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Publisher: Taylor & Francis

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UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gmcl16

Planned Multilayer Assemblies by Adsorption

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To cite this article: Lucy Netzer, Radu Iscovici & Jacob Sagiv (1983): Planned Multilayer Assemblies by Adsorption, Molecular Crystals and Liquid Crystals, 93:1, 415-417

To link to this article: http://dx.doi.org/10.1080/00268948308073545

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Mol. Cryst. Liq. Cryst., 1983, Vol. 93, pp. 415–417 0026-8941/83/9304–0415/\$18.50/0
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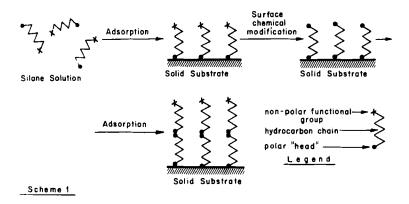
PLANNED MULTILAYER ASSEMBLIES BY ADSORPTION

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Adsorption at liquid solid interfaces is employed to construct organized multilayer structures on polar solid We have recently demonstrated that oriented compact monolayers of good quality can be obtained under suitable conditions either by physisorption or by chemisorption, using either pure compounds as adsorbates or mixtures of several components, and even using mixtures of both physisorbed and chemisorbed species. 1 Monolayer formation by adsorption offers certain important advantages as compared with the Lanmuir-Blodgett method; adsorption is a spontaneous process leading to thermodynamically film structures, there is no mechanical manipulation of the films, water is not indispensable for monolayer formation, monolayer composition and structure are usually dependent on the chemical nature and microscopic organization of the solid surface, covalent binding to the substrate and intralayer polymerization may take place simultaneously with the monolayer formation process, there are no restrictions regarding the macroscopic shape and size of the sub-However, the adsorption method has been so far shown to be suitable only for formation of single monolayers, l which limited severely its usefulness in the construction of multilayer assemblies.

It is the purpose of the present paper to describe a new monolayer assembling strategey designed to overcome

this drawback. The key step in the new method consists in the chemical activation of the monolayer coated solid surface in order to introduce polar sites for the anchoring of an additional monolayer on top of the activated one. The activation is achieved using bifunctional surfactants provided with a terminal non polar function that may be chemically modified into a polar group during the activation step. A multilayer film is thus constructed by repetition of a two steps sequence involving adsorption (chemisorption) followed by chemical activation of the surface, for each deposited monolayer (see Scheme 1).



SCHEME 1. Schematic representation of the stepwise formation of an adsorbed multilayer film.

Formation of adsorbed multilayer films of a model bifunctional surfactant, $\text{CH}_2 = \text{CH-(CH}_2)_{14}\text{-SiCl}_3$ (15-Hexadecenyltrichloro-silane, HTS), has been studied using contact angle measurements, ellipsometry, and infrared internal and external multiple reflection spectroscopy. ² The

monolayer-to-surface and monolayer-to-monolayer binding was realized through formation of covalent siloxane (O-Si-O) bridges, and the exposed monolayer surface was activated by oxidation of the vinylic groups to terminal hydroxyls.²

Our present results demonstrate that a molecular spontaneous organization process combined with a suitable chemical triggering procedure may result into a controllable route to the synthesis of an artificial super molecular organizate. The feasibility of this new approach is expected to lead to interesting developments in the field of monolayer assemblies as well as in other related areas of solid state chemistry.

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