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# Design and surface synchrotron X-ray structure analysis of Langmuir films for crystal nucleation

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Abstract: Crystal nucleation of glycine and sodium chloride has been studied under floating Langmuir monolayers at air/solution interfaces, and at glass slides coated with Langmuir-Blodgett films. The packing arrangements of the polar head groups of the monolayers were varied in a controlled manner by introducing different groups in the hydrophobic tails. The structures of some of these monolayers were independently elucidated by grazing incidence X-ray diffraction and reflectivity measurements using synchrotron light. It was found that the crystals nucleated at the interface exposed a top layer of molecules with an arrangement similar or complementary to that of the polar head groups of the monolayer. These results imply that the packing of the polar head groups determines the morphology and the nucleation rate of the attached crystal.

## INTRODUCTION

The processes of crystal nucleation, growth and dissolution are of central importance to the fundamental and applied sciences, ranging from the chemistry and physics of materials, through structural chemistry and biology, to biological and pathological crystallization. Yet, the degree of understanding and the ability to control them are still at a rudimentary level. Most previous studies were primarily of a thermodynamic and kinetic nature and directed at simple inorganic systems. The present approach is from the structural and stereochemical view point, taking also into account the molecular packing arrangement of the crystal and its morphology.

Crystal nucleation has been described classically in terms of two distinct consecutive steps (ref.1). In the first one, the dissolved molecules in the supersaturated solution aggregate to form structured embryonic nuclei. Upon formation they develop a surface which separates them from the environment. The free energy of formation of the new surface may be represented by $4\pi r^2\Delta G_s$, where r is the radius of the embryo and $\Delta G_s$ represents the surface free energy of the nucleus per unit area. $\Delta G_s$ is always positive and represents destabilization of these nuclei. On the other hand the driving force for the formation of the aggregate is provided by the internal forces between the molecules, as expressed by $-4/3\ \pi r^3\Delta G_v$ where $\Delta G_v$ is the free energy per unit volume of the nucleus relative to the parent phase. Thus the net change in free energy of nucleation is $\Delta G_n=4\pi r^2\Delta G_s-4/3\ \pi r^3\Delta G_v$. Once the embryo crosses the critical radius $r_c$ at which $d\Delta G_n/dr=0$, corresponding to

$r_c=2\Delta G_S/\Delta G_V$, continual growth of the nucleus will be a stable process. In the present approach we assume that a mature crystal develops from an embryo possessing the same structure. Thus, for example, materials which have the tendency to precipitate into polymorphic forms should contain in solution embryos of the same polymorphic crystalline forms. In order to gain information on the structures of these embryos we undertook the design of ordered surfaces that will induce, by a type of epitaxy, oriented nucleation of the desired crystal. We were faced with the problem of designing synthetic two-dimensional nets which should be either identical or complementary in structure to one of the molecular layers of the to-be nucleated single crystal. For this purpose we used monolayers composed of amphiphilic molecules at the air/solution interface so that the polar head groups form a two-dimensional structure which will induce nucleation of one of the faces of the crystal (ref.2). Furthermore, by modifying the hydrophobic tail, or by diluting the monolayer with other amphiphiles inert to nucleation of the crystal, it should be possible to vary, within limits, the packing arrangements of these head groups and their domain sizes, and so influence the crystallization process in a controlled manner. Finally, new analytical methods, such as grazing incidence X-ray diffraction and reflectivity using synchrotron light (ref.3), provide new means to elucidate the structures of such monolayers (ref.4) and the molecules attached to them, from which crystals start growing. These concepts and methods are illustrated with two model systems: the crystallization of α-glycine and sodium chloride.

## CRYSTALLIZATION OF α-GLYCINE UNDER α-AMINO ACID MONOLAYERS

Glycine crystallizes from aqueous solution in the α-form (space group $P2_1/n$), exhibiting a bipyramidal habit (ref.5). The glycine molecules form hydrogen bonded chiral layers parallel to the ac plane (Fig.1a,b,c). These layers are juxtaposed on one side of the b-axis by centres of inversion about which the molecules are interlinked to form centrosymmetric hydrogen-bonded bilayers (Fig.1c). These neighbouring bilayers make contact through weak CH...O interactions via the n-glide symmetry to complete the crystal packing. A densely packed Langmuir monolayer of amphiphilic homochiral α-amino acid molecules should exhibit at the air/water interface a hydrogen-bonded layer arrangement very similar to that of α-glycine (Fig.1b), provided the hydrophobic moieties of the monolayer have a cross-sectional area equal to or smaller than that of the α-amino acid head groups. Consequently, a monolayer of, say, resolved (R)-α-amino acids packed as tightly as in the ac layer of α-glycine, should simulate an r-layer of glycine molecules exposed at the (010) face of the crystal, (as shown in Fig.1), and thus might induce nucleation of a glycine crystal with this face attached to the monolayer (Fig.2a). By symmetry, the corresponding monolayer of (S)-α-amino acids should induce nucleation of a glycine crystal with its ($0\bar{1}0$) face attached to the monolayer (Fig.2b). A controlled variation of the packing pattern of homochiral α-amino acid head groups can be achieved by insertion of bulky groups at various sites along the hydrophobic chain. Slight changes in the packing arrangement of the polar head groups should affect both the rate of crystal nucleation and the degree of orientation of the glycine crystals at the air/solution interface. For example, α-amino acids bearing steroids as the hydrophobic moiety should, upon compression, interfere with the regular packing of the polar head groups. Such a film should not promote the crystal nucleation of glycine. Insertion of a less bulky group, such as a fluorocarbon chain, should cause some distortion in the regular arrangement of the α-amino acid moieties.

With these ideas in mind, we synthesized three classes (I-III) of resolved amphiphilic α-amino acids for crystallization studies. Some representative monolayers used are listed in the Table. Molecules 1 and 2, which belong to class I, bear hydrophobic moieties which

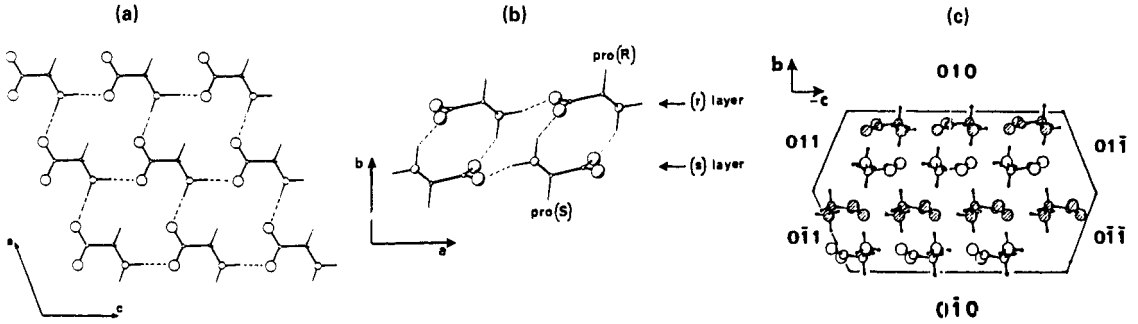


Fig. 1. (a) An ac layer of hydrogen-bonded glycine molecules viewed along the b axis. The layer is defined as r since the H atoms of the C-H bonds which emerge from the ac plane are of prochiral R configuration.

(b) A centrosymmetric bilayer of hydrogen bonded glycine molecules viewed perpendicular to the bc plane. The upper r layer is that shown in Fig.1a.

(c) Packing arrangement of α-glycine, delineated by its crystal faces. The bilayers (Fig.1b) are related by twofold screw symmetry along the b axis.

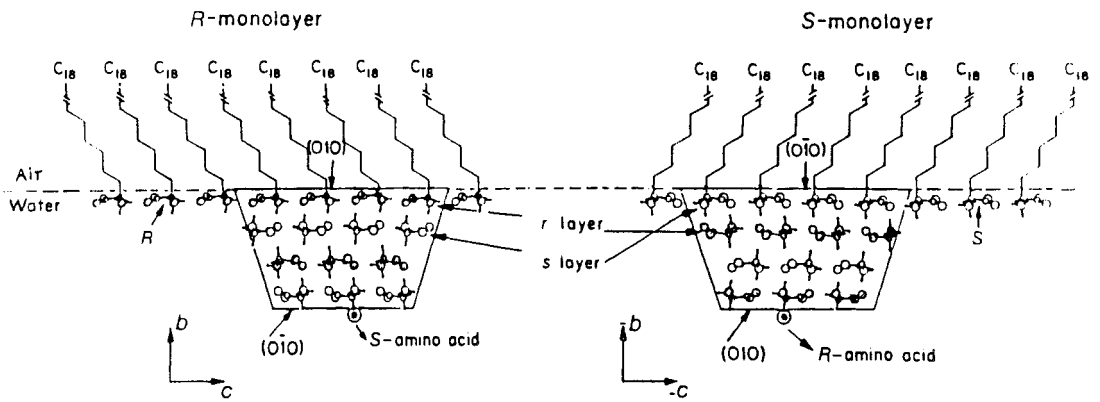


Fig. 2. Schematic view of pyramidal crystals of glycine grown under compressed R and S amino acid monolayers. The (010) face is attached to the R monolayer and the (0ī0) face to the S monolayer. S and R amino acids are shown adsorbed from solution at the (0ī0) and (010) faces, respectively.

have a cross sectional area larger than that of their polar head groups; class II is represented by the amino acid 3 in which the hydrophobic tail is partially fluorinated. Here, the cross-section of the hydrophobic tail is just slightly larger than that of the polar head group. Class III, represented by molecules 4-10 comprises molecules in which the cross-sectional area of the hydrophobic tail is smaller than or almost equal to that of the hydrophilic head group. In this class of monolayers, the glycyl head groups can in principle form a stable hydrogen-bonded two-dimensional net as found in the crystal structures of many α-amino acids, such as resolved valine, leucine or norleucine. When a Langmuir film of compound 1, with a limiting molecular area of 38 $Å^2$ and so belonging to class I, was compressed over saturated solutions of glycine, no crystallization of glycine at the monolayer-water interface was noticed in most cases. In the few instances where crystallization did occur, it was initiated inside the aqueous solution and only later on took place at the monolayer-solution interface. The crystals attached to the monolayer displayed the normal bipyramidal habit and generally assumed different orientations vis-a-vis the monolayer surface.

Table: Crystallization of α-glycine underneath floating Langmuir monolayers

| | | Monolayer | Limit. area per molec. ($Å^2$) | Degree of Orientation (%) | Face attached to monolayer | Rate of crystallization |
|---|---|---|---|---|---|---|
| 1 | S | 5-α-Cholestan-3β-OCO-$CH_2$-CH-($NH_3^+$)-$CO^-_2$ | 38 | No orient | -- | Slow (hours) |
| 2 | R | X N-CO-$CH_2$-CH-($CO_2H$)-S-$CH_2$-CH-($NH_3^+$)-$CO_2^-$ X: $CH_3$-$(CH_2)_{14}$-COO-$CH_2$-$CH_2$- | 77 | -- | -- | -- |
| 3 | S | $CF_3$-$(CF_2)_9$-$(CH_2)_2$-OCO-$CH_2$-CH-($NH_3^+$)-$CO_2^-$ | 30 | 50-79 | $(0\bar{1}0)$ | Fast (sec.) |
| 4 | S | $CH_3(CH_2)_{17}$-NH-CO-$CH_2$-CH-($NH_3^+$)-$CO_2^-$ | 27 | 39-77 | $(0\bar{1}0)$ | Fast (sec.) |
| 5 | S | $CH_3(CH_2)_{17}$-NH-CO-$(CH_2)_2$-CH-($NH_3^+$)-$CO_2^-$ | 27 | 51-96 | $(0\bar{1}0)$ | Fast (sec.) |
| 6 | R | $CH_3(CH_2)_{14}$-CO-NH-$(CH_2)_4$-CH-($NH_3^+$)-$CO_2^-$ | 27 | >99 | (010) | Fast (sec.) |
| | S | $CH_3(CH_2)_{14}$-CO-NH-$(CH_2)_4$-CH-($NH_3^+$)-$CO_2^-$ | 27 | >99 | $(0\bar{1}0)$ | Fast (sec.) |
| 7 | R | $CH_3(CH_2)_{14}$-CO-NH-$(CH_2)_2$-CH-($NH_3^+$)-$CO_2^-$ | 27 | >99 | (010) | Fast (sec.) |
| 8 | S | $CH_3(CH_2)_{14}$-CO-NH-$(CH_2)_3$-CH-($NH_3^+$)-$CO_2^-$ | 27 | 88-93 | $(0\bar{1}0)$ | Fast (sec.) |
| 9 | R | $CH_3(CH_2)_{17}$-OCO-$CH_2$-CH-($NH_3^+$)-$CO_2^-$ | 29 | >99 | (010) | Fast (sec.) |
| | S | $CH_3(CH_2)_{17}$-OCO-$CH_2$-CH-($NH_3^+$)-$CO_2^-$ | 29 | >99 | $(0\bar{1}0)$ | Fast (sec.) |
| 10 | S | $CH_3(CH_2)_{17}$-OCO-$(CH_2)_2$-CH-($NH_3^+$)-$CO_2^-$ | 29 | 73-93 | $(0\bar{1}0)$ | Fast (sec.) |

In contrast, films of the fluorinated monolayer of the resolved β-aspartate ester 3 (expressing a limiting molecular area of $30Å^2$, and so belonging to class II), induced a fast nucleation of glycine. When monolayers of S-configuration were used, well-shaped pyramids, with basal faces $(0\bar{1}0)$ and (010) attached to the interface were found with a preference of 50-79% for the $(0\bar{1}0)$ faces. (Note a).

Molecules of class III display limiting molecular cross-sectional areas in the range of $27\text{-}29Å^2$. All these resolved monolayers, when spread and compressed over supersaturated solutions of glycine, yielded fast nucleation of glycine, albeit with different degrees of (010) to $(0\bar{1}0)$ orientation. Complete oriented attachment of the expected crystal face was obtained with three monolayers, palmitoyl-lysine (6), palmitoyl-α,γ diaminobutyric acid (7) and stearylaspartate (9). This result is depicted in Fig.3 for a crust of glycine crystals grown under a monolayer of stearylaspartate from a supersaturated solution of glycine containing 1% of racemic glutamic acid; here the additive is used as a means for determining the ratio of (010) to $(0\bar{1}0)$ oriented glycine crystals. When monolayers of R-configuration were used, the resulting attached glycine crystals (Fig.3a) were found to contain as an occluded additive only (S)-glutamic acid, as established by HPLC analysis (Fig.3b). This enantioselective occlusion is possible only if the $(0\bar{1}0)$, but not the (010), faces of the attached crystals of glycine are exposed to the solution (ref.5b,c.). This crystal orientation was independently established by X-ray diffraction measurements on specimen crystals. By the same mechanism the S-monolayers yielded $(0\bar{1}0)$ oriented crystals which occlude exclusively the (R)-glutamic acid (see Fig.3c,d). Experiments conducted with monolayers of resolved palmitoyl ornithine (8), and stearyl glutamate (10), resulted again in a fast crystallization but with a lower degree of orientation (see Table). Crystallization of glycine under a monolayer of (S)-aspartic acid-β-stearyl amide (4), with a surface area similar to that of stearyl aspartate was slow; these attached crystals were either (010) or $(0\bar{1}0)$ oriented pyramids as well as non-oriented bipyramids. When a

Note a: We shall refer to crystals with their (010) or $(0\bar{1}0)$ faces attached to the monolayer as "(010 or $(0\bar{1}0)$ oriented" respectively.

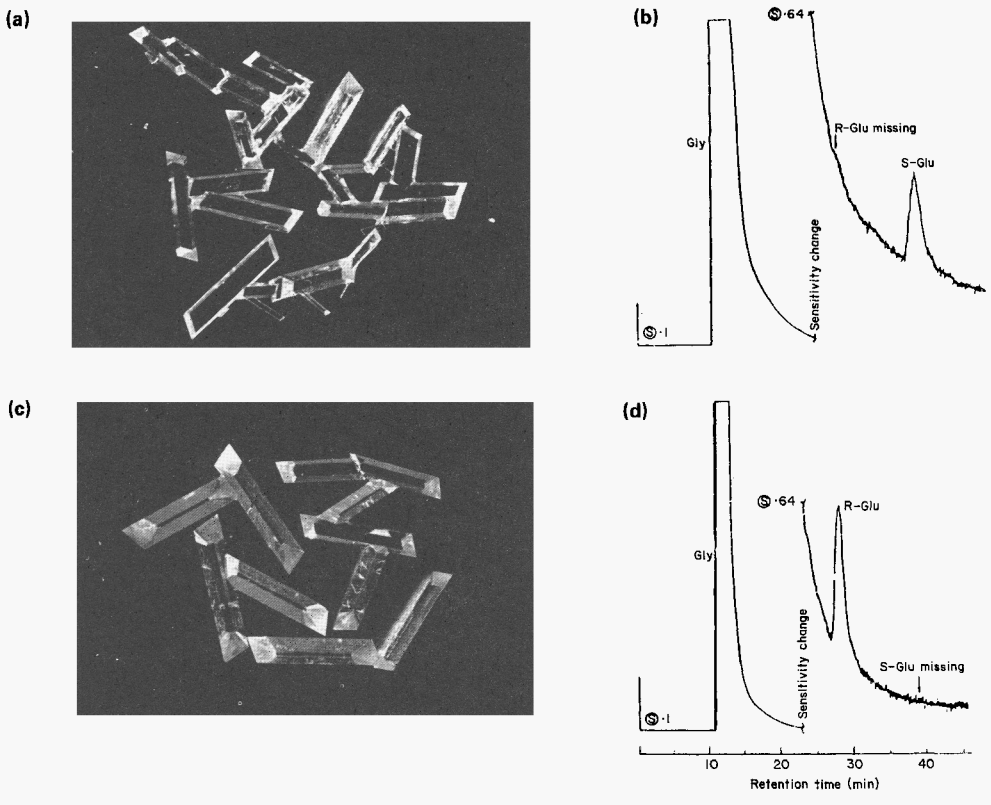


Fig. 3. (a) A crust of glycine crystals grown under a monolayer of compound 9 (R) in the presence of (R,S)glu. All the crystals expose their (010) faces to the monolayer and exhibit the same enantiomorphous morphologies.

(b) HPLC analysis of an ensemble of crystals grown as in (a). After washing with water, sensitivities as indicated.

(c) A crust of glycine crystals grown under a monolayer of compound 9 (S) in the presence of (R,S)glu. All the crystals expose their (0$\bar{1}$0) faces to the monolayer and exhibit opposite enantiomorphous morphologies of those in (a).

(d) HPLC analysis of an ensemble of crystals grown as in (c). After washing with water, sensitivities as indicated.

monolayer of resolved (S)-glutamic acid $\gamma$-stearyl-amide (5) was used, plate like crystals were obtained with a preferred (0$\bar{1}$0) orientation (see Table).

The results discussed above clearly indicate that a molecular surface area of the monolayer, as determined from the $\pi$-A isotherm, similar to that of $\alpha$-glycine, is a necessary condition for complete oriented growth of the $\alpha$-glycine. But this constraint was found to be insufficient, since monolayers with different hydrophobic chains, but with similar molecular surface areas, might assume different arrangements of their polar head-groups, leading to nucleation of crystals expressing different attached faces.

We may account for the appearance of oppositely oriented crystals of glycine [e.g., (010) oriented crystals underneath an S-monolayer], by examining how the crystal may "nucleate" below the pseudo-centrosymmetric hydrogen-bonded bilayer composed of amphiphilic molecules and the first glycine layer (ref.2a,b). The to-be-attached second glycine layer would normally make contact via a n glide plane, as shown in Fig.1c involving the top second and third layers. A similar contact geometry involving these two layers may be achieved via a pseudo-twofold screw symmetry about the a axis, leading to oppositely oriented crystals, (A detailed discussion thereon is given in ref.2b.).

## X-RAY ANALYSIS OF FLOATING LANGMUIR MONOLAYERS

Grazing incidence X-ray diffraction and specular reflectivity using synchrotron radiation provided independent yet complementary structural information on these monolayers (ref.4a,b,c). The first method probes the in-plane structure and size of the crystalline domains of the monolayer, whereas the X-ray reflectivity data can yield the variation in electron density of the monolayer perpendicular to the water surface as well as the average cross-sectional area per molecule.

Several monolayer systems were examined. Palmitoyl-R-lysine (6), which induced complete oriented nucleation of glycine crystals, was found by surface diffraction (ref.4a), to form crystalline domains at the air/solution interface. Fig.4 depicts the experimental in-plane diffraction pattern obtained from this monolayer which proved to be a two-dimensional powder with a "coherence length" (in other words a well-ordered domain size) of about 500Å. The reflectivity measurements yielded a model of the electron density variation across the monolayer from which we derived an area per molecule of 26.8Å$^2$ and a molecular thickness of 26.2 ± 1.0Å, which compares well with the layer thickness of 26.9 ± 0.3Å provided by X-ray powder diffraction data of crystalline palmitoyl-R-lysine. The molecular thickness of 26.2Å corresponds to a tilt of the molecular chain axis of 30° from the vertical. Based on the above information, a model for the packing of the monolayer molecules was proposed and is shown in Fig.5. Its cell axes are a=5.03, b=5.46Å, $\gamma$=117.8°. The packing of the α-amino acid head groups is very similar to that of an ac layer of glycine molecules in its crystal structure. It follows that this similarity in packing is responsible for the fast and complete oriented nucleation of the attached glycine crystals. From the packing arrangement of the monolayer we see that the amide group (CONH) incorporated in the hydrocarbon chain of the molecule, contributes to the structural stability of the monolayer by interlinking neighbouring molecules via linear N-H...O=C hydrogen bonds. The linearity is made possible by the 30° tilt (from the vertical) of the molecular axis (see Fig.5). When the location of the amide group is shifted by a single C-C bond as in palmitoyl ornithine (8), the monolayer cannot form an N-H...O=C hydrogen bond with the same tilt of the chain. An N-H...O=C bond, albeit weak, may yet be achieved if the chains are tilted differently than in palmitoyl-lysine. This would also imply that the glycine moieties of palmitoyl ornithine form an arrangement different from that of the monolayer of palmitoyl lysine and the layer structure of α-glycine, and so account for the lower degree of oriented glycine crystallization found under palmitoyl ornithine. Moreover, we have not

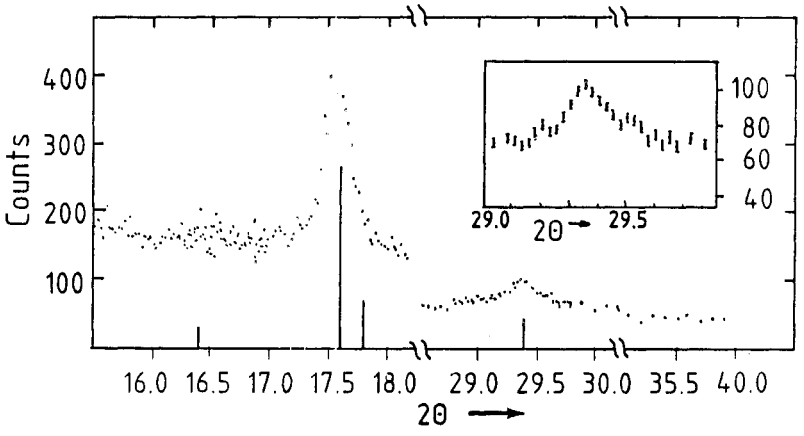


Fig. 4. Experimental X-ray diffraction pattern from a multidomain monolayer of palmitoyl-(R)-lysine. The insert shows an expanded view of the (1,2) peak.

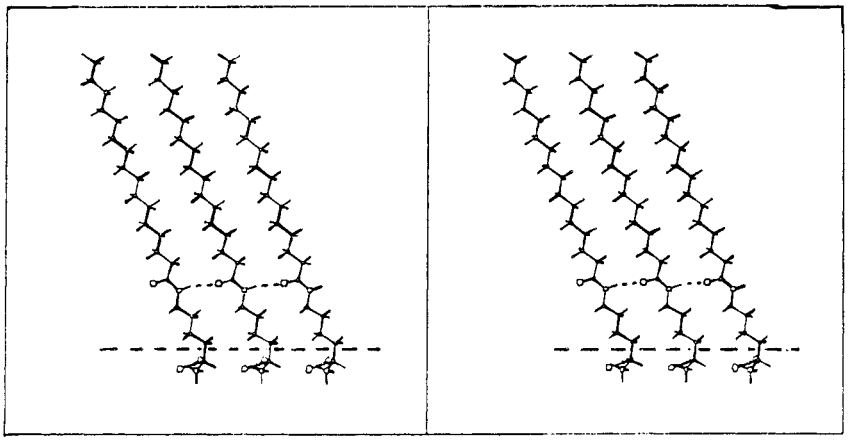

Fig. 5. A stereoscopic view of a monolayer of palmitoyl-R-lysine floating on water perpendicular to the monolayer plane.

yet been able to observe surface diffraction peaks from this monolayer, also indicative that the molecular arrangement is different from that of palmitoyl lysine. This deduction is strengthened by the observation that a further shift in the position of the amide group by another C-C bond as in (7), restores the ability of the molecules to form stable intermolecular N-H...O=C hydrogen bonds, as reflected by the completely oriented crystals of glycine underneath this monolayer.

Additional information on the effect of side chain modification on the packing arrangement of the head groups was extracted by surface X-ray diffraction on the fluorinated Langmuir monolayer 3 (ref.4c) which belongs to class II. A $\pi$-A isotherm of 3 (Fig.6a) shows that the monolayer undergoes a phase-transition at about 25 mN/m. The X-ray diffraction measurements mirror this observation. At high pressures one diffraction peak with a d-spacing of 4.97Å was observed. On decompression of the monolayer, this single peak split into two with d-spacings of 5.11 and 5.00 Å (see Fig.6b). These data, together with the reflectivity measurements yielded the following structural model. In the decompressed state ($\pi$ < 25 mN/m) the molecules pack in a distorted hexagonal net ($\underline{a}=\underline{b}=5.82$Å, $\gamma=118.5°$) with a molecular tilt of 20±10° (Fig.7a). For $\pi>\pi_s$, the lattice is hexagonal ($\underline{a}=\underline{b}=5.74$Å, $\gamma=120°$) and the molecules are vertically aligned. The hydrophobic chain is shown in Fig.7 . The $(CF_2)_9CF_3$ moiety of the chain adopts a helical conformation with a rotation of approximatly 15° per C-C bond. There is thus a distinct mismatch between the layer structure of the $\alpha$-amino acid moiety of the fluorinated monolayer and the layer structure of $\alpha$-glycine in terms of molecular tilt and cell axes ($\underline{a}=\underline{b}=5.74$Å, $\gamma=120°$ versus $\underline{a}=5.11$, $c=5.46$Å, $\beta=111.7°$).

The surface X-ray diffraction studies indicate well ordered domains of about 500 Å for compressed palmitoyl lysine and 1000Å for the fluorinated monolayer. But these results do not specify the minimum domain size required to induce crystal nucleation. In order to obtain information as to the threshold domain size of the monolayer required to induce nucleation of glycine, we made use of mixed monolayers. Crystallization experiments under mixed monolayers of (R,S)-palmitoyl-lysine were performed with the hope that these molecules would resolve spontaneously into enantiomeric clusters. Thus by varying their enantiomeric molar ratio [R:S] we would be able to vary their relative cluster size. By observing the ratio of the number of nucleating (010)/(0$\bar{1}$0) oriented glycine crystals, as a function of the enantiomeric [R:S] ratio, we would get a measure of the number of molecules required to induce crystallization. It was found that up to 16% of palmitoyl-R-lysine could

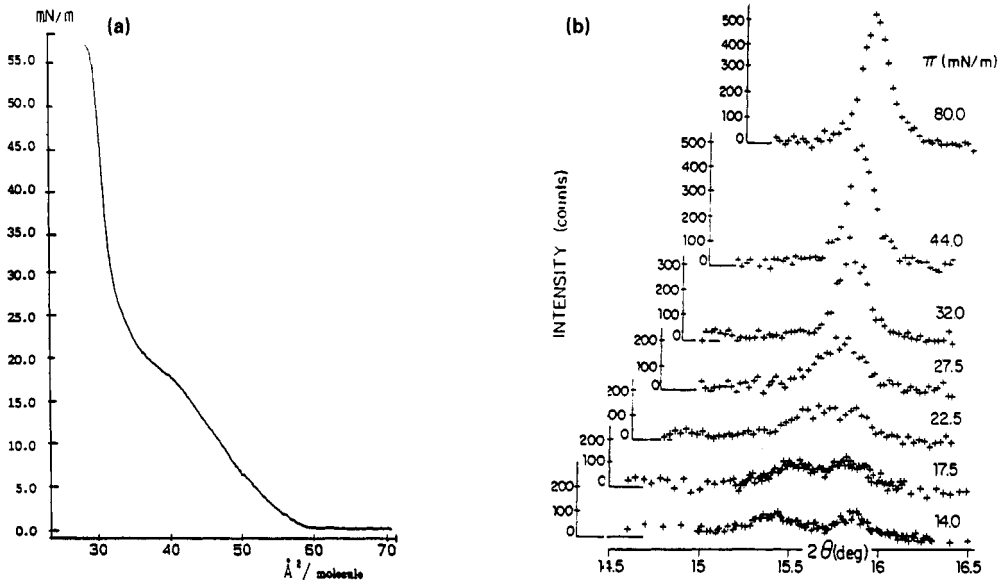


Fig. 6. (a) $\pi$-A diagram of 3 at 20°C; (b) Grazing angle diffraction data measured for a Langmuir monolayer of 3 at the surface pressures indicated in the Figure.

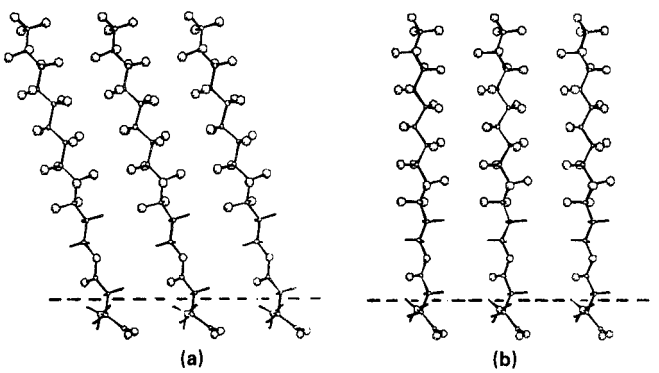


Fig. 7.
Models for the structure of a Langmuir monolayer of 3:
(a) Side view of the α-phase at surface pressures below 25 mN/m.
(b) Side view of the β-phase at surface pressures above 25 mN/m.

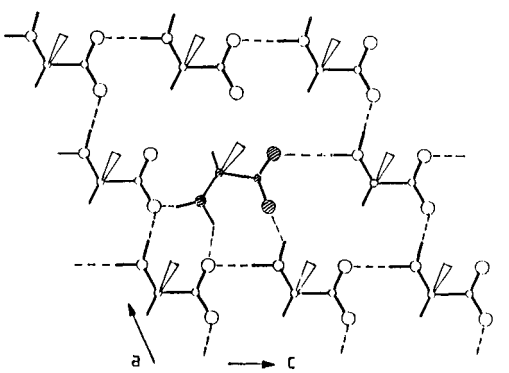


Fig. 8.
Possible packing arrangement for inclusion of one S-α-amino acid molecule in a layer of R-α-amino acid molecules. The wedges represent the molecular side chain and all point in the same direction.

be included in the S-monolayer before (010) oriented crystals of glycine also began to appear. However, surface X-ray diffraction measurements revealed that as little as 4% of the opposite enantiomer can destroy the diffraction peak, indicating that the lattice of the monolayer becomes sufficiently distorted to impart a glass-like packing. Fig.8 shows the possible packing for inclusion of one S-molecule in a layer of R-molecules. We may reconcile these diffraction and crystallization results by assuming that the "glass-like" structure of the monolayer is sufficiently ordered over several unit cells only to permit oriented nucleation of α-glycine.

## CRYSTALLIZATION OF NaCl UNDER MONOLAYERS

In the α-amino acid surfactant/glycine system the polar head groups at the interface may be regarded as forming the first layer of the to-be-grown single crystal. In principle, one may extend this approach by designing surfaces which may lead to the organization of a layer of atomic or molecular ions in solution. The structure of such an ionic layer may be similar or complementary to the layer structure of the underlying to-be-nucleated crystal. In order to probe the feasibility of this approach, we studied the nucleation of sodium chloride underneath several monolayers (ref.6).

Sodium chloride precipitates from aqueous solutions in the cubic space group Fm3m, $\underline{a}$=5.638Å, exhibiting {100} crystal faces. When crystallized under specific conditions, two other less stable faces, {110} and {111} can be expressed. The (110) face (Fig.9a) is composed of alternating rows of $Na^+$ and $Cl^-$ ions, separated from one another by 2.84Å. On the other hand, a pure (111) face is composed of ions of the same kind, (i.e., $Na^+$ or $Cl^-$) as shown in Fig.9b. The juxtaposed layers are of opposite charge, and so neutralize the system.

When monolayers of arachidic or stearic acid, which form hexagonal nets on compression (ref.4d), were spread over an NaCl solution, 70-90% of the sodium chloride crystals formed under the monolayer were attached thereto with their {111} faces. As mentioned above, this layer is comprised of ions of one type only. Were we to align $Na^+$ ions underneath a layer containing carboxylate head groups, the $Na^+$ ions would, in an ordered system, pack in an identical hexagonal net in order to conserve charge neutrality. The hexagonal lattice of the (111) face of NaCl is $\underline{a}=\underline{b}$=3.99Å, $\gamma$=120° with an area of 14.5Å$^2$. Thus, there can be no structural match between the top layer of $Na^+$ ions attached to the monolayer with an area/molecule of approximately 20Å$^2$ and the underlying (111) layer of $Cl^-$ ions of area 14.5Å$^2$, but we may deduce that the attached layer of $Na^+$ ions induces formation of the top (111) layer of $Cl^-$ ions by electrostatic forces, and so account for the observation that up to 90% of the NaCl crystals are attached with their (111) faces to the monolayer. When a monolayer of carboxylic acids which bear a styrene or diacetylenic group in the side tail was used, a pronounced reduction of the number of crystals was noticed.

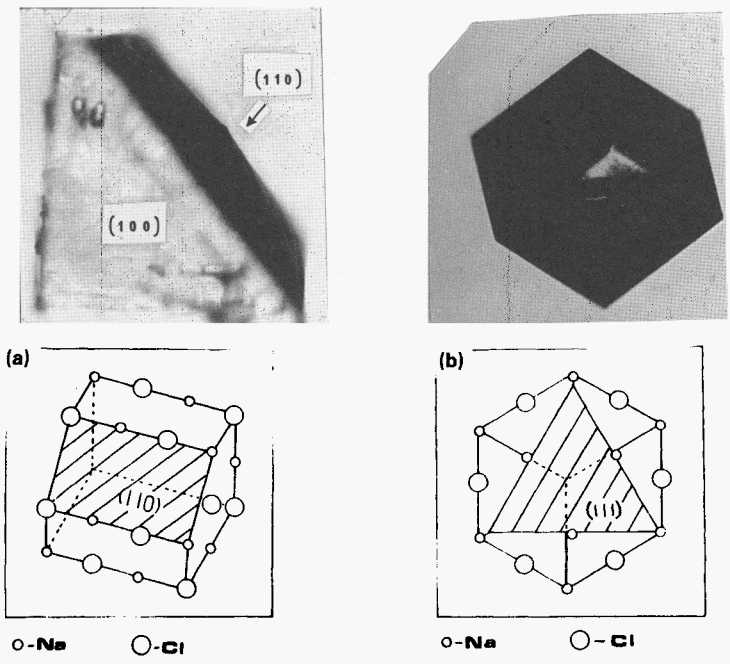


Fig. 9.
Crystals of sodium chloride grown under monolayer of
(a) stearyl-R-glutamate;
(b) stearic acid

This result is in keeping with the expectation that by further increasing the area per monolayer molecule, the "Stern" layer (ref.7) of $Na^+$ ions below the charged carboxylate layer is more diluted, so reducing the chances for attached nucleation of NaCl with its (111) face. Indeed, a compressed monolayer of cholesteryl succinate, with an area per molecule of ~ 38Å$^2$, does not induce crystallization of NaCl at all.

Monolayers of zwitterionic α-amino acids promote, in the pH range 3 to 10, a fast nucleation of NaCl. Over 90% of these crystals nucleate from the (110) face, the remainder from either (100) or (111) (ref.8). We may account for the preference of the (110) face on the following grounds. The distribution of $Na^+$ and $Cl^-$ ions at the (110) face of NaCl and that of the $NH_3^+$ and $CO_2^-$ zwitterionic groups of the glycine moieties of the monolayer are complementary to one another. The distance between adjacent rows of $Na^+$ and $Cl^-$ ions on the (110) face equals $\underline{c}/2$, that is 2.8Å (see Fig.9a); the average distance between adjacent rows of $NH_3^+$ and $CO_2^-$ groups along the $\underline{b}^*$ reciprocal direction in the monolayer of the fluorinated system is 2.5Å. These two values indicate that a strong electrostatic interaction may be achieved between the two layers involving nearest-neighbour contact between rows of ions of opposite charge, if the (110) net of NaCl in contact with the monolayer does not exceed three unit cells in its $\underline{c}$ direction. An NaCl net larger than three unit cells would lead to eventual contact between rows of ions of the same charge.

Spreading a monolayer of octadecylamine, which is positively charged, promotes nucleation of NaCl at the interface from the natural {100} face (Fig.9c). This monolayer has a limiting molecular surface area of 31.0Å$^2$ which is almost equal to the unit surface area of NaCl on its (100) face (31.8Å$^2$). The match between these two surfaces suggests that chloride ions penetrate between the positively charged octadecyl ammonium molecules in order to preserve charge neutrality, so inducing nucleation of the (100) face of NaCl.

## LANGMUIR-BLODGETT FILMS

The present studies suggest that in principle it should be possible to coat solid supports with a structured monolayer for the oriented growth of crystals. Indeed, we were able to coat glass with Langmuir-Blodgett films exposing their polar head groups to the solution for the controlled oriented growth of glycine and NaCl, enabling simultaneous comparison of the crystallization at the air/solution and solid/solution interfaces. Crystallization results for both NaCl and glycine were almost identical at these two interfaces. Thus, for example, when glycine was grown on glass coated with a monolayer of palmitoyl-R-lysine (from aqueous solution containing 1% of DNP-$N^\varepsilon$-S-lysine), yellow plates attached to the film with their (010) face were found. When the coated film was of S-absolute configuration, enantiomorphous transparent pyramids attached with their (0$\bar{1}$0) face to the film were obtained (ref.6). Analogous studies were carried out in crystallization of NaCl on surfaces coated with stearic acid and stearyl glutamate (10). Fig.10a shows a predominant number of crystals with their (111) face attached to the monolayer. Fig.10b shows crystals of NaCl with their (110) and (100) faces attached to the surface.

At least two possible mechanisms may explain the observed results. The first one is that nucleation starts at the floating Langmuir monolayer and crystal nuclei are transferred together with the monolayer onto the glass support. A second possibility is that the monolayers deposited on the glass slide assume a structure similar to that of the floating Langmuir film and so should initiate the crystal nucleation. Some support for the latter mechanism comes from the observation that crystal nucleation of sodium chloride crystals is faster with Langmuir-Blodgett films as compared to the floating Langmuir ones. Definite

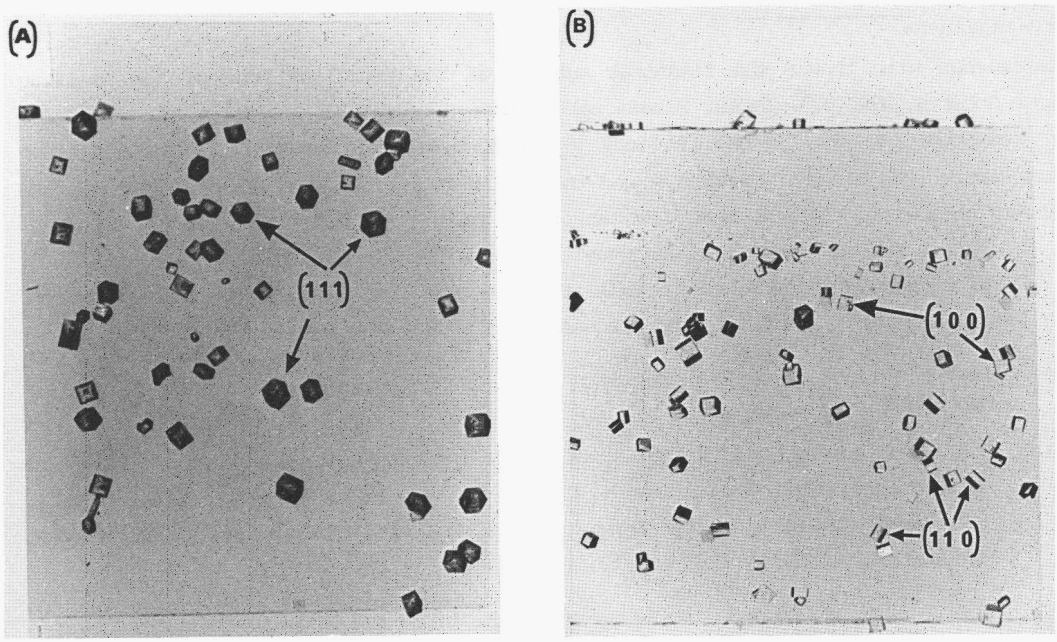


Fig. 10. Photographs of crystals of NaCl grown on glass supports coated with (a) stearic acid, (b) stearyl glutamate.

(a) Predominance of NaCl crystals with their (111) face attached to the monolayer appearing as hexagons. Note absence of crystals with their (110) face attached to the monolayer, which are rectangular with shaded edges. Three hexagons are denoted.

(b) Appearance of NaCl crystals attached with their (110) and (100) faces to the monolayer. Note the shaded edges of the (110) attached crystals.

determination of these possible mechanisms should become possible by independent assignment of the structures of Langmuir-Blodgett films by X-ray diffraction.

## CONCLUSIONS

Langmuir and Langmuir-Blodgett films have been used for the study of crystal nucleation. The monolayers were designed such that the polar head groups are arranged in a manner similar or complementary to a layer of molecules or ions belonging to the face of the to-be-nucleated crystal at the interface. The packing arrangement of some of the floating monolayers were studied by grazing incidence X-ray diffraction and reflectivity, using synchrotron light.

Oriented crystallization of glycine and sodium chloride was induced under a variety of monolayers. For both systems the structure of the nucleating face of the attached crystals proved to be a sensitive probe of the match or complementarity between the packing arrangement of the head groups of the monolayer and the layer structure of the nucleated face of the crystal. This stereochemical correlation may be utilized for obtaining structural information on domains of amphiphilic molecules at interfaces for those systems which are not yet amenable to present techniques, such as X-ray diffraction, but which are able to induce oriented crystallization. Such experiments should provide, eventually, information on the size and structure of molecular clusters en route to crystal nucleation. Finally, the design of surfaces on solid supports might prove to be of practical importance in crystal separation processes.

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