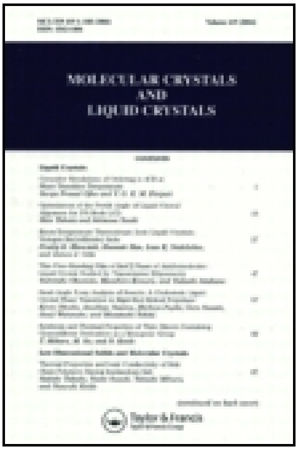

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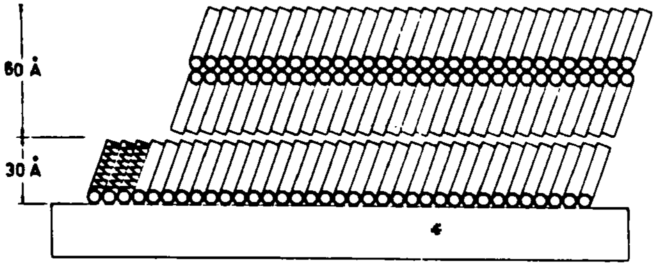
Abstract

Solid state chemical reactivity in L.B. films is used to insert inorganic or organic species in a layered organic matrix giving rise to organized insertion compounds with novel physico-chemical properties.

INTRODUCTION

The general trend in solid state chemistry is to consider that the reactivity is governed by the structure of the matrix [1-4]. Whereas current studies are usually performed in inorganic layered matrices (graphite, chalcogenides) or in clathrate cyrstals with urea, dextrin, etc., we would like to present here L.B. films as an organic matrix into which inorganic compounds can be inserted. We shall emphasize as well the influence of the structure upon the reactivity, and vice vetsa, in L.B. films. Here it is possible to confine small ions or molecules in parallel polar planes in which reactions can take place that are often, as a matter of fact, matrix controlled [5]. Hence metastable phases can be obtained and preserved for a long time. New species, free from the initial matrix, can also be synthesized in situ, in the form of very thin films (d < 10 Å, which is a mean value for the thickness of the polar planes). These inserted compounds are separated by equidistant layers of inert organic material (Fig. 1).



Layered structure of L.B. films.

PRINCIPLE

L.B. films are layered assemblies of amphiphilic molecules deposited by the now well-known Langmuir-Blodgett technique [6]. The long aliphatic chains act as packing pieces keeping apart the parallel polar planes where chemical reactions can take place under control. Hence the matrix is made of organic molecules and mineral species are introduced in the polar plane by diffusion followed by a reaction. Diffusion alone is not enough since the atoms or molecules have to be linked by a chemical bond to the matrix to produce stable, organized products. If no reaction takes place the diffused aqueous species do not remain after washing with pure water, or on re-exposure to air when the diffusion is performed from vapour. In short the technique consists in bonding the guest to the matrix in the first stage and freeing this guest afterwards by precipitating it in another combined form in the second stage. From this, it is obvious that the best analytical means is infrared spectroscopy which describes the reactivity of the organic matrix and gives proof of the bonding of the diffused guest to it, at the first stage. In the second stage, the initial IR spectrum of the matrix is recovered. The inorganic compound must be detected by another technique, for example, electron diffraction, electronic microscopy or UV-visible spectroscopy.

This is illustrated here by a few examples which are, of course, not exhaustive.

I. INSERTION OF INORGANIC GUESTS.

1.1. Silver [7].

An L.B. film (20 layers on each side of a calcium fluoride substrate) of behenic acid ($C_{21}H_{43}COOH$) is immersed in an aqueous solution of silver nitrate (10^{-2}M). The reaction is quantitative. Every carboxylic group shifts from COOH ($\nu_{C=O}$ 1708 cm^{-1}) to COO^- (ν = 1520 cm^{-1}) in the infrared spectrum. The silver salt is then obtained and one Ag^+ is bound to one molecule of the matrix (washing with pure water eliminates the excess of silver nitrate). Also the

X-Ray diffraction pattern is different from the initial pattern of the pure acid and is enhanced by the higher electron density of silver (COO Ag) compared to hydrogen (COOH) [8].

In a second stage, the silver behenate is reduced by hydrazine vapour and the infrared spectrum of the behenic acid matrix is recovered. However the acid is in a different metastable phase (a form instead of the initial b form) the crystal lattice of which is similar to the silver behenate one. Silver is deposited in situ, in the polar planes, as small clusters 10 to 20 Å in size as shown by transmission electron microscopy. To summarize the synthesis, the first reaction involves a structural change of the matrix due to the reactivity and the second one takes advantage of the matrix rigidity to prevent any extended aggregation.

1.2. Metal sulfides.

Silver or any metal salt of behenic acid in L.B. films reacts under a stream of hydrogen sulfide. This regenerates the acid (in form a or b depending on the structure of the salt) and precipitates the metal sulfide (CdS-AgS-CuS-ZnS-NiS-PbS) inserted in the polar planes.

1.3. Metal halides.

Instead of H_2S streams of HCl, HBr, HI deposit the metal halides.

In a more sophisticated matrix such as ω diyne pentacosanoïc acid (absorbing in the UV region) the copper acetylide (λ_{max} = 430 nm in the visible region) is formed by diffusing copper (I) chloride in an ammonia solution.

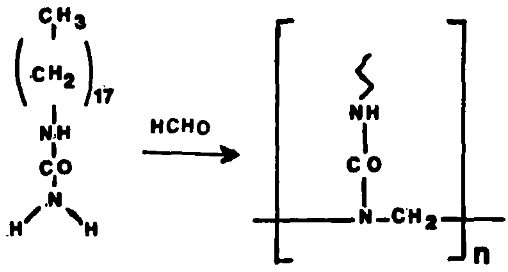
$$H-C\equiv C-C\equiv C-(CH_2)_{20}COOH \xrightarrow[NH_4OH]{Cu^+} Cu-C\equiv C-C\equiv C-(CH_2)_{20}COOH$$

($\nu_{\equiv C-H}$ at 3300 cm^{-1} vanished in the infrared spectrum). HCl vapour hydrolyses this acetylide, returning the diyne and precipitating CuCl in situ. The presence of CuCl is evidenced by passing iodine vapour which gives the following reaction: $CuCl \xrightarrow{I_2} CuI_3^-$. This periodide is detected at 290 and 360 nm in the UV spectrum). At this stage the recovered ω diyne pentacosanoïc acid can be polymerized under radiation giving the proof of a non disordered structure in spite of the presence of the insertion compound.

Other reactions in diynoïc acid matrices have been performed and interesting reactions obtained [9].

2. INSERTION OF ORGANIC GUESTS : OCTADECYL UREA-FORMOL.

This example deals with insertion followed by reactivity with the matrix, giving rise to a new matrix. Of course this guest matrix coupling can be extented to other couples of host and guest (phenol-formaldehyde, diketone-hydrazine...) [10]. Upon diffusion of formaldehyde vapour at room temperature in an L.B. film (30 layers) of octadecyl urea, addition and elimination reactions take place. The methylene bridges fit well the distances between two neighbouring polar heads in a close packed arrangement (Fig. 2)



A second diffusion of formaldehyde vapours, at higher temperature, cross-links the previous linear polymer by reaction of the remaining NH groups. The details and mechanisms have been described elsewhere [11]. Here is also emphazised the role of the organized assembly since, in bulk, no reaction is detected.

3. INSERTION OF ORGANIC + INORGANIC GUESTS.

Among the numerous goals to be reached on the way towards molecular electronics, one is to achieve electron transportation, i.e., conducting monomolecular films. An opportunity was given by the well-known stacking of TCNQ molecules in the form of complexes between a donor and an acceptor. It was obvious that a molecular arrangement of TCNQ free from the matrix was needed: the stacking of TCNQ must not be too strongly matrix-controlled since an accurate value of 3.3 Å is required for the intermolecular distance in a stack. The aliphatic chains, in a close packed assembly provide at least a distance of 4 to 5 Å between two neighbouring polar groups. The strategy chosen involves the synthesis of an amphiphilic charge transfer salt of TCNQ with the aliphatic chain bound only to the donor or cation and the fabrication of an L.B. film from its solution. $TCNQ^-$ is found dimerized and parallel to the substrate in the polar planes [12]. In the first stage, diffusion of iodine vapour provides the oxidation of $TCNQ^-$ into $TCNQ^\circ$ molecules. These molecules are now free from the matrix and can reorient independently of the amphiphilic donor periodide formed in the reaction (N-docosyl pyridinium was the donor in the experiment as described in [13]).

In the second stage, diffusion of aqueous lithium iodide leads to monomolecular conducting films of $LiTCNQ_x\ (I_3)_{1-x}$ regularly inserted and confined in the polar planes.

An example related to another TCNQ conducting complex is published elsewhere [14].

CONCLUSION.

These non exhaustive experiments are presented to focus on the high reactivity of these organized assemblies called L.B. films and on the chemistry involved at the molecular scale. The influence of the layered matrix, together with the relative freedom of the polar heads inside the volume allowed by the polar planes, gives rise not only to important chemical reactivity but also the possibility of reorganization of the guests if necessary (such as conducting stacks of TCNQ). The flexibility in these matrices (L.B. films) is tremendous compared to rigid monocrystals which are often either destroyed by the introduction of the guests or are non reactive.

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