

Polymer decoration of layer silicates: crystallographic interactions at the polyethylene–talc interface

J. C. WITTMANN, B. LOTZ

Centre de Recherches sur les Macromolécules, CNRS and ULP, 6, rue Boussingault, 67083 Strasbourg, France

A recently developed technique of "polymer decoration" which makes use of the condensation and crystallization of polymer vapours is used to investigate the crystallographic interactions between polyethylene (PE) and talc, a well known nucleating agent of polymers. The interactions are of epitaxial character. The relationship involves the talc (001) and PE (110) contact planes, and is characterized by alignment of PE chains parallel to either [110], $[1\bar{1}0]$ or [100] directions of the talc substrate with matching of the 0.445 nm PE inter-chain and 0.457 nm talc inter-row distances. The PE–talc interactions underline the non-hexagonal symmetry of the substrate surface layer, as either one, two or all three of the above mentioned crystallographic directions are selected in the polymer–talc epitaxy. Polymer decoration is therefore proposed as a valuable new tool in investigating layered silicates as it provides information on the surface structure; it complements the classical gold decoration technique which provides information on the surface topography. Finally, crystallization of amorphous selenium on talc is shown to take place via an epitaxial relationship comparable to the polyethylene–talc one, with matching of selenium 0.4355 nm inter-chain and talc 0.457 nm inter-row distances.

1. Introduction

In spite of the widespread use of talc as a heterogeneous nucleating agent in the crystallization of polymers, its mode of action remains little understood. To our knowledge, the only extensive structural investigation of interactions between talc and any crystallizable polymer deals with polyethylene [1]. It concludes to an epitaxial interaction on the basis of morphology (i.e. oriented overgrowth of the polymer) but the precise structural relationship was not established because of experimental difficulties in electron diffraction for this system. A more recent investigation of polyethylene and polypropylene crystallization on the phyllosilicate muscovite mica which has a related structure has also pointed to epitaxial growth of the polymer on the mineral substrate [2].

In the present article, the crystallographic interactions between talc and polyethylene are determined by means of transmission electron microscopy and electron diffraction. The emphasis in this work is put on a set of newly developed experimental techniques which make it possible to obtain composite diffraction patterns of both polymer and substrate. In particular, use has been made of a vapourization technique of polymers, (and notably polyethylene) which allows investigations of the polyethylene–talc interactions in some detail. As a matter of fact, this "polymer decoration" technique [3] appears to be a valuable new experimental tool well adapted to investigate the surface structure of layered silicates (and by extension,

most probably of other materials as well), while the familiar "gold decoration" introduced by Bassett [4] is mainly suited to investigate the surface topography. As will become apparent, the two decoration techniques complement each other and can even be used in association to reveal the surface topography and structure of certain layered silicates.

2. Experimental details

2.1. Samples

The talc specimens used originate from the quarries of Luzenac (south-west part of France) and Samatta (Sardinia, Italy), and were provided by Drs G. Fourty and J. Yvon, respectively.

The polyethylene sample used was a fraction obtained by preparative gel permeation chromatography (provided by Dr A. Panaras, Research Centre of Elf Aquitaine, Lacq, France); its molecular characteristics are: $M_w = 22\,000$, $M_n = 20\,000$, $p = 1.1$. Hexatriacontane is of commercial origin (Eastman Organic Chemicals, Rochester, New York).

2.2. Techniques

The talc specimens were prepared for experimentation by taking small chips of the original block, suspending in ethanol, and submitting them to ultrasonic treatment (Power, ~ 12 W for ~ 15 min). The treatment results in the formation of a hazy suspension of talc particles, of which the thinner ones, separated from the larger ones by sedimentation, can be used in

transmission electron microscopy (thickness; < 40 to 50 nm). Small drops of the suspension are deposited on either glass cover-slides or carbon-covered electron microscope copper grids; the suspending solvent is allowed to evaporate, and the talc particles are coated with polymer or paraffin vapours.

Vapourization of PE or paraffin is performed by gentle heating of small amounts (~2 to 5 mg) of the sample deposited on a tungsten wire. Heating time is of the order of 1 min, and the polymer-substrate distance is ~10 cm. In the process, chain scission of PE occurs, and the vapourized material has a M_w of the order of 1300 [5]; hexatriacontane vapourizes without significant degradation. After polymer decoration, the sample is either decorated with gold or shadowed with Pt-C, and is carbon coated. The most illustrative pictures are obtained with the combined polymer and gold decorations which, being both performed under normal incidence, avoid spurious orientational effects as with Pt-C shadowing. These pictures have therefore been preferred for this article.

Samples formed on glass cover-slides are detached with the help of a polyacrylic acid backing, floated off on water and picked up with electron microscope grids.

For comparison purposes, thin films of selenium were also produced by vapourization. The selenium pellets are heated in a tungsten boat. The condensed, initially amorphous selenium films are thermally treated (annealing between 70 and 160°C) to induce crystallization.

Examination was made either in the transmission or selected area diffraction mode with a Hitachi electron microscope set at 75 kV.

3. Results

3.1. Crystallization of PE vapours on talc

As indicated in the experimental section, ultrasonic treatment results in the formation of thin talc flakes which, when deposited on a glass substrate, are oriented with their large (001) cleavage faces exposed to polymer vapours. Crystallization of the condensed PE vapours reveals various aspects of the underlying talc structure, mainly through characteristic preferential orientation of the lamellae. Three typical decoration patterns have been observed, which are characterized by three, two and a single orientation of the PE chains and lamellae, respectively.

3.1.1. Three-fold orientation

Fig. 1a illustrates the crystalline habit of polyethylene vapours deposited on a thin, relatively uniform talc flake. The figure displays three sets of double rows of gold particles, oriented nearly 120° apart. This pattern is obtained in the following manner: upon deposition of the PE vapours, crystallization results in the formation of lamellae standing edge-on on the substrate. Since only small amounts of vapourized polymer are deposited, mostly isolated lamellae are formed on a relatively "clean" (i.e. polymer-free) substrate. Subsequent gold decoration underlines both "walls" formed by the isolated lamellae, i.e. results in a double row of gold particles which is easily distinguished on a rather featureless substrate.

The crystallographic relationship between PE and talc is established by the composite diffraction pattern of Fig. 1b. It is characterized by a hexagonal array of sharp $hk0$ spots arising from the talc substrate, and by three sets of arced PE reflections oriented 120° apart. The three sets of 002 reflections characterize three PE chain orientations. On the corresponding equators, the only observed reflections are at 0.297 and 0.221 nm, indexed as 210 and 310 of the normal, orthorhombic unit-cell of PE; the contact plane, normal to the diffracting planes, is therefore (110). The crystallographic relationship is of epitaxial character. It may be summarized as:

$$(001)_{\text{talc}} // (110)_{\text{PE}}$$

and

$$[001]_{\text{PE}} // [110], [1\bar{1}0] \text{ or } [100]_{\text{talc}}$$

and is based on an important one-dimensional lattice matching of the PE distance between chains in the (110) plane (0.445 nm) with the talc 0.457 nm periodicity [6] in directions normal to the three above mentioned ones.

3.1.2. Two-fold and single orientations of the PE decorating lamellae

Besides the decoration pattern of Fig. 1 characterized by three orientations of the PE rods, two additional patterns of PE decoration were observed for cleaved talc particles. On rare occasions decoration patterns as shown in Fig. 2 have been observed. These are characterized by the selection of two out of the three above-mentioned orientations.

More frequently however, a single orientation of the PE chain is found over relatively large areas of the substrate cleavage faces, as illustrated in Fig. 3a. The corresponding composite diffraction pattern is shown in Fig. 3b. The unique orientation may change when cleavage of the talc particle exposes different layers. Fig. 4, which displays this behaviour, provides at the same time a very illustrative example of the possibilities of the combined polymer and gold decoration techniques. It shows a cleaved talc particle with ten different cleavage planes, designated in sequence A to J. Cleavage steps between these planes are visible through both PE crystallization and gold decoration characteristics. Plane A displays the three PE orientations. All the other planes are characterized by a single (or a vastly dominant) orientation of the PE lamellae, except for Plane F which appears rather featureless. These orientations are parallel to those found in Plane A, but sudden 120° (or 60°) changes in orientation occur at cleavage steps which are also underlined by the gold decoration pattern. These 120° changes in lamellar orientation correspond to changes of 120° in the chain axis orientation (which is normal to the lamellar extension). The changes are apparently unrelated from one cleavage plane to another, as plus and minus 120° changes are observed, or no change at all: the latter possibility is represented by Planes I and J, which are however clearly distinct, as revealed by the cleavage step shown by the gold decoration pattern.

It may be noted in particular that the polymer orientations bear no correlation with the orientation of the cleavage steps, which thus cannot be considered as active features of the substrate in the nucleation of the polymer. The crystallization behaviour of the PE vapours therefore establishes that in these cleaved talc particles, the silicate layers depart from the hexagonal symmetry they are supposed to have from their accepted crystallographic structure. In addition, the different behaviour of Plane F in Fig. 4 suggests that it is of a different nature than its neighbours. These observations will be further examined in the discussion section in conjunction with very similar results obtained previously by other authors, using different depositing materials and substrate layered silicates.

3.2. Crystallization of paraffin vapours on a talc substrate

Deposition and crystallization of paraffin vapours instead of PE ones results in a crystallographic relationship with the talc substrate similar to that observed with PE, i.e. (1 1 0) contact plane of the paraffin and matching of the paraffin 0.445 nm inter-chain distance and talc 0.457 nm periodicity. Several differences in the crystalline morphology are however observed; they are examined with the aim to evaluate the suitability of paraffin as a decorating material for layered silicates.

Deposition and crystallization of paraffin vapours gives rise to a crystalline morphology as shown in Fig. 5a. Typical wide and low angle selected area

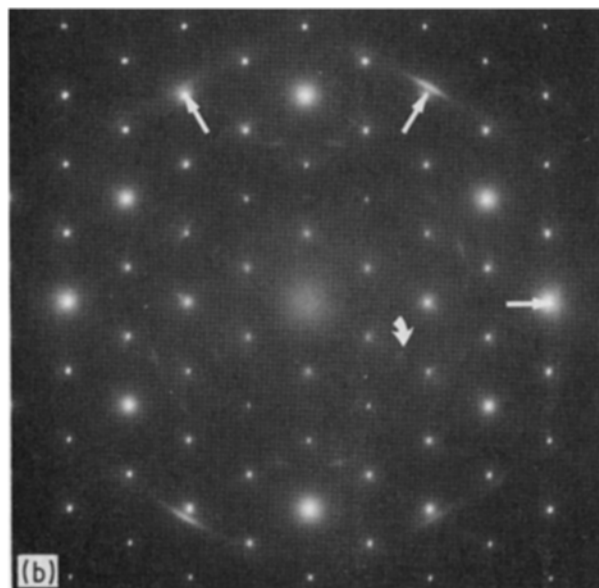
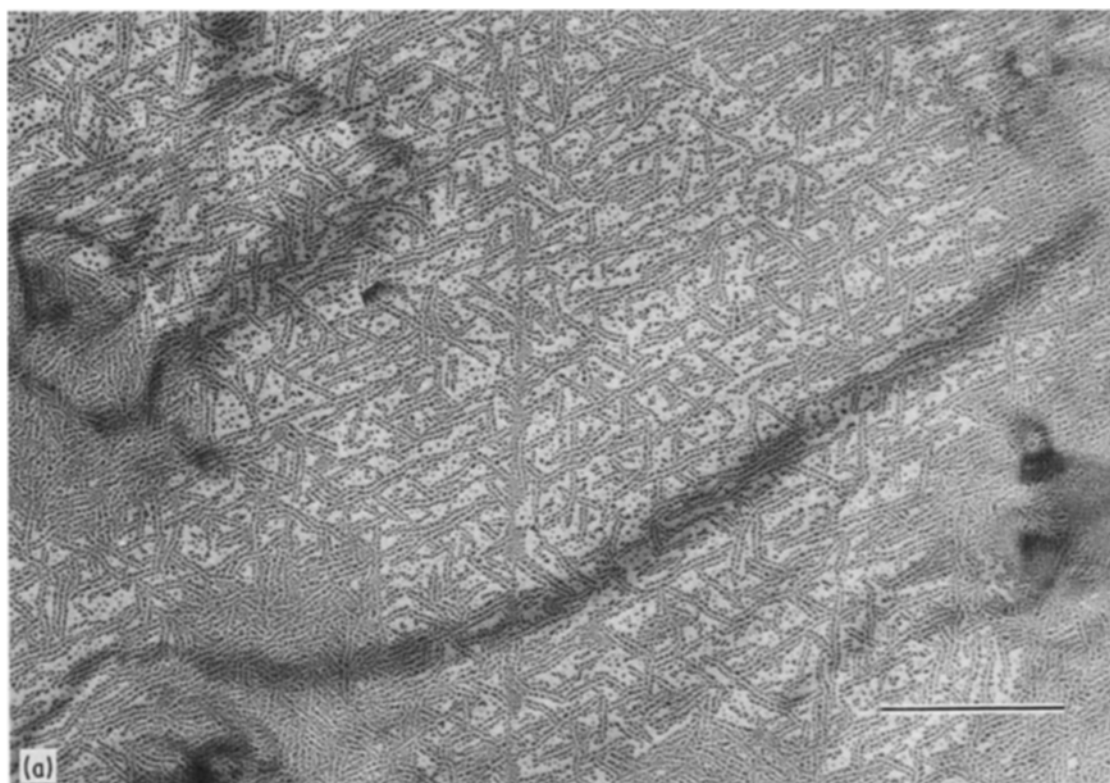


Figure 1 (a) Decoration pattern of a talc particle obtained by successive deposition of vapours of polyethylene and gold. Note that the gold particles underline both edges of the polymer lamellae standing edge-on on the substrate surface. Thickness of polymer lamellae is ~ 12.0 nm, which combined with the known [5] molecular weight of the deposited material (~ 1300), suggests that the chains are fully extended in the lamellae, with virtually no chain folding. Note the three orientations nearly 120° apart of the decorating lamellae and their length which on occasion reaches the micrometre range. Presence of the talc substrate is attested by the dark fringes crossing the picture, which are due to diffraction contrast of the particle. The experimental conditions are identical for the bright fields shown in Figs. 1 to 4. Scale bar: $0.5 \mu\text{m}$. (b) Electron diffraction pattern of an exposed talc layer with the three orientations of the polymer decoration as in (a), but more heavily polymer-decorated, and with no gold decoration. Note the hexagonal net of sharp spots due to the talc substrate and the three sets of arced reflections arising from the polymer overgrowth. The PE chain axis directions are marked (outer arrows pointing to the PE 002 reflections) and one of the PE 210 reflections (which define $\{110\}$ as the PE contact planes) is indicated with a bent arrow.

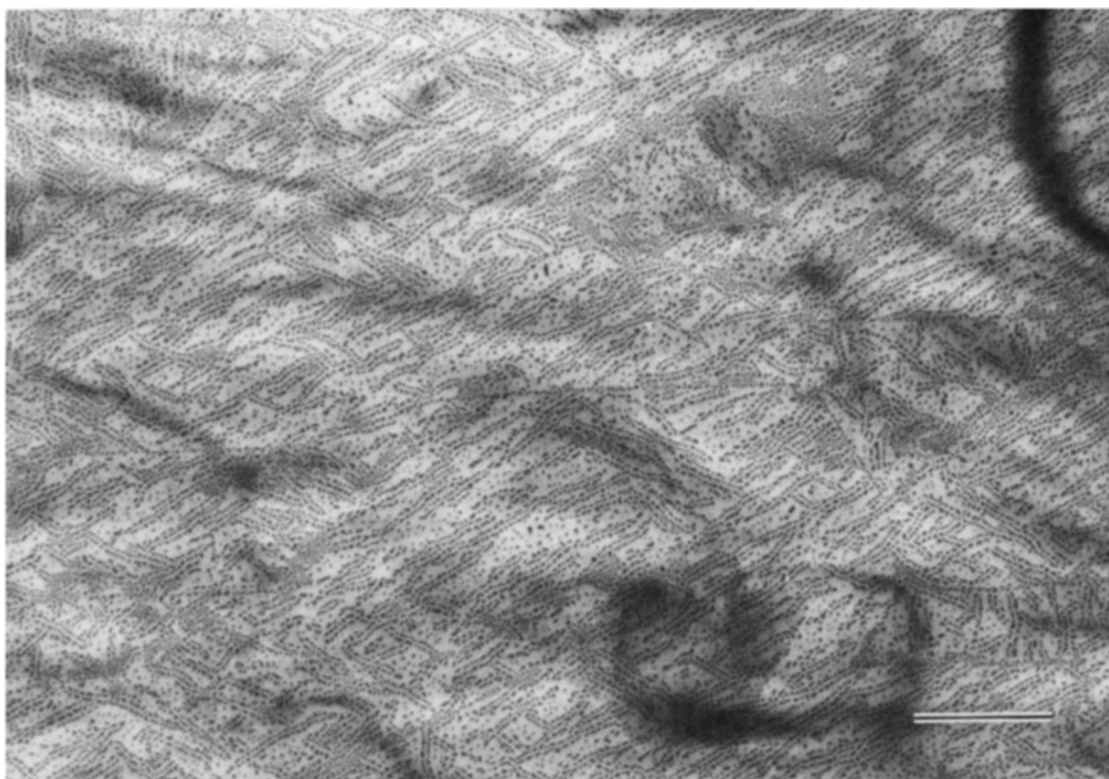


Figure 2 Decoration pattern obtained as in Fig. 1 but showing only two orientations of the PE lamellae. Note that this orientation pattern extends over successive cleavage planes of the substrate. The cleavage planes are revealed by an additional row of gold particles which crosses the figure horizontally. This decoration pattern is observed only rarely.

electron diffraction patterns are shown in Fig. 5b and c, respectively. The paraffin lamellae crystallize also edge-on, with the paraffin chain parallel to the substrate (001) plane of talc. When the amount of deposited paraffin material is sufficient, these lamellae build up stacks which give rise to a low angle diffraction pattern with the characteristic 4.76 nm periodicity (for a $C_{36}H_{74}$ material, cf. Fig. 5c).

Several features of the paraffin crystallization make it less suited than PE as a decorating material. First, due probably to its lower melting temperature, and therefore lower undercooling at the (room) temperature of the substrate, nucleation frequency appears to be lower for paraffins than for PE: paraffins tend often to gather on a (relatively) few nucleation sites, which supposes considerable molecular movement in the supercooled, condensed vapours. Second, it was observed (Fig. 6) that the decoration pattern produced upon evaporation changes when the preparation is stored at room temperature. This evolution is quite spectacular, and manifests itself by the migration and rearrangement of paraffin islands. The time scale of this process is of the order of days or weeks, which would make a second examination of a given preparation somewhat inconclusive. Since such modifications of the PE decoration do not take place, and since the PE decoration is more uniform due to its higher nucleation density, the use of polymer rather than paraffin as a decorating material seems preferable.

3.3. Crystallization of amorphous selenium on talc substrates

Previous investigations have shown that the crystal-

lization behaviour and the epitaxial relationship with some organic substrates of selenium and polyethylene are similar [7] despite the different conformation (3₁ helix) of the inorganic polymer. This similarity in behaviour was attributed to the close correspondence of the chain packing distances in the PE (110) and selenium (10.0) planes (0.445 and 0.4355 nm, respectively) and of the periodicities along the chain axes ($2c_{PE} = 0.508$ nm, $c_{SE} = 0.495$ nm). Thus, *p*-terphenyl and *p*-quaterphenyl which induce the epitaxial crystallization of PE with a (110) contact plane are also suitable substrates for the epitaxial crystallization of selenium. By a similar reasoning, talc should also be a good substrate for the epitaxial crystallization of selenium.

Selenium has been vapourized on cleaved talc particles. Condensed selenium vapours are amorphous at room temperature, but annealing of the sample in the temperature range 70 to 160° C results in the epitaxial crystallization of the selenium film on the talc particles. As illustrated in Fig. 7, which is a composite talc-selenium diffraction pattern, three orientations of the selenium chain are present, and matching of the 0.4355 nm of selenium and 0.457 nm talc periodicities is again realized.

4. Discussion

The observed preferential orientation of the PE chains on cleaved talc particles raises a number of questions on the talc structure, which need be analysed with reference to other reported epitaxial crystallizations of organic materials and polymers on layer silicates, and especially on its most frequently used example, muscovite mica. Next, the nucleation activity of talc

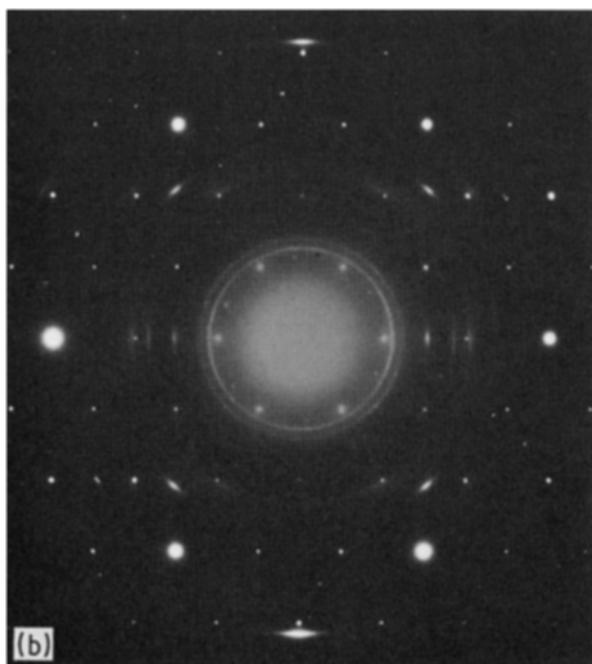
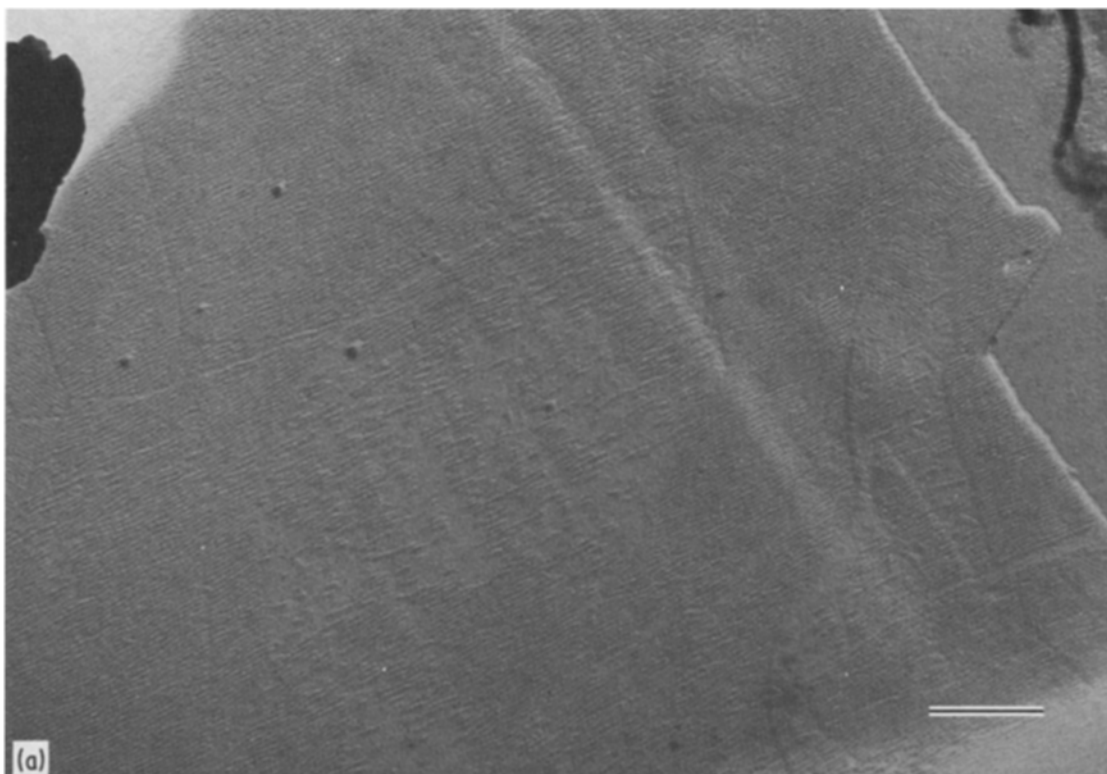


Figure 3 (a) Polyethylene decorated and Pt/C shadowed talc particle which displays a single orientation of the polyethylene lamellae. Note that the Pt/C shadowing also underlines the cleavage step of the talc particle. The origin of large scale variations in decoration density, as observed in the centre of the micrograph, is not known. Scale bar: 0.5 μm . (b) Diffraction pattern of a talc particle with a mostly single orientation of the decorating polyethylene lamellae. The chain axis is vertical for the major population of PE lamellae.

towards polymers will be examined in the light of the observed epitaxial relationship between polyethylene and the talc cleavage plane. Finally, the suitability and usefulness of polymer decoration as a tool for surface structure analysis will be discussed.

4.1. The structure of the talc layer and cleavage plane

Talc is a clay mineral with a sheet structure. The individual sheet is of the three layer type: it is made of two external silica layers which sandwich a brucite layer [6] (Fig. 8). The silica layers are made of an hexagonal array of SiO_4 tetrahedrons with their tips pointing inward in the sheet. The brucite layer is made

of octahedrons which share atoms with the silica layers (cf. Fig. 8). Easy cleavage is possible between neighbouring silica layers of successive sheets, which gives rise to the characteristic flake morphology with (001) cleavage planes made of an array of oxygen triangles arranged hexagonally. The crystal structure of talc departs however from hexagonal symmetry since the two silica layers of any given sheet are shifted relative to one another (in the c^* -axis projection). The shift can be in any one of three equivalent directions 120° apart in the plane of the sheet and results in a unit-cell that must be defined as monoclinic rather than hexagonal (cf. Fig. 8). Since no detailed X-ray structure analysis of talc is available, it is not known whether this monoclinic character exerts an influence on the structure and therefore the symmetry of the silica layer, i.e. on the symmetry of the cleavage plane. A comparison with the better known situation prevailing in muscovite mica is therefore helpful.

Muscovite mica, a member of the illite minerals, has a multilayered structure very similar to that of talc. Partial replacement of Si by Al^{3+} requires however the presence of additional positive ions in order to balance the net charge of the structure. This is provided for by potassium ions located between silica layers of successive sheets [6]: structurally, the muscovite mica cleavage plane is essentially similar to that of talc, with the addition of some potassium ions.

The existence, regularity and consequences on the

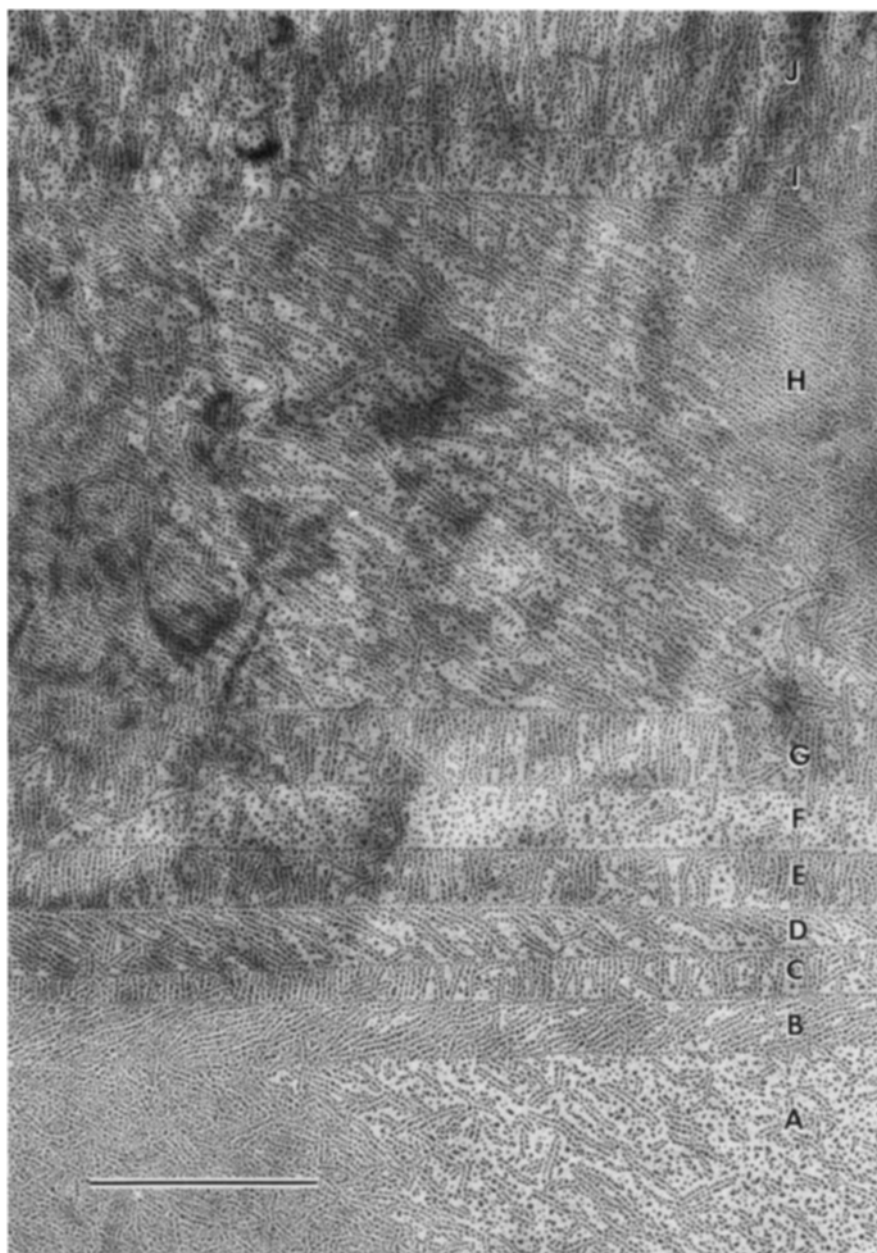


Figure 4 Polyethylene and gold decorated talc particle displaying several cleavage steps. The cleavage steps run horizontal; they are underlined by the gold decoration, and correspond often to 120° changes in the PE decoration orientation. The successive cleavage planes are marked (A to J). Note in particular the similar orientations of the decoration in Planes I and J, and the different decoration density of both PE and gold in Plane F (cf. section 3.1.2). Scale bar: $0.2 \mu\text{m}$.

crystal structure and growth habit of the displacement of successive silica layers and sheets has been investigated with particular care in micas. A regular pattern of displacements is often observed through the depth (i.e. cross-section) of a mica sample, which led to the description of a large number of mica polytypes [6]. The regular pattern of displacements appears to arise from growth on screw dislocations with a Burger's vector normal to the sheets and intensity equal to an integral number of sheets [8, 9]. The crystal structure of the most common polytype of muscovite mica, the two layer monoclinic form ($2M_1$) has been analysed by Radoslovich [10]. In agreement with other investigations on related layer silicates, he observes that the "ideal" open hexagonal network of basal oxygen atoms in the Si-O tetrahedra are significantly distorted, due to the rotation of whole Si-O tetrahedra; the rotation ranges from 5° in vermiculite [11] to $\sim 13^\circ$ in muscovite: "the surfaces thus have a marked ditrigonal rather than hexagonal symmetry" [10] (Fig. 9). In addition, the Si-O tetrahedra in mus-

covite are slightly tilted, which results in differences (admittedly small: $\sim 0.012 \text{ nm}$) in the z-co-ordinates of one third of the oxygens which build up the contact surface of muscovite mica. Radoslovich also suggests that "the distortions in the oxygen network are (...) primarily due to (dimensional) misfit between the tetrahedral and octahedral layers". These dimensions depend on the cationic substitution of the layers. From available formula which make it possible to compute the dimensions of the layers from their chemical composition [12], he suggests that, in talc, "there should be practically no misfit between the octahedral and tetrahedral layers (...): the silica layer in talc is therefore probably fully extended and undistorted".

Results on "orientation overgrowth of condensed polycyclic aromatic compounds vacuum-evaporated onto cleaved face of mica" reported by Uyeda *et al.* [13] were not analysed with reference to the structure determined by Radoslovich, but strongly support the view that the cleavage face of mica departs from

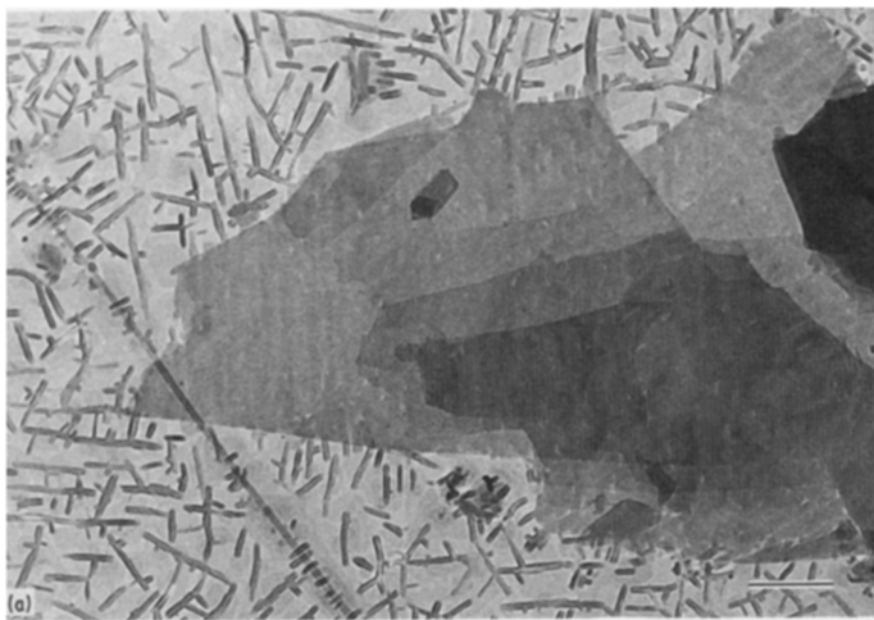


Figure 5 (a) Cleaved talc particle decorated with paraffin ($n\text{-C}_{36}\text{H}_{74}$) vapours. Note the different nucleation density on the talc particle, which displays mostly a single orientation of the paraffin deposit in any one cleavage plane. The decoration pattern of the substrate (glass slide) is produced by initial crystallization of paraffin molecules with their chain axis normal to the glass surface. Subsequent deposition of paraffin vapours on these first-formed lamellae is made with the chain axis parallel to their end-surface, which is a characteristic feature of polymer and paraffin decoration of polymer or paraffin lamellae [3]. Scale bar: $0.5\ \mu\text{m}$. (b) Selected area electron diffraction pattern of a talc particle with single orientation of the paraffin decoration. Note the presence of 0034 and 0036 reflections in the chain axis direction (arrowed) and the 210 reflections on the equator (bent arrow). (c) Low angle electron diffraction pattern of a paraffin decorated talc particle. Note the $00l$ reflections with basic repeat distance of $4.76\ \text{nm}$. This distance corresponds to the length of the fully extended paraffin chains; its presence suggests that vapourization of the paraffin takes place with no significant degradation.

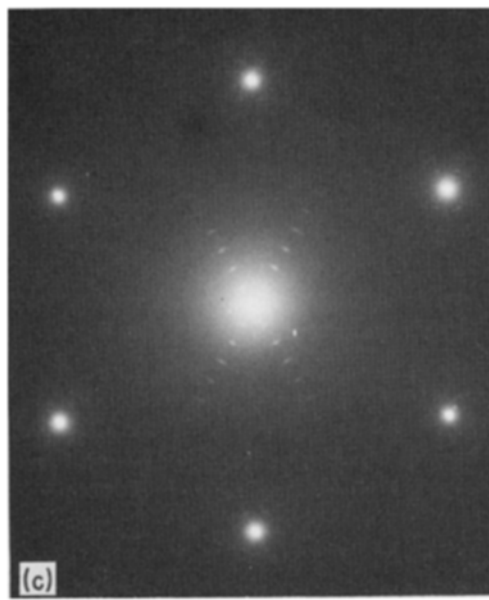
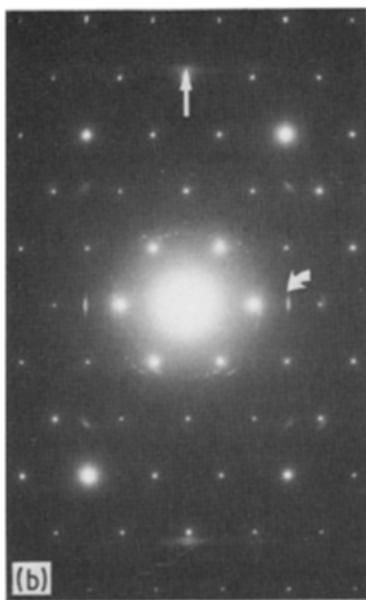
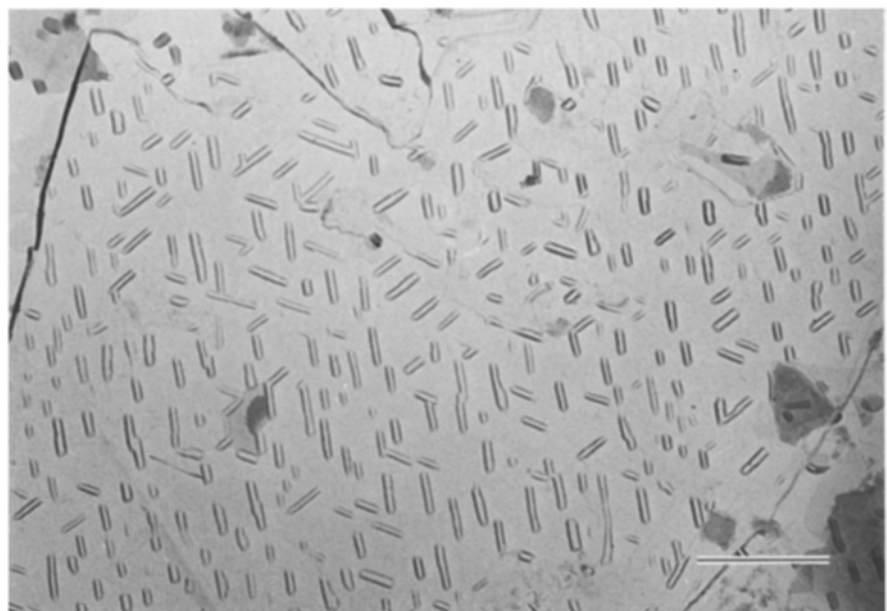


Figure 6 Paraffin-decorated talc particle in which the paraffin molecules have gathered into relatively large, multilayer aggregates; three orientations of these aggregates are clearly visible. Such patterns are observed after storage, due to paraffin decoration rearrangement. Scale bar: $1\ \mu\text{m}$.



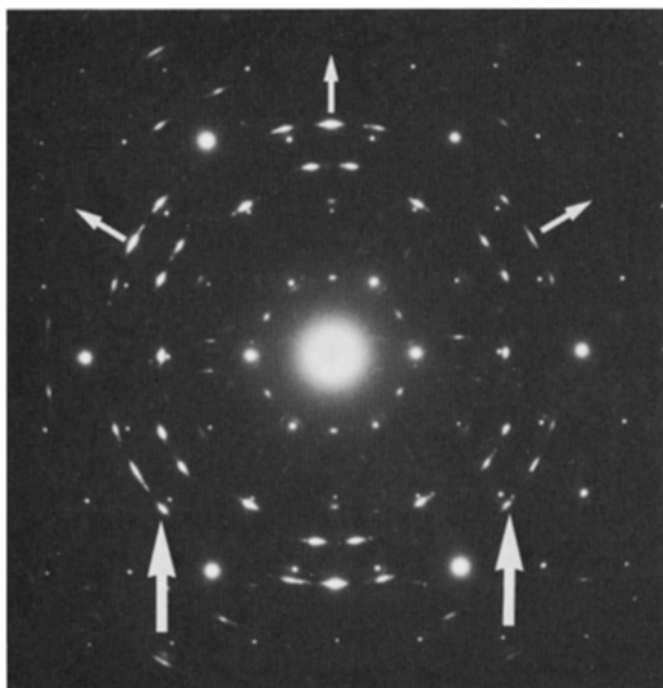


Figure 7 Selected area electron diffraction pattern of a cleaved talc particle decorated with selenium vapours and annealed to 125 to 135°C. This complicated pattern is made of the usual hexagonal array of sharp spots arising from the talc substrate. Superposed on it are three sets of selenium diffraction arcs. The selenium chain axes are indicated by arrows starting from the 003 reflections of selenium. The two vertical rows of 20l reflections are arrowed (200 on the equator of this figure). All the other observed arcs can be obtained from this single selenium pattern by plus and minus 60° rotations.

hexagonal symmetry. These authors establish in particular that the symmetry of the orientation overgrowth changes with the substrate temperature. At lower substrate temperature ($150^\circ < T < 170^\circ \text{C}$) a single directional orientation of the evaporated film is observed. At higher substrate temperatures ($200 < T < 250^\circ \text{C}$) a double (for Zn-phthalocyanine) or triple (for Pt- and Cu-phthalocyanines) orientation is formed; in the latter case, the electron diffraction pattern shows however two-fold symmetry in spite of the apparent triangular configuration.

The observations of Uyeda *et al.* [13] would be difficult to explain on the sole monoclinic character of the top sheet, assuming an ideal hexagonal structure of the silica layers, since the interactions between the overgrowth and the bottom silica layer of the surface mica sheet, which are ~ 0.8 to 1.0 nm away, can provide no more than a small contribution to the total interaction energy. The concept of deformed silica layers appears more satisfactory, as it provides a built-

in asymmetry of the crystal surface which directly interacts with the overgrowth.

An important contribution of the work of Uyeda *et al.* rests in the demonstration that the symmetry of the outermost silica layer can be modified, in the present case by heat treatment. It can also be inferred from their work that layer structures which induce double and triple orientations are more elusive and more common, respectively.

Before closing the discussion on mica substrates, mention must be made of a recent short report on the epitaxial crystallization of thin films of PE on muscovite mica [2]. The most common PE contact plane was found to be (110). The lamellae have the PE *c*-axis parallel to the mica $\langle 110 \rangle$ or $[100]$ directions, with matching of the PE 0.445 nm periodicity and mica 0.457 nm one, as observed in our work on talc.

The epitaxial crystallization results of Uyeda *et al.* [13] and Lovinger [2] using muscovite mica substrates have been discussed in some detail as they bear strong

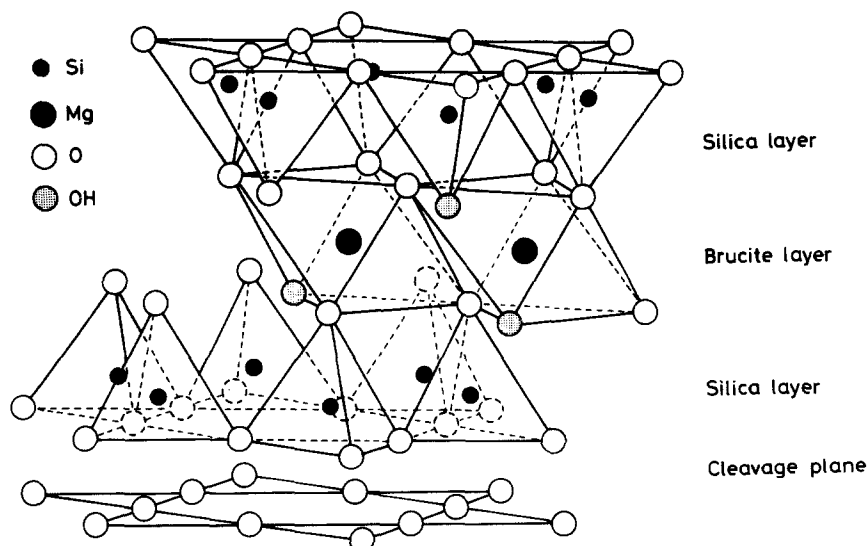


Figure 8 Diagrammatic sketch of the sheet structure of talc, as adapted from reference [6]. The silicate tetrahedra form on the outer surfaces of the layer an hexagonal array of oxygen atoms (see the top surface of the bottom sheet). The central brucite layer is made of octahedra with a central aluminium atom, while the outer atoms are either oxygens shared with the silica layers or hydroxyls shared with neighbour octahedras of the brucite sheet.

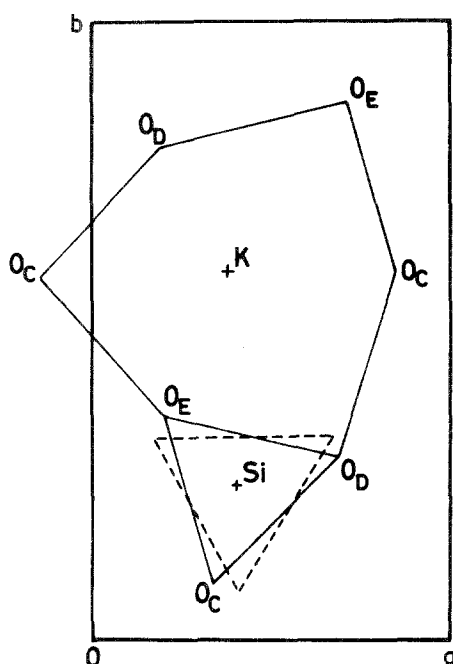


Figure 9 Normal projection onto the ab face of some of the atoms in muscovite mica, as adapted from reference [10]. The "ideal" position of the oxygens in the silicate network are indicated by dashed lines. The departure from this ideal position by rotation of the tetrahedra (here by an angle of some 15°), together with the uneven height of these oxygens (O_D is shifted downwards, but by only 0.012 nm), gives rise to the ditrigonal character of the mica surface. A similar departure from hexagonal symmetry of the silica layer in talc is suggested by the identity of decoration behaviours of talc and mica (see text).

resemblance with the present ones using talc substrates. The close parallelism of Uyeda *et al.* and our own observations makes it possible to better evaluate the importance of substrate nature and experimental conditions.

The observation of a single orientation of the polyethylene decoration on cleaved talc flakes suggests that the cleavage surface, i.e. the silica layer departs from the hexagonal symmetry it is assumed to have in the classical structure of talc. The similarities with the epitaxies on mica suggest that these departures must be of a related type, i.e. creation of a lower symmetry induced by the rotation of the silicate tetrahedra from the ideal structure. This experimental observation is at variance with the inference made by Radoslovich [10], namely that, in view of the dimensional matching of tetrahedra and octahedra, the talc structure must be virtually undistorted. Conversely, observation of similar epitaxial crystallization behaviour on talc and mica suggests that the possible presence of potassium ions on the cleavage surfaces of mica interferes little in the epitaxial growth.

The observation of two and three orientations of the epitaxial overgrowth on talc and mica suggests also that the substrate exposed layer may lose its asymmetry, although no precise structural picture can be given at this stage. In muscovite mica, the loss of the unique decoration orientation has been linked to specific thermal treatments. From our experience, it would appear that, in talc, freshly cleaved surfaces are more prone to giving the single orientation. The precise experimental conditions which give rise to the

various decoration habits on talc need however be determined in further detail. In this respect, comparison with polytypes of muscovite mica whose structure is better known, and for which the sequence of structural transitions has been established by Uyeda *et al.* will be helpful. In particular, the 1M polytype of mica may well provide a suitable substrate for establishing a correlation between the polymer or low molecular weight organic material decoration orientation and the precise orientation of the monoclinic unit-cell in the exposed sheet of the substrate. Further work along these lines is in progress.

4.2. Talc as a nucleating agent for polyethylene

The present experimental results on talc-polymer interactions confirm the suitability of talc as a nucleating agent for crystallizable polymers. They provide further experimental support for the epitaxial character of the relationship, as suggested by Rybnikar [1] and give a structural basis to the reported morphologies. For example, the variation of the length of "epitaxial (PE) rods" as well as the "cooperative direction change of about 60° " [1] must be related, with reference to Fig. 4, to the presence of cleavage steps on the talc surface. Also, the suggested [1] epitaxial relationship between PE and talc needs to be modified; while the PE chain axes are indeed parallel to the talc a -axis (or at 60° to it), the PE contact plane is (110) rather than the proposed (100) one. It follows that, contrary to the opinion once expressed [14], lattice matching is an important parameter in the epitaxial crystallization of PE.

4.3. Polymer decoration as a new investigation tool

Polymer decoration is similar to gold decoration in its experimental set-up and can be performed with the substrate held at room temperature. It requires equipment that is already available in most materials science laboratories. In contrast to gold decoration, it makes use as the evaporated material of elongated molecules which have aspect ratios (length over diameter) of roughly $13.0\text{ nm}/0.5\text{ nm}$, i.e. 20 or 25. These geometrical and structural characteristics of the decorating molecules are well suited to revealing the anisotropic character of surfaces. It has been used in our laboratory to investigate the fold surface structure of polymer lamellar crystals and the interactions between polymers and crystals of low molecular weight organic materials, but is clearly suited for most surfaces of organic or inorganic solid materials.

The potential of polymer decoration (here combined with gold decoration) in investigating the surface structure of layer silicates is fully illustrated by Figs. 1 to 4. The observed anisotropies are not, strictly speaking, new: besides the work of Uyeda *et al.* [13], Friedel [15] reports that Royer has observed already in 1925 single orientations of epitaxially grown crystals of ammonium iodide on the cleavage surface of mica. The correlation of "geographical" limits (cleavage steps) with the underlying structure at a submicron scale offered by polymer decoration alone, or by the

combined decoration techniques is however exceptional. Changes in decoration orientation are clearly related to the orientation of the crystal axes and have already been discussed. Changes of the decoration pattern may also be informative: for example, the different decoration density of surface F in Fig. 4 suggests that it is of a different nature than the other layers: it may well correspond to an exposed layer of brucite, either of a talc sheet, or interleaved as an additional feature in the structure, as would be the case in chlorite: interleaving of "foreign" sheets is quite possible and actually rather frequent in talc and in layered silicates.

5. Conclusion

Interactions between talc and polyethylene are shown to be of epitaxial character: the nucleating activity of this additive towards the polymer appears to be linked to its high dispersion (related to its easy cleavage), associated with an epitaxial relationship which matches the 0.445 nm interchain distance in the (1 1 0) plane of PE and the 0.457 nm (i.e. $b/2$) in the (0 0 1) cleavage plane of talc. A related epitaxial relationship also prevails in crystalline selenium–talc interactions. Topographical features of the talc particles (cleavage steps, cracks or crevices, etc) appear to play no role in the nucleating activity of talc towards crystalline polymers.

The polyethylene–talc interactions have been established with the help of a decoration technique which is based on the crystallization of condensed polymer vapours. This technique has been recently used for characterizing the surface structure of chain-folded polymer lamellae [3]. When applied to talc it displays characteristic single, double or triple orientations on the substrate surface. Similar orientational behaviour has been observed in the epitaxial growth of phthalocyanines deposited on muscovite mica, and must be associated with the departure of the surface silica layer from hexagonal symmetry, i.e. it reveals the monoclinic character of

layer silicates. On this basis, polymer decoration should be a helpful new tool in structural investigations of layered silicates and, more generally, in revealing anisotropies in the properties or structure of the surface of solid materials.

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References

1. F. RYBNIKAR, *J. Macromol. Sci. Phys.* **B19** (1981) 1.
2. A. J. LOVINGER, *Polymer Preprints* **21** (1980) 253.
3. J. C. WITTMANN and B. LOTZ, *J. Polym. Sci. Polym. Phys. Ed.* **23** (1985) 205.
4. G. A. BASSETT, *Phil. Mag.* **3** (1958) 1042.
5. M. ASHIDA, Y. UEDA and J. WATANABE, *J. Polym. Sci. Polym. Phys. Ed.* **16** (1978) 179.
6. R. E. GRIM, in "Clay mineralogy" (McGraw-Hill New York, 1953) pp. 43–83.
7. J. C. WITTMANN and B. LOTZ, *J. Mater. Sci.* **19**(1984) 1439.
8. F. C. FRANK, *Phil. Mag.* **42** (1951) 1014.
9. A. BARONNET, *Prog. Cryst. Growth Charact.* **1** (1978) 151.
10. E. W. RADOSLOVICH, *Acta Cryst.* **13** (1960) 919.
11. A. McL. MATHIESON and G. F. WARNER, *Amer. Min.* **94** (1954) 231.
12. G. W. BRINDLEY and D. M. C. MAC EWAN, *Ceramics; a symposium* (British Ceramic Society, 1953) p. 15.
13. N. UYEDA, M. ASHIDA and E. SUITO, *J. Appl. Phys.* **36** (1965) 1453.
14. J. A. KOUTSKY, A. G. WALTON, E. BAER, *J. Polym. Sci.* **B5** (1967) 185.
15. G. FRIEDEL, "Leçons de Cristallographie" (Berger-Levrault, Paris, 1926).

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