Polymer and Organic Molecules Ordered via Epitaxy: Geometrical and Molecular Interactions

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SUMMARY: Control of structural order at the molecular level for both conventional linear polymers and conjugated polymers with valuable opto-electronic properties has major consequence on the macroscopic properties of these polymers. Though the traditional means of orientation of polymer was mechanical deformation, presently extensive works are concerned with a more controlled way of orientation: epitaxial crystallisation. Most of the first documented examples of epitaxial growth of conventional polymers on single crystals followed the well-established geometrical rules of best matching. However, recent examples show off more subtle rules of selection. Analogous cases, following or breaking the matching rules, have been observed for diacetylenes ordered via epipolymerisation on single crystals. Hereafter, representative examples of the structural matching rules are depicted first, and then recent examples, which depart from the simple geometrical fitting, are described. The analysis of the former leads to define the subtle matching rules applying for polymers linked to their conformational adaptability. The analysis of the latter gives the opportunity to discuss the relative influence of geometrical and molecular interactions between the deposit and the substrate.

Introduction

Epitaxial crystallisation of polymers is used nowadays in materials science. For instance, addition of nucleating agents which act via epitaxy(1) in bulk semi-crystalline polymers reduces the spherulite size, thus improves the optical and mechanical properties of polymer films(2). The transcrystalline layers induced by epitaxial nucleation between fillers and polymer matrix reinforce polymer composites(3). Epitaxial orientation is also a basic tool to tailor ordered thin films of specific polymers. The single–crystal like structure, more ordered than the fibre-texture achieved by common mechanical processes, highlights at the

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macroscopic scale the intrinsic molecular anisotropy of the chain characteristics. For instance, thin films of poly(sulfur nitride)[4)], a polymeric metal, or of polydiacetylenes[5)] with large non-resonant third order susceptibilities (χ^3), have been successfully epipolymerised on alkali halides (epipolymerisation (EP) is a short used for epitaxial crystallisation plus polymerisation).

Epitaxy, first introduced by Royer[6)], from the Greek epi, which means "on" and taxos which means "organised deposition" defines the oriented overgrowth of a crystal upon a foreign crystal. Traditionally, epitaxy is associated with dimensional matching rules between the contact planes of the interacting species; these rules were established by Royer himself for minerals, which crystallise essentially in cubic systems. But linear polymers crystallise with a more sophisticated organisation; the chain-folded lamellae growth gives rise to thin single crystals a few nm thick or to spherulites[7,8)]. Will these strange crystals interact in a classical way with the deposit? Willems[9)] and Fisher[10)] gave a positive answer to this question. They observed the oriented deposition of polyethylene, the simplest polyolefin, on alkali halides: the macromolecular chains lay down parallel to the substrate contact plane and the lamellae are edge on. Another singularity of polymer crystals is their propensity in developing various crystalline polymorphs[11,12)]; the same polymer can adopt different chain conformations (planar zigzag, and/or diverse helical conformations); it can also adopt different packing of the chains. How does this «flexible» crystallisation influence the selection rules? More specifically what are the prominent features, which govern the selection of a given contact plane rather than another one?

The present paper examines the relative orientation(s) of a polymer (or a monomer, later polymerised via topotactic polymerisation: epipolymerisation (EP)), on a crystalline substrate (alkali halide or organic molecules, more specifically aromatic ones). The orientation is looked at by diverse microscopic techniques (optical, electron, and near-field microscopy). The final relative orientation of the two crystals (deposit and substrate) is described, and the analysis of orientation mechanism allows tracing back the deposit/substrate interactions at the molecular level during the deposition process where the deposit is, previous to crystalline nucleation, in its vapour or liquid state. Consequently the driving forces ruling the relative orientation may be attainable.

In what follows, we describe the preparation methods for polymer/substrate thin bilayers adapted to electron microscopy. It is followed by the description of some cases where best matching applies with subtle selection rules due to the above mentioned crystallisation habits of polymers. Finally, after some cases where geometrical fitting does not suffice to justify the epitaxial growth are considered. The comparison of both cases helps depicting certain of the rules governing epitaxial growth of polymers.

Experimental part

Techniques:

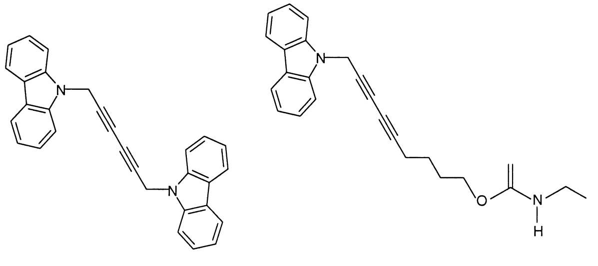
Optical, electron (EM) and atomic force (AFM) microscopy are the most appropriate techniques to investigate the mutual orientation(s) of the deposit and the substrate. Electron diffraction is especially well adapted to probe the relative orientation(s) of the two crystal cells; electron bright field images give access at the scale of crystalline lamellae. Atomic force microscopy (AFM) permits finer analysis of the molecular arrangement in the contact plane at the sub-molecular level13).

Film preparation of linear polymers:

Electron microscopy techniques for organic polymers require thin films, typically in the range of 5 to 60nm. Bilayers suitable for both electron and atomic force microscopy are grown in different ways depending on the physico-chemical characteristics of the species. When the polymer is soluble in the substrate and re-crystallises after it, both compounds are co-melted between glass cover slides and then cooled down. For infusible substrates, the substrate crystals produced separately are deposited on an already grown polymer film. The polymer is molten and re-crystallised. For both types of preparation, the substrate is then partially or totally dissolved for EM, totally dissolved for AFM.

Film preparation of polydiacetylenes (pDA):

The thickness requirement for pDA is identical to that of linear polymers but the film preparation is fundamentally different. pDA have a rigid conjugated chain grown by topotactic polymerisation14,15), thus the films are produced by epipolymerisation. A monomer film is produced by sublimation on a freshly cleaved surface of the substrate and later polymerised. Up to now, we have always been able to preserve the epitaxial orientation of the monomer during polymerisation, even in the case of phase transition during polymerisation. During deposition, the vacuum is typically of the order of 10^{-8} to 10^{-6}mbar; the deposition rate varies from 0.1nm/sec to 0.1nm/min and the substrate temperature is kept constant in the range going from room temperature to 100°C. The polymerisation proceeds differently with the nature of the lateral substituents. The symmetrically substituted 1,6-di(N-carbazolyl)2,4-hexadiyne (DCH) is heated at 150°C for one day to produce pDCH, the non-symmetrically substituted 9-(9-carbazolyl)-5,7-nonadiyn-1-ol ethylurethan (CNEU) is annealed at 100°C and then polymerised by UV irradiation at 254nm for 10 min to yield pCNEU. The schematic chemical formula of DCH and CNEU, not showing the hydrogen atoms, are drawn in structural formula 1. Note the common carbazolyl substituent on one side of the rigid core of the molecules.



DCH CNEU

1

Results and discussion

General rules:

In epitaxy, the contact faces (or planes) are often the natural growth faces; they are usually dense crystallographic planes with similar structural organisation for the deposit and the substrate. Thus the lattice matching rules compare corresponding dimensions of the substrate d_{subs} and of the deposit d_{depos}. The mismatch is defined as:

$$\textbf{Mismatch (in \%)} = 100[(d_{depos} - d_{subs})]/d_{subs}$$

A long accepted rule of thumb is that oriented overgrowth requires a mismatch smaller than ± 15%. Large mismatches cannot be accommodated over large distances and will force the formation of dislocations or defects hence the disorientation of the deposit. For polymers, the matching may be one or two-dimensional and the chain is usually laying down in the contact plane. Some exceptions[16)], not considered hereafter, have been reported of ordered crystallisation with the polymer chains orthogonal to the contact plane. It seems hard to understand a matching via the fold plane of the crystal; a growth transition between a thin transient layer with chains flat on the substrate and chains standing up may account for these observations.

Simple geometric matching:

The geometrical matching rules holding for epitaxial crystallisation just recalledare now illustrated with some examples.

1) Linear chains (the case of polyolefins):

Though works describing epitaxial crystallisation of linear polymers[17)] report examples for nearly all-common linear chains (polyolefins, polyethers, polyesters, polyamides,), the best-documented cases concern the polyolefins. Rather than trying to make an exhaustive compilation, we relate hereafter the established facts for polyolefins, the main family of polymers in terms of industrial production; the rules set up for polyolefins have been proved to apply for other linear polymers[18)]. To be complete, we have to stress that polyolefins do not bear any polar groups thus their interactions with the substrates are restricted to weak van-der-Waals interactions.

The geometrical fitting rests for polyolefins, on the shape of the chain. Epitaxy of polyethylene, a nearly featureless cylinder with a zigzag conformation, is governed by the inter chain distances. For polypropylene and other helical chains, epitaxy is governed by the 2-D organisation of the prominent substituents or by the helical path in the contact plane.

1) a. Polyethylene (PE):

Despite of a very simple molecular architecture, PE crystallises at atmospheric pressure in two different modifications -a stable orthorhombic form[19)], and a metastable monoclinic form[20)]-. Both polymorphs orient on alkali halides[9, 10, 21-23)] going from LiF to KI with cell parameters ranging from 0.401 to 0.705nm, $d_{(110)}$ ranging from 0.284 to 0.499nm. Considering the significant variations in periodicities, these early works wrongly attributed the alignment of PE chains to long-range electrostatic forces rather than to epitaxial crystallisation. However, a systematic investigation of the deposition of PE[24)] on alkali halides and organic crystals discloses six different contact planes, three for each polymorph. The selected polymorph and selected contact plane correspond to the best geometrical fitting between the substrate and the nearest inter-chain distances (four cases) or second nearest neighbours. This selection rule happens to be very critical. Not only the crystal form is chosen but there is always a unique contact plane selected even when two possible planes may fit the 15% thumb rule: on p-terphenyl (pTer) and anthracene (An) with isomorphous (001) planes, PE lays down respectively and solely in the $(110)_{PE/pTer}$ and $(100)_{PE/An}$ planes with respective mismatch –2,6% and 0% though the respective deposition of the $(100)_{PE/pTer}$ and $(110)_{PE/An}$ planes would introduce acceptable mismatches of –2,6% and –9%.

Another proof of geometrical adaptation is the deposition of the metastable phase. It exists just as a thin transient layer close to the substrate; it then develops into the orthorhombic stable form via a growth transition in the upper part of the thicker films. A similar epitaxy-induced transient layer has been reported for polyoxymethylene, for which a metastable orthorhombic phase gives rise to the stable hexagonal one by growth transition or by annealing[25)].

1) b. Polypropylene:

Three crystal phases of isotactic polypropylene (iPP) are known which rest on different modes of packing of the same 3_1 helix. The unit cell of two of them are built on successive left or right isochiral helices layers, but with different alternations, the stable α monoclinic[26)] and the γ orthorhombic[27)]; the latter is the only polymer form known with non-parallel chains in the unit cell. The third form, β a trigonal form[28)] is based on isochiral helices. Though some works will be soon published on the β phase of iPP, we will focus our attention on the epitaxial crystallisation of the stable α phase and more precisely of the αiPP in its very symmetric (010) plane[29)]. The prominent features in this plane are methyl (Me) groups ordered in a lozenge shape (cf Figure 2, ref 29) which moreover govern via homoepitaxy the original quadrite morphology of αiPP[30,31)]. The pattern of Me groups in this $(010)_{\alpha iPP}$ plane is very special. It is highly symmetric and the density of Me differs in the (010) and $(0\bar{1}0)$ plane. The density is related to the orientation of the base and top of the 3_1 helix projection in the plane. Previous AFM micrographs have demonstrated that the contact plane is the less dense one. The lozenge organisation gives rise to rows of Me with three characteristic repetitive distances: 0.425nm parallel to the short diagonal, 0.505nm parallel to the long diagonal and 0.65nm along c ≈0.65nm or along a (exactly 0.655nm). Up to this year, the epitaxial orientations described for αiPP in the (010) plane reposed uniquely on the 0.505nm geometrical matching of Me rows parallel to the long diagonal with either rows of aromatic rings for nucleating agents based on organic crystals[32)], or the 0.495nm inter-chain spacing in the bc plane of PE. Recently, a more thorough examination[29)] of diverse substrates has proved that the nucleation of the $(010)_{\alpha iPP}$ is not restricted to the Me rows 0.5nm apart but can also match the other Me rows already mentioned 0.425nm and 0.65nm, creating a potential "multiple" nucleation in this (010) face. It explains for instance epitaxy on different alkali halides, based on a KI <110> 0.498nm matching the 0.5nm long diagonal and a KCl <110> 0.44nm matching the 0.425nm short one. Various aromatic crystals yield also new epitaxies in $(010)_{\alpha iPP}$. For instance, rows of aromatic rings 0.39nm apart in the ab plane of 2Bromo-benzoic acid fits the 0.425nm spacing when rows of benzene rings of 4Fluoro-benzoic acid 0.638nm apart in the bc plane fits the 0.65nm one. The respective disregistries –8,7% and -2% satisfy the thumb rule. However, the case of 2Bromo-benzoic acid is very discriminating and deserves some more comments. b axis of 2Bromo-benzoic acid is 0.41nm, closest to

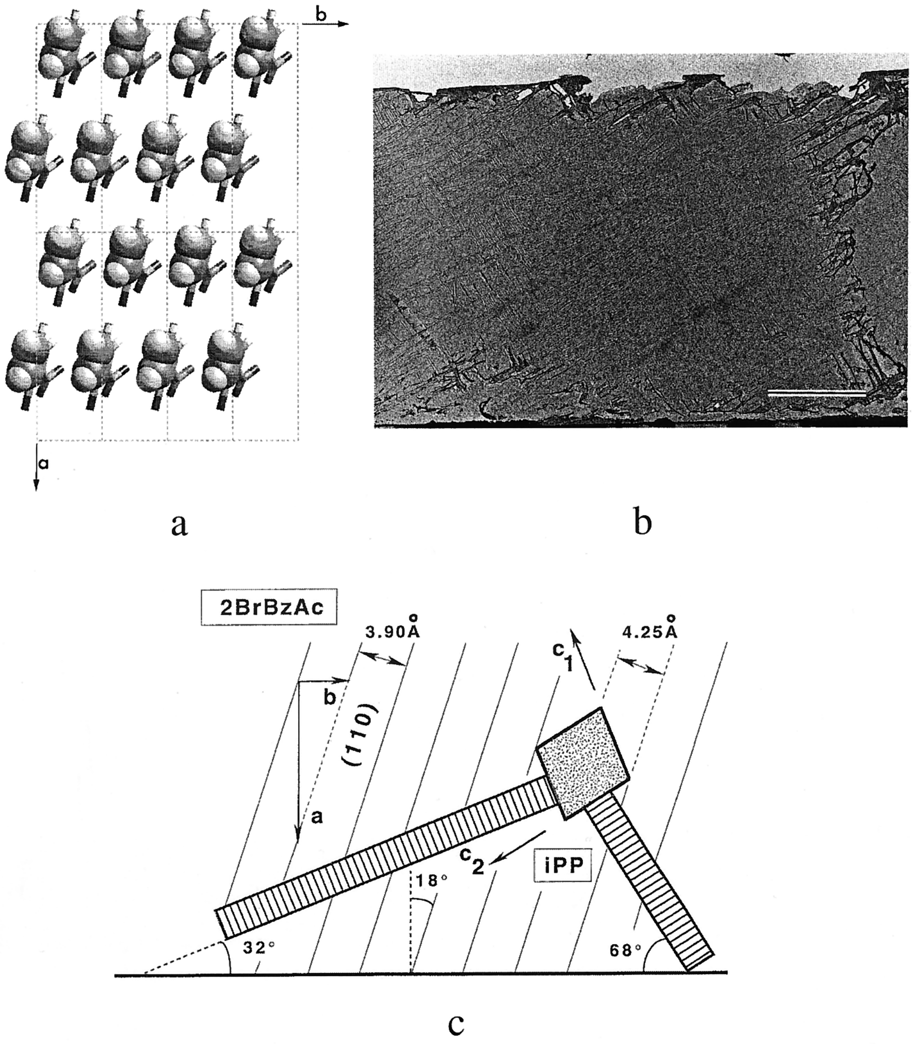
0.425nm than the inter-rows distance (0.39nm) of benzene rings between (110); the difference comes from well defined furrows of benzene. As clearly seen in Figure1, they favour the intercalation of prominent Me groups. This comment anticipates in part our conclusions, the features to be taken into account for geometrical epitaxy are the more prominent atoms (or group of atoms) lining the contact plane.

2) Epipolymerisation of 1,6-di(N-carbazolyl)2,4-hexadiyne (DCH) on alkali halides:

Epipolymerisation (EP), corresponds to the orientation of monomer onto a substrate plus a polymerisation (polymerisation and crystallisation may be simultaneous or not). EP is a valuable tool for controlling molecular engineering of polymeric, fold-free, single crystal-like films with few defects. It has been applied more or less successfully to polymers as diverse as polyacetylene33), rigid polyxylylene34), photoreactive 2-5distyrylpyrazine35) etc..., on alkali halides, aromatic crystals and oriented polymer films. Most of these examples have not scrutinised the epitaxial orientation(s) with the nature of the substrates and with the modification of the molecular architecture of the deposit. The only attempt at such a diversification has been developed on carbazolyl-substituted polydiacetylenes (pDA). pDA films are prepared by EP of their diacetylene monomers (DA). For a given DA the geometrical or molecular epitaxy depends on the nature of the substrate, hence on the potential interactions of this DA with the deposit.

pDA are useful for optical devices because of their large non-resonant third order susceptibilities, their rapid response time and their high damage threshold to intense light flux36). Poly(1,6-di(N-carbazolyl)2,4-hexadiyne) (pDCH), the pDA symmetrically substituted with carbazol, is most attractive for its important resistance to heat and oxidation, and high degree of conversion (~ 98%). However, DCH crystals 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. EP is one way to overcome this drawback and obtain films with valuable optical qualities.

DCH films have been grown by rapid sublimation on fused quartz, NaCl, KCl, KBr and KI kept at room temperature and then converted to pDCH by heating37). The experiment on fused quartz is performed to control the chemical purity of the film. UV-visible transmission optical spectroscopy shows no absorption, except that of carbazol, for the as deposed film. Heating to 150°C induces the polymerisation, thus the characteristic low energy adsorption peak of pDCH at 655nm appears; the polymerisation rate follows the classical thermal polymerisation38). On quartz and NaCl, the pDCH film is constituted of needles 1-3μm long and of shorter irregular platelets without any privileged orientation.



a b

c

Fig. 1: Epitaxial orientation of isotactic Polypropylene on 2Bromo-benzoic acid (2BrBzAc) a) Molecular model of the ac contact plane of 2BrBzAc, b) α iPP lamellae on 2BrBzAc (scale bar=2μm), c) Schematic representation of the orientation of α iPP on 2BrBzAc (a, b: cell axes of the substrate 2BrBzAc, shadowed lozenze = (010) plane of αiPP with c_1 and c_2 = chain directions of the quadrite). Parts a, b and c in proper relative orientation.

The film organisation on the other alkali halides is very different. We still observe needles and tiny rectangular platelets, however the long axis of the needles and the main side of the rectangles are well oriented along two directions at right angles. This cross hatched bi-oriented texture, illustrated in Figure 2 marks an epitaxial orientation of the deposit, the two orientations at right angle arising from the cubic symmetry of the substrate. The diffraction pattern is composed of slightly arced spots, the angular width of which is ± 4°. The main contact plane has been indexed as $(\bar{2}03)_{pDCH}$. DCH does not follow the Baughman's rule $^{\text{see in } 13)}$; it undergoes a phase transition (at around 25% conversion) during polymerisation. If we assume that during transformation of the DCH crystal into pDCH the b direction is maintained and the transformation proceeds by shearing in the (010) plane parallel to the [001] direction, $(\bar{2}03)_{pDCH}$ comes from the original natural growth face $(\bar{1}02)_{DCH}$.

On one hand, the b repetitive distance of DCH in $(\bar{1}02)_{DCH}$, (= 0.455nm) matches $d(110)_{KCL, KBr, KI}$ ones ranging from 0.444 to 0.499nm. $d(110)_{KBr}$ (=0.465nm) it fits nearly perfectly b_{DCH} and the films on KBr have the smallest angular dispersion. On the other hand, neither a_{NaCl} (0.563nm), nor $d(110)_{NaCL}$ (0.397nm) fit the b value. We have here a clear case of a 1-D geometrical epitaxy. Substrates having similar nature and same crystalline organisation, induce an oriented crystallisation only when the disregistry is lower than10%.

AFM examination of thin films of DCH and pDCH on KBr at the very first stages of growth reveals isolated three-dimensional "islands or crystals", a morphology typical of a Volmer-Weber growth.

<u>Molecular matching</u>:

This part of the presentation, though less documented, describes some cases of epitaxial orientation, which cannot be analysed with the matching rule only.

1) Epipolymerisation of 1,6-di(N-carbazolyl)2,4-hexadiyne on potassium acid phthalate:

The orientation of DCH on KBr was satisfactory on an academic point of view. Some people, misled by a restrictive interpretation of the matching rule to lattice matching, stated in 1985 that: "DA cannot be oriented by EP due to their large cell parameters" (for instance: a_{DCH}= 1.36nm, c_{DCH}= 1.76nm) $^{\text{see in } 13)}$. But the bi-orientation attained on cubic crystals is not fully adequate for optical devices. Our approach has been to choose organic crystals with a lower degree of symmetry. DCH was vaporised on the easy cleavage plane of potassium acid phthalate crystals (KAP)$^{39)}$ which may be as long as 10 cm. [Note, for this work we use the now standard unit cell for KAP, $Pca2_1$ with a= 0.9609, b=1.332, c=6.466nm]. EM bright field observations (Figure 3) indicate an excellent polycrystalline texture, fine and homogeneous.

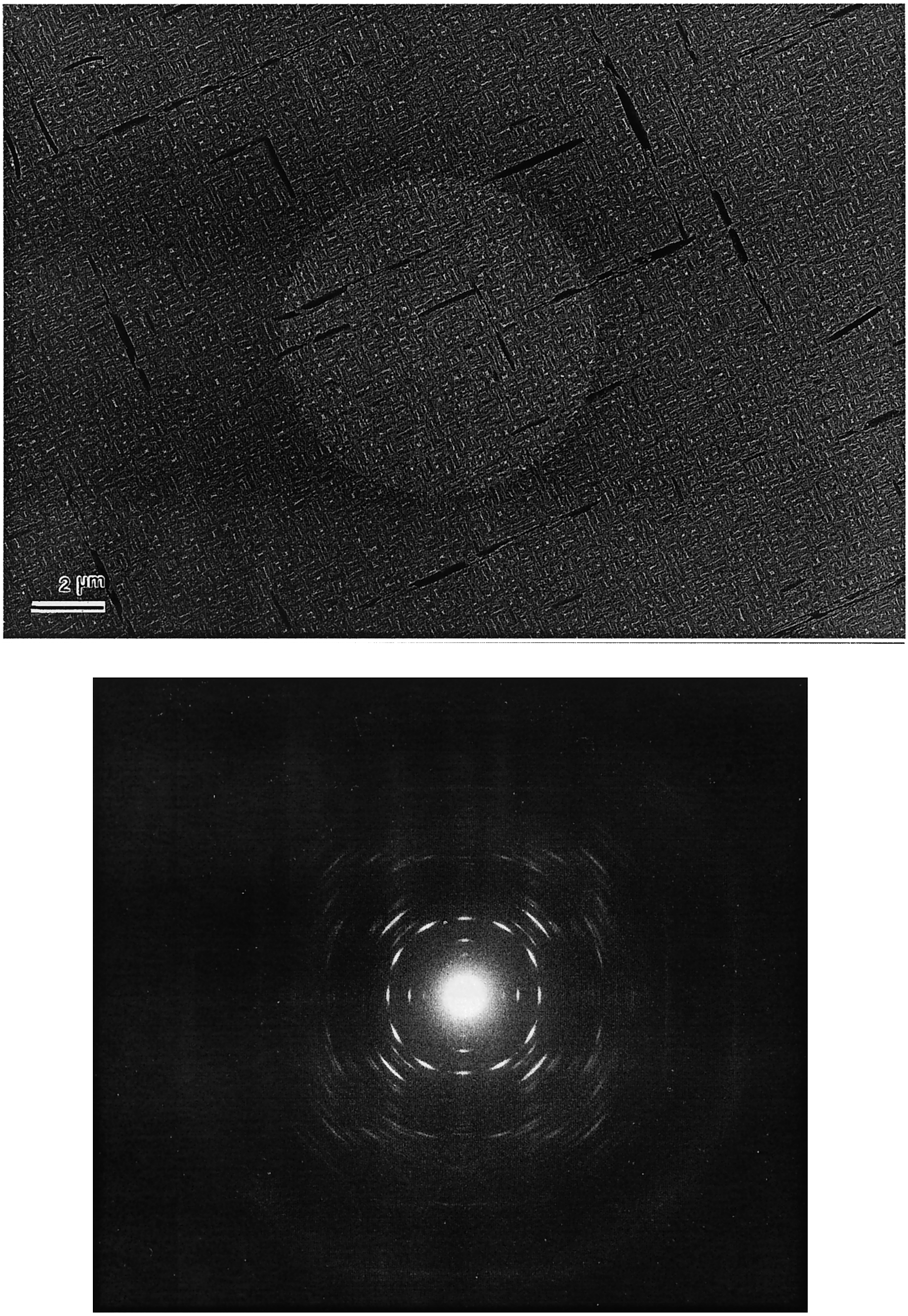


Fig. 2: Electron micrograph of a bioriented film of pDCH on KBr, KBr kept at 100°C: Upper part bright field image, lower part selected area diffraction.

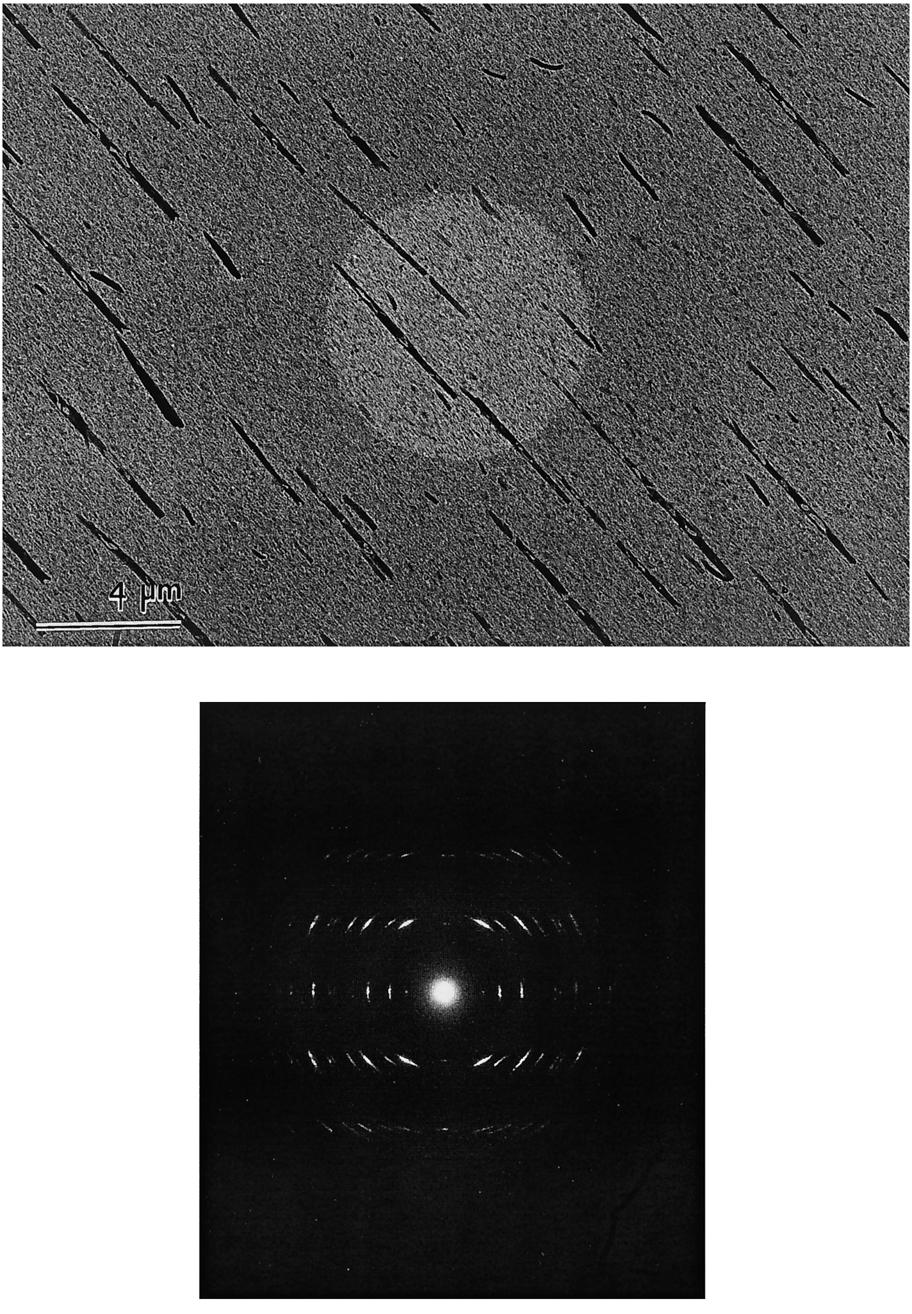


Fig. 3: Electron micrograph of an oriented film of pDCH on KAP, KAP kept at room temperature: Upper part bright field image, lower part selected area diffraction.

Compared for instance to the films just described on KBr the width of the crystallites is 1/3 to 1/5 smaller and they lie down in a unique direction. The relationships derived from the composite diffraction pattern of pDCH on KAP are the following:

contact planes $\Rightarrow (\bar{2}03)_{pDCH} // (010)_{KAP}$

directions $\Rightarrow b_{pDCH} // c_{KAP}$ and $[101]_{pDCH} // a_{KAP}$

Therefore, taking into account the modification involved during phase transformation, the initial orientation of the DCH monomer on KAP can be traced back and is as follows:

contact planes $\Rightarrow (\bar{1}02)_{DCH} // (010)_{KAP}$

directions $\Rightarrow b_{DCH} // c_{KAP}$

These well-established relationships are non-typical for epitaxy. Considering the parameters, the mismatch will be 30% along c_{KAP} and 38% along a_{KAP}. Since the orientation of DCH on KAP has been reproduced many times, at different temperatures and vaporisation rates, always with very good results, we believe that the orientation of DCH 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 41.8° and 32.8°for DCH and KAP respectively. The spacing between the two carbazols of DCH is equivalent to that of the deep wells delimited by the parallel rows of aromatic rings along a_{KAP}. The rigid core is thinner than the carbazol; therefore, there is no steric hindrance with the other row of phenyl groups intercalated on the cleavage plane of KAP. The position of the first DCH molecule is probably stabilised through π–π interactions between the phenyl group of deposit and substrate. We thus call this mechanism molecular epitaxy.

Increasing the temperature (below 100°C) of the substrate increases the quality of the orientation, and decreases the cracks in the needles related to the phase transition (Figure 4).

2) Epipolymerisation of 9-(9-carbazolyl)-5,7-nonadiyn-1-ol ethylurethan (CNEU):

Molecular epitaxy being related to local interactions, it is worth checking the influence of chemical architecture of the deposit. DCH is not soluble, thus restricted to deposition by vacuum sublimation. Therefore we have synthesised a non-symmetric DA; one carbazolyl substituent is maintained, the other one is replaced by an alkyl-urethane group similar to the substituents of the well known symmetric soluble BCMU[15] series. Though the exact crystalline structure of CNEU has not been determined yet, the examination of its behaviour on KAP compared to the one of DCH on KAP happens to be very telling.

When CNEU is vaporised on KAP maintained at room temperature, it develops a polycrystalline film composed of extremely thin crystals[40]. Most of them are oriented along c_{KAP}; but a few others are oriented at 57° or 122° to c_{KAP}, along [101] and $[10\bar{1}]$ KAP.

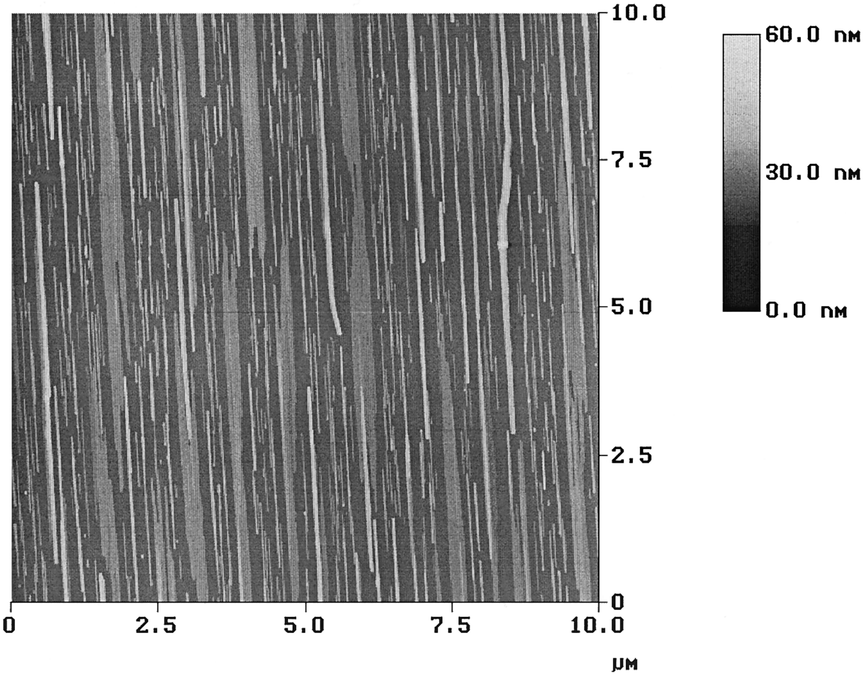


Fig. 4: Atomic force image of an oriented film of PDCH on KAP, KAP kept at 100°C.

All the crystals are distributed along these three directions (Figure 5), thus we deal with an epitaxial growth. The orientations along [101] and [10$\bar{1}$] KAP are a minority; they do not appear in the EM diffraction pattern. We can estimate that they represent less than 5% of the volume of the film. The EM diffraction shows a layered organisation with 0.48nm as repetitive distance, the typical spacing along the chain axis of pDA$^{15)}$. The chain axis runs along the long axis of the needles, we call it b_{CNEU} by analogy with the DCH structure. If the film is prepared by flash vaporisation, some streaking is detected in the first layer of the diffraction pattern, which reveals some disorder along the chain axis, quite analogous to that observed for the BCMU series.

The evolution of the morphologies from the monomer to the polymer film can be examined by AFM. Just after evaporation of CNEU, smooth crystals are badly oriented. After one minute heating treatment at 100°C elongated needles of CNEU have grown along the three directions mentioned above; after polymerisation the crystallites are longer.

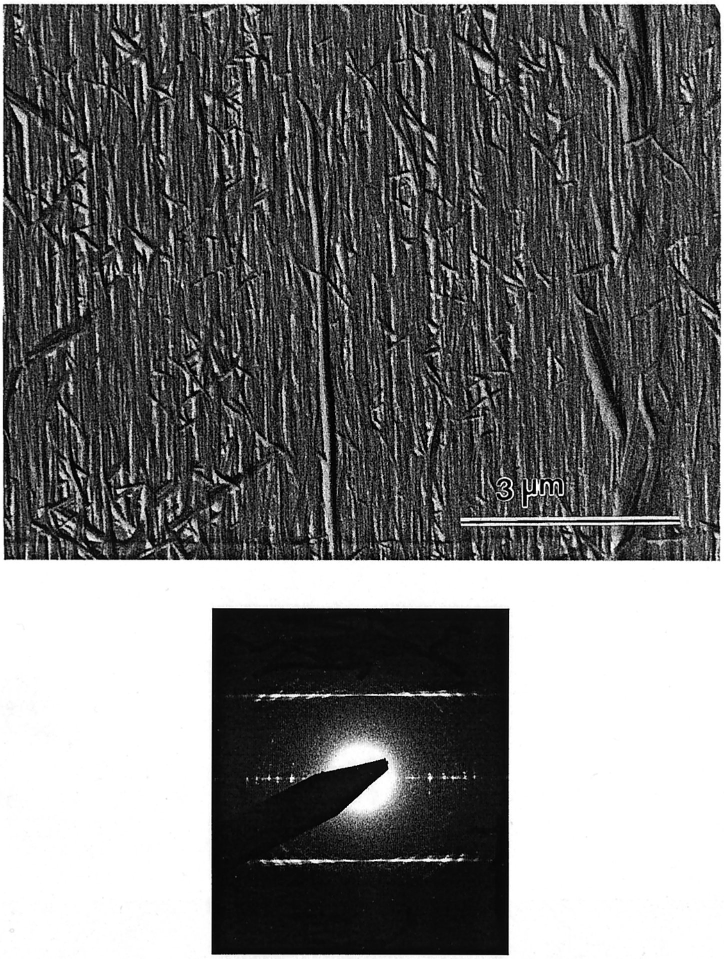


Fig. 5: Electron micrograph of an oriented film of pCNEU on KAP: Upper part bright field image, lower part selected area diffraction.

Experimental parameters have comparable effects on the orientation of CNEU/KAP than on the orientation of DCH/KAP. The optical quality of the films is better when vaporisation rate is low and the temperature is high (below100°C). More specifically, the two minor orientations are not observed at all for the optimal conditions.

What information can we get when comparing these two epitaxial growths? A single carbazolyl group induces a weaker epitaxy than the twin groups. Nevertheless, the main orientation, which is unique at high temperature (b_{CNEU}//c_{KAP}), corresponds to that of DCH/KAP. It means that the specific molecular interaction between the carbazolyl group and the rows of benzene of the phthalate surface can be extended to other molecules bearing carbazolyl groups. However, the other substituent is also able to interact with KAP, in a way which is similar to that of PE, [the epitaxy of PE on KAP1) gives rise to two orientations of the chains at 67° to one another, the PE chains lay down in the valley along <101> directions of KAP]. This epitaxy is probably linked to the shape of the substituent. Therefore, for the non-symmetric DA we have a sophisticated epitaxy which changes with the temperature of the substrate. It is the result of the competition between the π–π interactions for molecular epitaxy and the geometrical interactions. We thus confirm the previous results (DCH/KAP) and demonstrate that several types of interactions can control epitaxy in the field of organics.

Comments on other results:

Before drawing conclusions from our work, it is worth summing up another example where chemical affinity seems to play an important role. The bc plane of the α phase of polyvinylidene fluoride (PVF2) interacts with the ac plane of polytetrafluoroethylene (PTFE) with a 17% disregistry41). The density of fluor in this bc plane is very high. Two other planes of the PVF2 α phase and one from the β phase have more favourable repetitive distances but they are less dense in fluor. Another plane of the β phase has a similar density of fluor, but a mismatch of 24%. This means that epitaxy corresponds here to the best compromise to have a good balance between geometrical matching and chemical affinity.

Conclusion

Investigation of epitaxial growth of very diverse types of polymers helps refining the original lattice matching rules for polyolefins and reveals the chemical influence of non-inert molecules. For polyolefins with all trans backbone, epitaxy involves inter-chain distances. For polyolefins with helical conformation, the above rules may apply to inter-helix distances but sometimes more subtle rules are at play, like matching with rows of prominent groups [Me for (010) αiPP], or interstrand distances42). However, more recent works on linear polymers or on epipolymerisation suggest that the geometrical matching, even considering the detail of the topology in the contact planes, may be overcome by chemical interactions or affinity, as shown for DCH/KAP, CNEU/KAP and PVF_2/PTFE. In the near future, when research on epitaxy will be expanded to more diverse polymers, the influence of polar groups, dipoles, hydrogen bonding etc…may be more clearly demonstrated.

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