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

Anisotropic Incorporation of Functional Molecules and Synthesis of Low - Dimensional Clusters in Cast Multibilayer Films

Toyoki Kunitake [a]

[a] Faculty of Engineering, Kyushu University, Fukuoka, 812, Japan

Version of record first published: 23 Sep 2006.

To cite this article: Toyoki Kunitake (1994): Anisotropic Incorporation of Functional Molecules and Synthesis of Low - Dimensional Clusters in Cast Multibilayer Films, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 255:1, 7-16

To link to this article: http://dx.doi.org/10.1080/10587259408029771

Mol. Cryst. Liq. Cryst. 1994, Vol. 255, pp. 7–16
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ANISOTROPIC INCORPORATION OF FUNCTIONAL MOLECULES AND SYNTHESIS OF LOW - DIMENSIONAL CLUSTERS IN CAST MULTIBILAYER FILMS

TOYOKI KUNITAKE
Faculty of Engineering,
Kyushu University, Fukuoka 812, JAPAN

1. MOLECULAR DESIGN OF SYNTHETIC BILAYER MEMBRANES[1]

The phospholipid molecules, the major component of biomembrane bilayers, usually contain two fatty acid chains as the hydrophobic moiety and a phosphate derivative like phosphocholine as the hydrophilic moiety. Double-chain ammonium salts were found to be a simple synthetic analogue of phosphocholine lipids.[2] These ammonium salts form bilayer membranes spontaneously by dispersion in water, when the alkyl chain length is C_{10} to C_{20}. Subsequent studies demonstrated that the ammonium head group may be replaced with other hydrophilic units. Anionic double-chain amphiphiles(sulfonate, phosphate, carboxylate) have been shown to produce bilayer membranes. Nonionic(e.g.,polyoxyethylene) and zwitterionic counterparts also form bilayers.

A second class of bilayer-forming compounds are single-chain amphiphiles. Monoalkyl surfactants form fluid micelles in dilute solution. When aromatic units are introduced as rigid segments, surfactant molecules become better oriented in aggregates and produce bilayer assemblies. The rigid aromatic segment includes biphenyl, azobenzene, anthracene, etc. More recently, ammonium salts with three and four long alkyl chains were shown to undergo spontaneous bilayer formation. Furthermore, alkyl tails in the single-chain, double-chain, and triple-chain amphiphiles could be replaced with perfluoroalkyl groups.

When the hydrophilic heads are attached to both ends of appropriate(linear and cyclic) molecules, stable monolayer aggregates become available. Polymerization of bilayers and bilayer formation by polymeric amphiphiles are also possible. Examples of these bilayer-(or monolayer-) forming amphiphiles are given in Table 1. The molecular design can be summarized in terms of the module concept given in Figure 1.

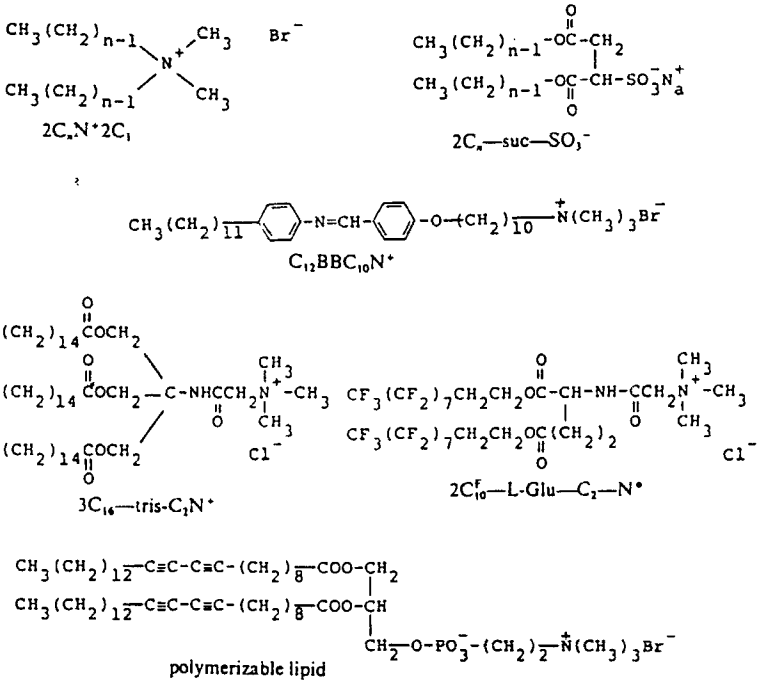


Table 1. Selected examples of bilayer-forming Amphiphiles

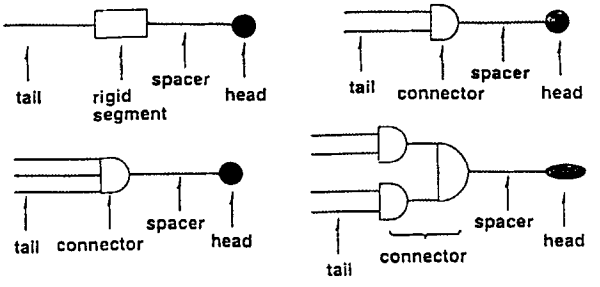


Figure 1. Structual elements(modules) of bilayer-forming amphiphiles.

2. ANISOTROPIC INCORPORATION OF FUNCTIONAL MOLECULES INTO CAST MULTIBILAYER FILMS

Aqueous bilayer membranes can be immobilized in solid forms by the following techniques[3].

(a) blending with hydrophobic polymers such as poly(vinyl chloride)
(b) coating of porous polymer films and capsules.
(c) direct casting on solid supports.
(d) as composites with hydrophilic polymers such as poly (vinyl alcohol).
(e) formation of polyion complexes with oppositely-charged polymers.
(f) build-up of multilayers by the Langmuir- Blodgett technique.

The formation of transparent cast films was first reported from aqueous bilayer dispersions of double-chain ammonium amphiphiles by Nakashima, Ando and Kunitake.[4] The maintenance of the bilayer structure in the film was confirmed by the phase transition behavior and by spectral changes of bound cyanine dyes. Subsequently, this technique was applied to bilayers of single-chain and to polymerized bilayers.

Specific incorporation of metalloporphyrins in biomimetic membranes and their functions are of great interest in relation to molecular organizations of enzymatic redox chain and of the photosynthetic reaction center. Anionic $Cu^{(II)}$ porphyrins can be readily introduced in multi-bilayer films of ammonium bilayer membranes by simple casting of the mixtures. The 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. As shown schematically in Figure 2. the porphyrin orientation is determined by the distribution of anionic charges on guest porphyrins, and the supramolecular structure of the host bilayers. Specifically, porphyrins which possess

evenly distributed anionic substituents, are incorporated horizontally on the ammonium bilayer surface. When anionic substituents are localized on one side of the porphyrin ring, the guest molecule is inserted into the spacer portion of the bilayer parallel to the molecular axis.[5]

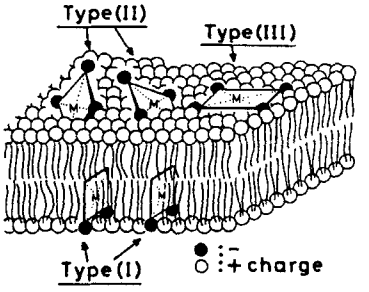


Figure 2. Schematic representation of three types of anionic porphyrin in a cast multilayer film. Type I porphyrins are inserted into the bilayer along the molecular axis of the spacer chain. Type II porphyrins are randomly placed on the bilayer surface. Type III porphyrins lie flat on the bilayer.

These results are subsequently applied to orientational control of protein molecules.[6] When aqueous myoglobin is cast together with a bilayer dispersion of a phosphate amphiphile, the resulting cast film gives anisotropic ESR patterns, as in the above porphyrin case. It is concluded that myoglobin molecules are placed in the interbilayer space in fixed orientations as shown Figure 3. The orientation is apparently determined by optimized electrostatic attraction between positively charged residues of the protein surface and phosphate anions on the bilayer surface. Chemical modifications of the protein surface that cause orientation changes endorse this supposition.

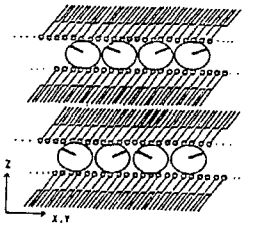


Figure 3. Schematic illustration of myoglobin orientationin bilayer membranes.

By this technique, myoglobin can be organized together with NADH and FMN coenzymes on the surface of aqueous synthetic bilayer membranes.[7] Myoglobin molecules bound onto a mixed bilayer of ammonium and phosphate amphiphiles efficiently accept an electron from NADH via FMN and subsequently release its electron catalytically to dioxygen and 1,2-naphthoquinone-4-sulfonate. Thus, myoglobin is converted from an oxygen storage protein to a redox enzyme. ESR examination of a cast film of the aqueous mixture indicates that myoglobin is bound to the mixed bilayer in a precise orientation comparable to conventional membrane-bound enzymes.

Subsequently, we successfully conducted directionally controlled anchoring of myoglobin on a dipalmitoylphosphatidylcholine(DPPC) bilayer.[8] Lipid-anchored myoglobin is obtainable from a monoalkylated heme derivative and apomyoglobin. Gel filtration and ultrafiltration studies indicate that the lipid-anchored myoglobin , but not native myoglobin, is bound to the DPPC bilayer membrane in aqueous dispersion. A cast film of the phospholipid and the anchored myoglobin displays anisotropic ESR signals, which depend on the disposition of the cast film in the magnetic field. These results suggest that myoglobin molecules are placed on the lipid bilayer in a fixed orientation by inserting the anchor alkyl chain into the bilayer, as in Figure 4. The ESR anisotropy is not observed without the anchor.

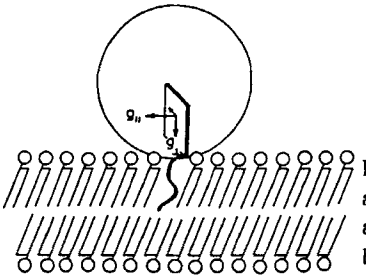
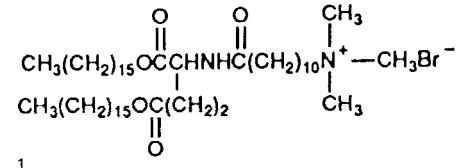
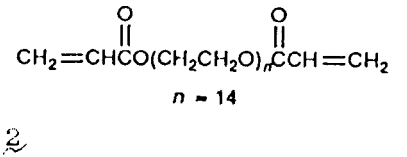


Figure 4. Schematic illustration of anisotropic incorporation of lipid-anchored myoglobin into the DPPC bilayer membrane.

3. PREPARATION OF MULTILAYERED 2D POLYMER NETWORKS BY POLYMERIZATION AND CROSSLINKING

Cast films of glutamate-based double-chain amphiphile 1 are transparent and self-supporting when prepared by itself as well as together with guest monomer 2.[9] An equimolar cast film shows diffractions up to 15th order due to a single spacing of 74 Å before and after photopolymerization. The electron density matching of the X-ray data produces the molecular packings shown in Figure 5, in the absence and presence of equimolar monomer 2.





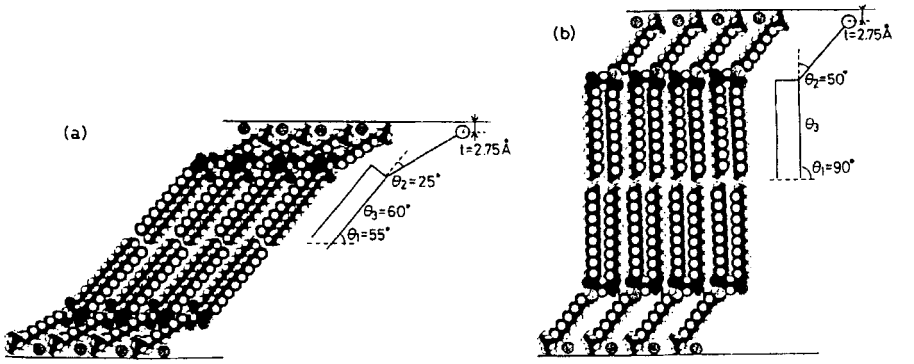


Figure 5. Most plausible molecular packings in cast films, as inferred from XRD data: (a)single-component cast film of 1; (b)composite cast film of 1 and 2, molar ratio 1:1. The θ_3 value cannot be determined in (b), as the alkyl tail is oriented parallel to the z axis.

The equimolar composite film was subsequently immersed in methanol at room temperature in order to wash out the bilayer matrix. The remaining film is flexible and self-supporting. A sufficiently dried film gives elemental analyses that are in good agreement with those of a bulk-polymerized film(3-D polymer). No significant IR differences are found between these polymers, and the

amount of the residual vinyl unit is not detectable by FT-IR spectroscopy.

The swelling ratios of the 3-D polymer film are essentially the same in the lateral as well as perpendicular directions. In contrast, the perpendicular swelling is ca. 5 times greater than the lateral swelling in the case of the 2-D polymer film. This is a strong indication of the presence of anisotropic cross-linking. The solvent would be readily accommodated in between the two-dimensional polymer networks.

The anisotropic structural characteristics are also evident in some mechanical properties. The tensile strength of the 2-D film is 3 times greater than that of the 3-D film and the ultimate elongation of the former is also ca. 5 times greater. The monomer molecules in an equimolar composite film must be uniformly distributed with thicknesses of several tens of angstroms and cross-linking is expected to extend uniformly in the two-dimensional space.

Figure 6 illustrates the preparative scheme of the multilayered polymer network.

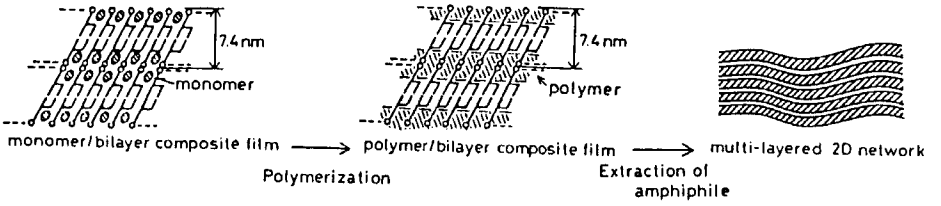


Figure 6. schematic illustrationof template synthesis of a multilayered two-dimensional polymer network.

A similar 2D network is prepared also by crosslinking of linear polymers which are incorporated in the interbilayer space of cast films.[10] Equimolar cast films are prepared from amphiphile 1 and poly(allylamine) and allowed to react with glutaraldehyde. X-ray diffraction of the film shows the presence of a layered structure with 60 Å spacing. The matrix bilayer component can be washed out by methanol. Scanning electron microscopy of a cross section proves that the film is composed of the multilayer

with less than 10 nm unit thickness.

4. MULTILAYERED ULTRATHIN INORGANIC FILMS

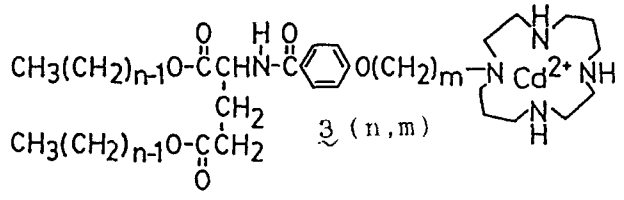
Inorganic 2-D networks are similarly prepared by taking advantage of bilayer templates. When aqueous dispersions of alkoxysilanes and bilayer membranes are cast on solid supports and treated with NH_3 gas for hydrolysis and condensation, stable composite films consisting of extended bilayers and polysiloxane 2D networks are formed. Extraction of the bilayer component provides stable films of multilayered polysiloxane 2D networks. SEM observation of its cross section shows that ultrafine polysiloxane structures are present including ultrathin layers with 20-Å thickness.[11,12] The morphology of the film cross section is variable in accordance with component structures and casting conditions.

Ultrafine particles of metal oxides have become widely available. They are suitable as starting materials of inorganic multilayers. For example, composite cast films are obtainable from aqueous Al_2O_3 sols(diameter, 10-100 nm) and an ammonium bilayer dispersion. Calcination of the film at temperatures above 300 °C produces a multilayered Al_2O_3 film.[13] A much larger surface area is retained in the template-synthesized film when compared with that of the non-templated alumina.

5. STRUCTURE CONTROL OF INORGANIC CLUSTERS

Preorganization of metal ions on bilayer surfaces may lead to structure control of inorganic clusters. Regular cast films are obtainable from a double-chain amphiphile with the cyclam head group. Stoichiometric Cd^{2+} complexes 3 are readily formed by immersion in aqueous CdX_2. Treatment with H_2S gas gives rise to a CdS-bilayer composite which is soluble in organic media. Absorption spectra of Figure 7 display considerable blue shifts of the absorption edge when H_2S treatment is conducted at

temperatures below phase transition of the matrix bilayer. This result is indicative of formation of quantum-sized CdS particles. ^{113}Cd MAS-NMR data suggest that neutral CdS particles are adsorbed to the charged bilayer surface.[14]



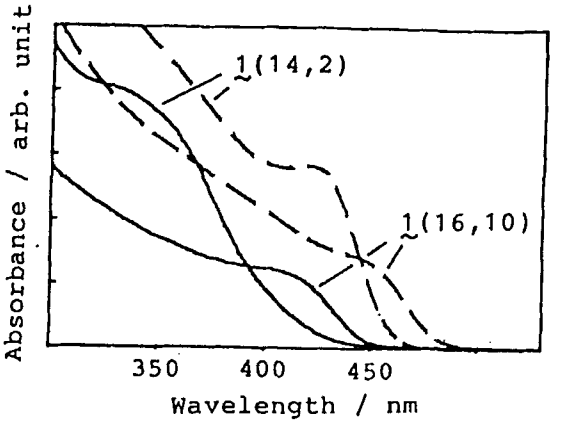


Figure 7. Absorption spectra of 3(n,m)-CdS complexes in $CHCl_3$. Solid line, 15° C; broken line, 80° C.

Metal halide clusters may be specifically formed on bilayer templates. It is known that PbX_4^{2-} n-alkylammonium complexes give 2-D crosslinked perovskite structures as in Figure 8.[15] PbX_4^{2-} anions are incorporated by ion exchange or by cocasting into the interbilayer space of ammonium cast films. Absorption spectra of the resulting neutral composite are blue shifted more than that of the 2-D perovskite compound.[16] It is conceivable that a less-than-two dimensional cluster is formed because the molecular area of the ammonium bilayer component is much larger than on half area of PbX_4^{2-}.

This approach is applicable to preparation of other metal halide clusters and novel bridged clusters.

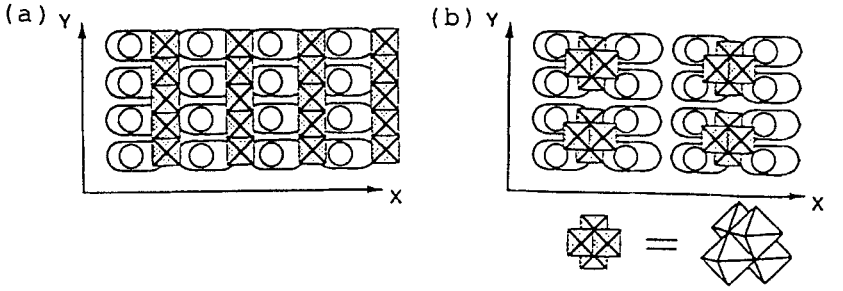


Figure 8. Schematic in-plane view of dimension-diminished clusters of the composition $3_2^{2+}PbBr_4^{2-}$
(a) linear type (b) dot type

REFERENCES

1. T.Kunitake, Angew. Chem. Int. Ed. Engl., 31, 709(1992)
2. T.Kunitake and Y.Okahata, J. Am. Chem. Soc., 99, 3860(1977)
3. T. Kunitake, Colloid Surfaces, 19, 225(1986)
4. N.Nakashima, R.Ando and T.Kunitake, Chem. Lett., 1577(1983)
5. Y.Ishikawa and T.Kunitake, J. Am. chem. Soc., 113, 621(1991)
6. I.Hamachi, S.Noda and T.Kunitake, J. Am. Chem. Soc. 112, 6744(1990)
7. I.Hamachi, S.Noda and T.Kunitake, J. Am. Chem. Soc., 113, 9625(1991)
8. I.Hamachi, K.Nakamura, A.Fujita and T.Kunitake, J. Am. Chem. Soc., 115, 4966(1993)
9. S.Asakuma, H.Okada and T.Kunitake, J. Am. Chem. Soc., 113, 1749(1991)
10. T.Ueno and T.Kunitake, Chem. Lett., 1927(1990)
11. K.Sakata and T.Kunitake, Chem. Commun., 504(1990)
12. K.Sakata and T.Kunitake, Chem. Lett., 2159(1989)
13. N.Tsutsumi, K.Sakata and T.Kunitake, Chem. Lett., 1465(1992)
14. N.Kimizuka, T.Miyoshi, I.Ichinose and T.Kunitake, Chem. Lett., 2039(1991)
15. J.Calabrese et al., J. Am. Chem. Soc., 113,2328(1991)
16. N.Kimizuka, T.Maeda, I.Ichinose and T.Kunitake, Chem. Lett., 941(1993)