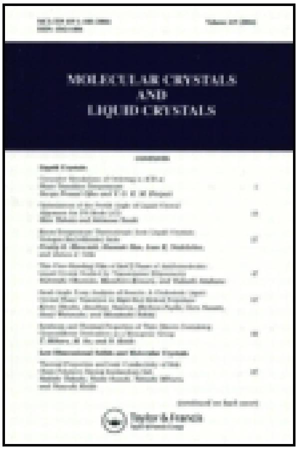

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Template Synthesis of Inorganic Clusters and 2D Molecular Networks in Multilayered Cast Films

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Version of record first published: 24 Sep 2006.

Mol. Cryst. Liq. Cryst. 1994, Vol. 240, pp. 1–7
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Printed in the United States of America

TEMPLATE SYNTHESIS OF INORGANIC CLUSTERS AND 2D MOLECULAR NETWORKS IN MULTILAYERED CAST FILMS

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Abstract Synthetic bilayer membranes are highly organized molecular aggregates and their characteristic organizations are maintained in aqueous dispersions as well as in their cast films. The interbilayer space of the cast film acts as extended two-dimensional matrices. Cocasting of aqueous bilayers and aqueous monomers/polymers can produce regular composite films. The subsequent polymerization/ cross - linking and removal of the bilayer matrices lead to multilayered 2D-networks. Ion exchange combined with chemical treatments can produce ultrathin inorganic layers and well-defined inorganic clusters.

INTRODUCTION

Biomembranes provide one of the most important structural units in the organization of the biological cell. It has been demonstrated that molecular bilayers are formed spontaneously from aqueous lipid dispersions, thus establishing that among the constituents of biomembranes, the lipid bilayer plays a most central role in maintaining biological molecular organization.

Similar bilayer membranes are prepared from a variety of synthetic amphiphiles including single-chain, double-chain, and triple-chain amphiphiles, as shown in Figure 1.[1] Because of strong self-assembling properties, these compounds become suitable as components of surface monolayers and planar bilayer membranes(BLM). The aqueous bilayer dispersion can be additionally transformed into free-standing cast films. The rich variety of the bilayer component and facile self-assembling of the unit bilayer render the cast film system very appealing as matrices for anisotropic ordering of functional molecules and for preparing two-dimensional organic and inorganic materials.

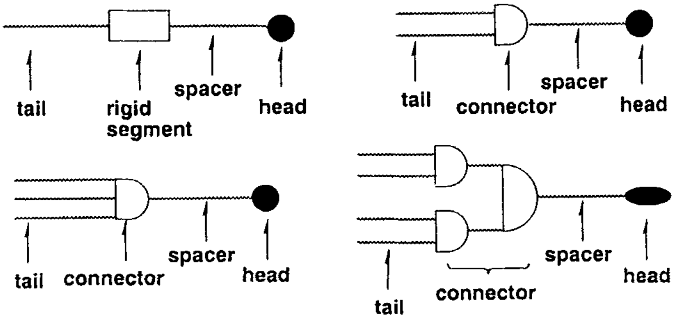


FIGURE 1 Structual elements(modules) of bilayer-forming amphiphiles.

Very recently, we directly observed individual molecular bilayers in cast films by transmission electron microscopy.[2] Minor structural differences of component molecules exerted a profound influence on the supramolecular structure of the cast film.

ANISOTROPIC INCORPORATION OF GUEST MOLECULES AND PREPARATION OF TWO-DIMENSIONAL POLYMER NETWORKS

Macroscopic anisotropy of cast multi-bilayer films is closely related to the microscopic(molecular) anisotropy of the unit bilayer. For instance, anionic Cu(II) porphyrins can be readily introduced in cast films of ammonium bilayer membranes by simple casting of mixed dispersions.[3] The spatial orientation of doped Cu(II) porphyrins is estimated by anisotropies of ESR spectral patterns that are dependent on the disposition of the film in the magnetic field. It was found that the porphyrin orientation was determined by the distribution of anionic charges on guest porphyrins and the supramolecular structure of host bilayers.

These results were subsequently extended to orientational control of protein molecules. When aqueous myoglobin is cast together with bilayer dispersions, the resulting cast film gives anisotropic ESR patterns, showing that myoglobin molecules are placed in the interbilayer space in fixed orientations that are apparently determined in a typcal case by optimized electrostatic attraction between positively-charged residues of the protein surface and phosphate anions on the bilayer surface:see Figure 2.[4] When a lipid anchor is attached to myoglobin, the anchor chain becomes inserted into bilayer, resulting in the correspondingly fixed orientation.[5]

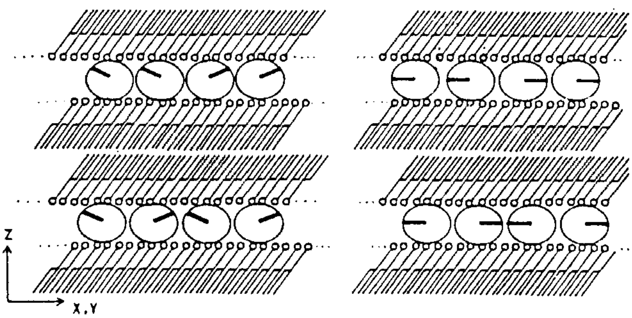
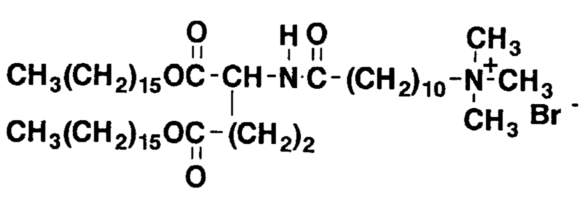


FIGURE 2 Schematic illustrations of myoglobin orientation in bilayer membranes.

Cast multibilayer films are obtainable from mixed dispersions of double-chain ammonium amphiphile 1 and bis-acrylate monomer 2.

1



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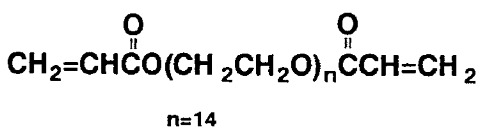


The monomer occupies the regular interbilayer space and this composite structure is not destroyed by photopolymerization. Extraction of the bilayer component with methanol leaves behind a multilayerd film of the 2D-polymer network,[6] as schematically illustrated in Figure 3.

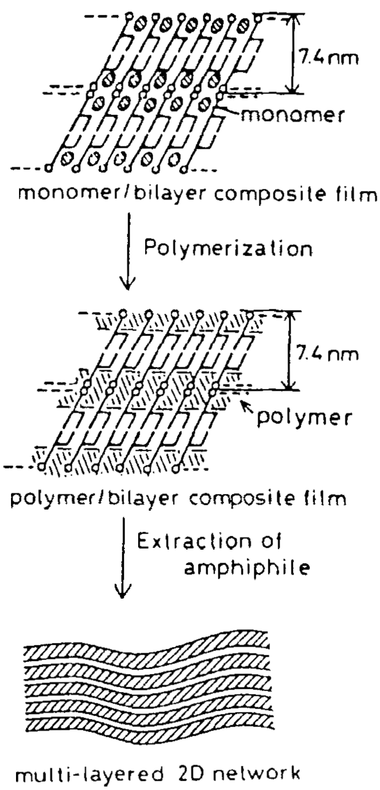


FIGURE 3 Schematic illustration of template synthesis of a multilayered two-dimensional polymer network.

Solvent swelling and some mechanical properties reflect the characteristic structural anisotropy. Charged monomers such as tetraallylammonium bromide[7] and linear polymers such as chitosan and poly(vinyl alcohol) can be used as starting materials.

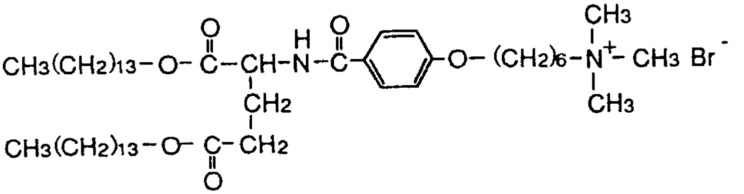
TEMPLATE SYNTHESIS OF MULTILAYERED ULTRATHIN INORGANIC FILMS

The preceding approach is applicable to synthesis of molecularly controlled siloxane networks and oriented iron oxide particles. When mixed dispersions of alkoxysilanes(e.g.,$(MeO)_3SiMe$) and bilayer components are cast and subjected to ammonia treatment, extensive hydrolysis and condensation of the alkoxysilane unit proceed, and stable films of polysiloxane 2D-network are formed upon extraction of matrix bilayers. The SEM observation of the cross section of the film demonstrates that ultrathin layers with 20-Å thickness are produced parallel to the film plane under proper conditions.[8] The morphology of the cross section is highly variable(thin layer, plates, pores, etc.) depending on the casting conditions.[9] The pore distribution of the multilayer film as measured by N_2 adsporption changes correspondingly.

In cast films of ammonium bilayers, bromide counterions are readily replaced with silicate anions. The subsequent treatment with hydrobromic acid generates silicate layers and bromide anions. This procedure can be repeated at least four times and the increment of the anionic silicate unit is stoichiometric in each cycle. Removal of the matrix bilayer by $CHCl_3$ extraction gives a self-supporting silicate multilayer.

Ultrafine particles of metal axides can be used as starting materials of inorganic multilayers. A homogeneous mixture of ammonium amphiphile 3 and an aqueous sol of amorphous Al_2O_3 particles(diameter, 10-100 nm) produces a composite cast film, which subsequently is converted to a multilayered Al_2O_3 film upon calcination at temperatures beyond 300 °C.[10]

3



Crystalline anisotropoy is found for the calcined film by X-ray diffraction and SEM observation, as opposed to an Al_2O_3 film obtained without the bilayer template.(Figure 4) A large surface area is retained in the template-synthesized film even after calcination at 1500 °C.

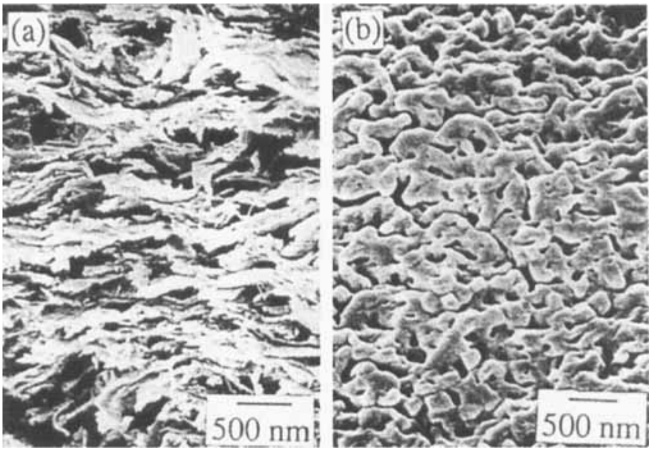


FIGURE 4 SEM photograph of α-Al_2O_3 thin films calcined at 1000 °C. The films were prepared by using the template(a) or without a template(b).

Other metal oxide sols similarly give rise to self-supporting multilayer films.

CONTROLLED SYNTHESIS OF INORGANIC CLUSTERS

Quantum-sized CdS particles are prepared by reaction of H_2S gas with $CdCl_2$-cyclam complexes preorganized in cast multibilayer films.[11] The particle size is affected by the chemical structure of the bilayer component as well as by the physical state of the matrix. Neutral CdS particles are stabilized seemingly by physical adsorption of protonated cyclam head groups, and the bilayer surface does not act as a template that can define guest structures. On the other hand, in the case of an ammonium bilayer-$CdBr_3^-$ composite film, one S atom is introduced per four Cd^{2+} ions without substantial changes in the coordination structure, suggesting the formation of a novel Cd-Br-S cluster.

Lead halide clusters are formed by ion exchange of counterions of an ammonium cast film with $PbBr_4^{2-}$ through dipping.[12] It has been known that primary alkylammonium salts of PbX_4^{-} form layerd perovskite compounds. The ion-exchanged cast film that maintains the regular layer structure displays electronic absorption at wavelength shorter than that of the 2D-cross-linked perovskite structure(PbI_4^{2-} cluster). This suggests that PbB_{r4}^{2-} clusters of lesser dimensions(linear or dot-shaped) are formed due to imbalance of the molecular area with that of the ammonium bilayer, as illustrated in Figure 5.

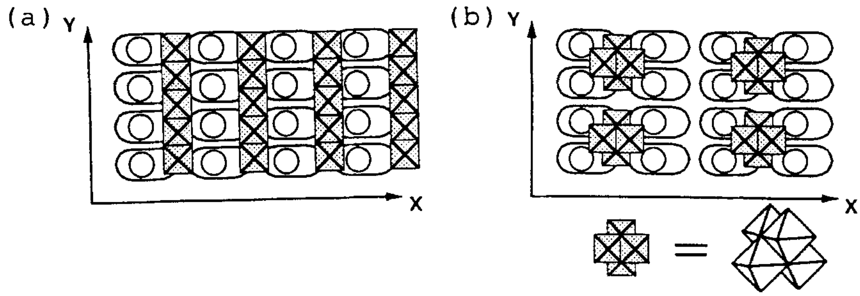


FIGURE 5 Schematic in-plane view of dimension-diminished clusters of the composition $\underline{3}_2^{2+}PbBr_4^{2-}$
(a) linear type (b) dot type

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