefore, we have examined the orientation of the crystals, the other important feature for active layers, by laying down 4T and α,ω -DH4T on silica or KAP (the experimental conditions are summarised in Table 4) [40,41]. As already mentioned, KAP is a valuable organic orienting substrate; large single crystals of KAP are commercially available, the interface in the easy cleavage plane (010)_{KAP} is lined with non-polar aromatic rings and is molecularly flat [28]. Nevertheless, the morphology of 4T films grown on KAP happens to be quite complex. The polycrystalline films are made of islands and platelets as shown by both AFM and EM bright field images. SAED indicates that the 4T polymorph deposited is the low temperature one (α -4T) reported by Siegrist et al. ($a = 0.609$ nm, $b = 0.786$

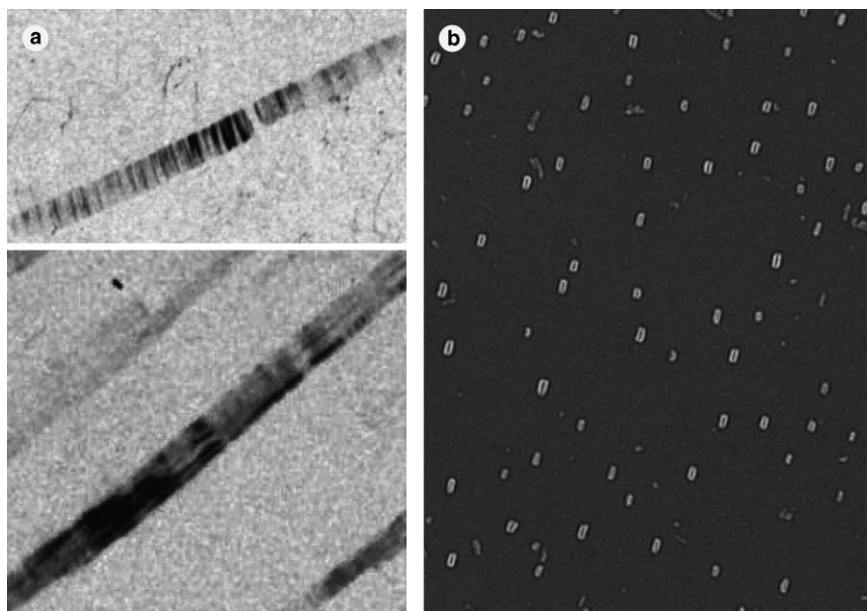
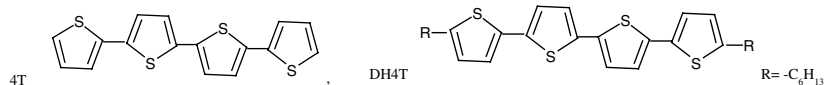


Fig. 6. Transmission electron micrographs taken on PSP films grown on mica (001). (a) Dark field images of two different needles taken from (213) reflexions for a 20 nm thick PSP film. (b) Rectangular precursor of the PSP needles for a thin film of PSP observed in defocused selected area diffraction (film nominal thickness 1 nm) rectangles size 60 nm × 30 nm (reproduced from Ref. [35] by permission).

Table 4
Experimental conditions and growth mode for the oligo-thiophenes thin films deposited on KAP

Substrate	Deposit	Deposition method	Growth mode
KAP (010)	4T	MBE ^a	“Volmer–Weber”-like ^b
KAP (010)	DH4T	MBE ^a	“Volmer–Weber”-like ^b



^a The thiophenes films are grown by OMBD. The Knudsen effusion cells are heated at 165 °C for 4T (190 °C for DH4T); the substrate is at 25 °C, the pressure is kept at 8×10^{-10} Pa for 4T (8×10^{-8} Pa for DH4T).

^b “Volmer–Weber”-like growth mode refers to the islands. However, two types of morphology are observed at the first stage of growth when the substrate is KAP. Therefore, it would not be appropriate to use the term Volmer–Weber growth without reservation. More work is needed to clearly define epitaxial growth process of molecular crystals thin films.

nm, $c = 3.052$ nm $\beta = 91.2^\circ$ monoclinic $P2_1/c$) with two different contact planes indexed (001)_{4T} and (100)_{4T}. The molecular axes of 4T are tilted at 61° and 30° with respect to (010)_{KAP}. The projection of the molecular axis, determined from polarised optical spectroscopy, is essentially parallel to c_{KAP} . Thus KAP promotes the quasi-epitaxial growth of 4T films, but the interaction

between 4T and KAP are weak and cannot impose a unique orientation to the 4T molecules.

Alkyl-substituted organics are more easily processable than the purely conjugated rigid systems. Therefore it is particularly interesting to orient alkyl-substituted active molecules on different substrates. α,ω -DH4T films were grown on silica and KAP. These polycrystalline α,ω -DH4T films

have morphologies very similar to that observed with 4T. On silica, 4T-islands are observed, the SAED shows that these islands have a unique contact plane of the deposit, the diffraction pattern allows to define a 2-D rectangular lattice of 0.606×0.816 nm, as already observed for silica at 100 °C [42]. The orientation of this plane at the interface is completely random. On KAP, like for 4T, islands and needles co-exist. As on silica, a 2-D rectangular SAED pattern is observed matching the same distances, but in this case, the orientation of the pattern is unique. Thus the polycrystalline film has a “single-crystal like” organisation which points to an epitaxial orientation of α,ω -DH4T on KAP. The exact character of the epitaxial relation is difficult to assess due to the lack of crystalline structure determined by X-ray diffraction for α,ω -DH4T, thus a detailed analysis of the epitaxial relation is postponed until this crystalline structure is determined. However, a modelling of the structure based on the known parameters and an analogy with the structure of α,ω -dihexylsexithiophene already suggest the possibility of both a geometrical and a topological epitaxy that is consistent with a residual adsorption observed in optical spectroscopy.

4. Conclusion

Recently, organic materials and polymers have attracted much interest as functional layers in the field of light-emitting devices, field effect transistors, sensors, solar cells, etc. Epitaxial growth is a most convenient method allowing to build up large and highly ordered thin films of these materials used as active layers in the different devices. The efficiency of the devices depends strongly on various features of these films: for instance, the nature of the polymorph, the degree of ordering, the grain sizes, the type of defects, etc. This implies that the structural characteristics of the films have to be studied in detail, including the organisation of the films that also requires the knowledge of the epitaxial relations between the deposit and the substrate.

The above reported description of a number of epitaxially grown films shows that EM is a most

appropriate technique to characterise, ex-situ, both the orientation and the morphology of these organic thin films. EM can investigate both the real and reciprocal spaces; it provides detailed informations at a scale of a few nm. While bright field imaging looks at the overall morphology (shape and size of different crystallites), dark field imaging explores their defects. EM diffraction is well adapted to analyse the epitaxial relations through the determination of the contact planes and of the relative orientations of the two components. HREM is able to directly visualise rows of atoms throughout the whole sample.

Recent developments both in methodology and in techniques extend the traditional practicable field of EM. Crystalline structures of polymers have been determined directly from electron diffraction data collected on single crystals [43]; *thus the determination of metastable polymorphs sometimes induced by epitaxial growth and/or OMBD can be envisaged*. Further extending EM potentiality, the *diffraction of a monomolecular thick film of sexithiophene (6T)* has been recently recorded with a CCD camera [44].

The described cases demonstrate the difficulty to rationalise and fully predict the overgrowth of a crystalline deposit on a crystalline substrate. However, some necessary characteristics can be deduced from these four examples. They will be specified further on. The very first studies on epitaxial crystallisation emphasised the major role of geometrical (dimensional) matching. However, the above examples show that more subtle rules are at play. The orientations of polypropylenes and polydiacetylenes demonstrate that exceptions to the common matching rule do exist. For polypropylenes, two members of the polyolefin group for which no strong interactions are at play, the overgrowth is controlled by a *topographic adaptation* of the rows of prominent groups of the deposit inserted between the rows of prominent groups of the substrate. For the symmetric polydiacetylene, the overgrowth is controlled by *molecular interactions* between the aromatic groups lining up the contact planes of both the deposit and the substrate. For the non-symmetric polydiacetylene, the overgrowth is controlled by the competition between molecular interactions and geometrical adaptation; as a result

of this competition, the degree of order in the film depends strongly on the temperature of the KAP substrate and on the evaporation rate. Finally, the oriented overgrowth of two foremost molecular crystals, sexyphenyl and thiophenes, demonstrate that diverse interactions control the growth of molecular films on various substrates. The orientation of PSP on GaAs (001) based on a 1-D fitting between b_{PSP} and a_{GaAs} results in a complex organisation in the films. It involves the growth habits of the bulk crystal via different twins, whereas the orientation of PSP on mica is suspected to be influenced by Coulombian interactions.

To sum up, some general features have to be taken into account to choose the most favourable substrate for growing ordered thin films. The prominent groups which are lining up the corresponding contact planes have to be arranged in similar arrays: same 2-D symmetry, same distances between rows. The lower the symmetry of the contact plane of the substrate, the better it prevents multiple orientations. It implies that organic crystals based on aromatic derivatives must be preferred to inorganic crystals with cubic symmetry. On top of these topological prerequisite relationships, the nature and strength of the interactions between the two crystals influence to a great extent, the deposition of the molecules in the very first layers for polar compounds.

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