Dried Foam Films

Dried Foam Films: Self-Standing, Water-Free, Reversed Bilayers of Amphiphilic Compounds**

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Foam films and lipid membranes are typical two-dimensional assemblies of amphiphiles with an inverse molecular arrangement.[1–3] In contrast to lipid membranes, which are spontaneously formed in water, foam films are formed in the air. Thin foam films are composed of a water layer sandwiched between two layers of amphiphiles that direct their hydrophobic moieties outwards.[4,5]

The first historical observation of thin foam films was probably made by Hooke as early as 1672. He reported the films as "holes in soap bubbles", as some parts of the colored bubbles turned black upon draining the water.[6] When interstitial water drains away, the foam film becomes much thinner than the wavelength of visible light and thus appears black as a result of the diminished reflection intensity.[7–9] Such films are named Black Films, and it is possible for the thickness of the water layer to be less than a few nanometers. Bélorgey and Benattar have reported that the thinnest film of ionic surfactant has only three hydration water molecules per counterion.[10] Thin foam films are usually formed in open frames placed in a sealed cell that is filled with saturated vapor, and the films are stable as long as water exists in the interstitial space.[11–14] However, they are so transient in ambient air that the interstitial water molecules have long been deemed to be indispensable to maintain the structure.[15] Herein, we report for the first time that some kinds of foam films exist even after being dried in ambient air. As illustrated in Figure 1, the dried foam films are formed by slowly evaporating the solution of amphiphilic compounds in the holes of substrates. The amphiphilic compounds spontaneously organize into a head-to-head arrangement with their hydrocarbon chains directed towards the air, and give self-standing reversed bilayers. The films form on porous substrates with micron to submicron pores and are stable under ultrahigh vacuum and at temperatures greater than 100 °C.

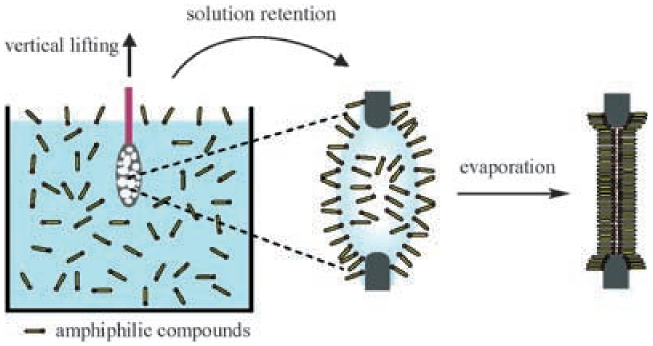

Figure 1. The formation of dried foam films; amphiphilic compounds in solution are illustrated in the monomeric dispersion in conditions below the critical micelle concentration (CMC).

A small amount of an 8.2 mM aqueous solution of dodecyltrimethylammonium bromide (DTAB, Figure 2 A) was retained in the holes of the porous substrate by the vertical lifting method. Initially, a perforated polymer membrane on a 150-mesh microgrid (Figure 2 B) was used as the substrate. The holes of a few micrometers in the polymer membrane are slightly hydrophobic and are therefore suitable for capturing small droplets of DTAB solution. The substrate was then allowed to stand for one hour in air at a humidity of between 40 and 50 %. The dried foam films obtained were too

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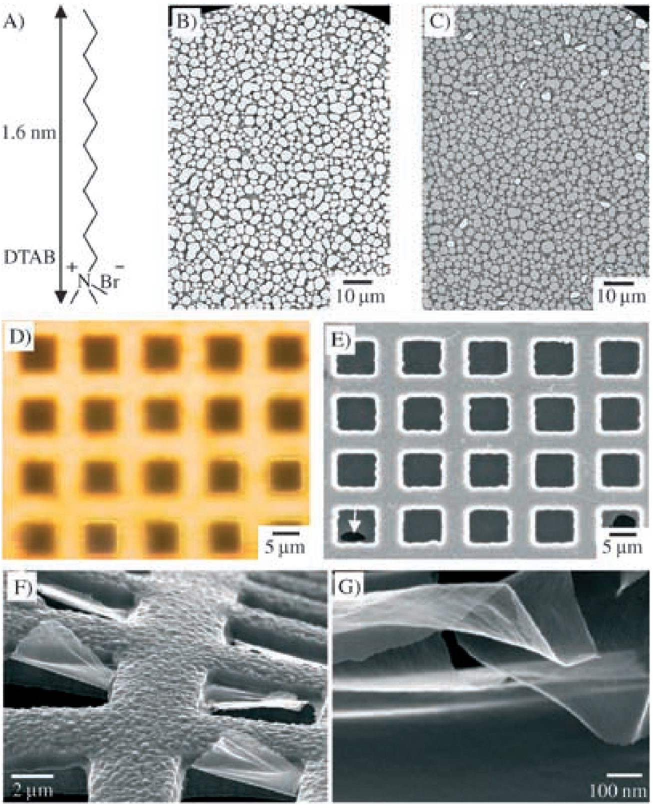

Figure 2. A) Molecular structure of DTAB; B) TEM image of a perforated polymer membrane on a 150-mesh microgrid; C) TEM image of DTAB films formed on the holes of the polymer membrane; D) confocal micrograph of DTAB films formed on a 2000-mesh copper grid; E) FE-SEM image of DTAB films formed on a 2000-mesh copper grid; F) cross-sectional FE-SEM image of DTAB films formed on a 2000-mesh copper grid; G) high-magnification of image in part F).

weak for the focused electron beam of a transmission electron microscope (TEM). However, this problem was successfully solved by coating the specimens with a thin layer of Pt nanoparticles by using a mild ion-sputter. As shown in Figure 2C, DTAB films uniformly cover the holes of the polymer membrane except for a few broken parts; the covered areas are dark because of the presence of the thin Pt layer. The films are extremely smooth and flat without any cracks. We then examined a 2000-mesh copper grid with 7-µm cells. Confocal microscopy, which has a detection limit close to 10 nm, is not useful for the observation of DTAB films owing to their thickness (Figure 2D). However, field-emission scanning electron microscopy (FE-SEM) gave a clear image of the films covering the holes of the copper grid (Figure 2E). Fully covered cells are easily distinguished from the cell; a black broken part is marked with an arrow. This sample was carefully torn and used for cross-sectional observation. As shown in Figure 2F, the film is flexible and prone to be warped by the electron beam when isolated from the wall of the copper grid. The film is transparent, which indicates that the film is thinner than the mean free-path of secondary electrons (≈5 nm) in the SEM observation. By scrutinizing the edge of the film, the thickness was estimated to be 6.5 ± 1.0 nm. The total thickness of Pt layers on both sides of the film was calculated to be about 4.0 nm from the deposition parameters. Therefore, the net thickness of the DTAB film is 2.5 nm, which means that the film probably has a bilayer structure, as the molecular length of DTAB is 1.6 nm.

Many different types of amphiphilic compounds were employed for the preparation of dried foam films. For example, double-chain-type didodecyldimethylammonium bromide (DDAB), zwitterionic dodecylphosphocholine (D-PC), nonionic polyoxyethylene dodecyl ether (Brij-35), natural egg lecithin, and two alkylsilane compounds—octadecyltrimethoxysilane (C18-Si) and octadecyldimethyl(3-trimethoxysilylpropyl) ammonium chloride (C18-N-Si)—were examined. Their dried foam films are shown in Figure 3. DDAB, D-PC, C18-Si, and C18-N-Si gave uniform films on 2000-mesh copper grids. The C18-Si film was prepared from ethanol solution (8.2 mM) because of its low solubility in water. This means that water is not indispensable for the formation of dried foam films. Interestingly, the C18-N-Si film was stable enough to withstand a focused electron beam without Pt coating. This stabilization is probably caused by the hydrolysis of methoxysilane groups and the subsequent formation of a siloxane network.

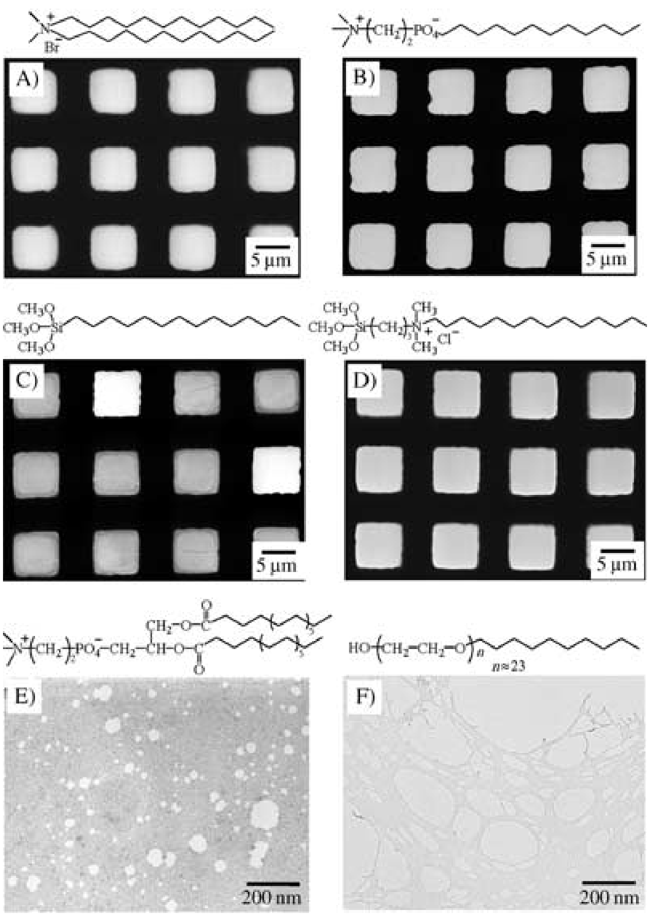

Figure 3. TEM images of the dried foam films of A) DDAB, B) D-PC, C) C18-Si, and D) C18-N-Si prepared on 2000-mesh copper grids; E) lecithin and F) Brij-35 films prepared on the holes of perforated polymer membranes. All films except C18-Si were prepared from aqueous solutions (8.2 mM) of the corresponding amphiphilic compounds.

The lecithin and Brij-35 films are very different from the others. As shown in Figure 3E, many circular pores are observed for the lecithin film. It is known that this compound spontaneously forms vesicular assemblies known as liposomes, and such a structure might be reflected in the circular pores of the dried foam film. The film made of Brij-35 appears to be a torn plastic film (Figure 3F). Natural lipids and nonionic surfactants have been extensively studied by many researchers,[16–19] who have reported that stable and densely packed foam films are readily formed because of the weak electrostatic repulsion between the two monolayers.[17,18] However, these liquid foam films are subject to serious morphology changes after evaporation of the water layer.

In previous studies, the amount of interstitial water has been estimated by transmission FTIR spectroscopy[20,21] as the water layer gives a strong absorption peak in the range from 3200 to 3600 cm^{-1}. The sensitivity of FTIR measurements is very high, and it is possible to detect a water layer not less than 0.2 nm thick.[18] To confirm the disappearance of water from the dried foam films, we recorded FTIR measurements. As shown in Figure 4, the characteristic peaks of water are not detected at all. It is clear that all the dried foam films have no liquid water and, moreover, no fluidic properties of liquids. Being skeptics, we assumed that a trace amount of water of crystallization should remain in the films. However, we could not find any evidence for the existence of this water. For example, DTAB, which has a trimethylammonium group and a bromide ion in its hydrophilic moiety, cannot strongly bind water molecules by hydrogen bonding, coordination bonding etc. Furthermore, TEM and FE-SEM observations were conducted under high vacuum conditions (lower than 1×10^{-6} torr). In these cases, all the interstitial water should have completely evaporated. What is to be emphasized is the structural stability of the dried foam films. The existence of water or a hydration layer is not necessarily essential to maintain the self-standing reversed bilayer structure.

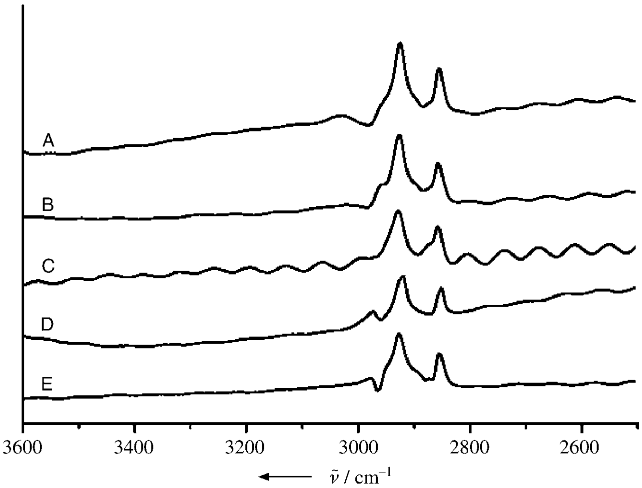

Figure 4. Transmission FTIR spectra of the dried foam films of A) DTAB, B) DDAB, C) D-PC, D) C18-Si, and E) C18-N-Si on porous alumina membranes.

What is the role of alkyl chains in the structural stabilization of the reversed bilayer structure? In the crystalline state DTAB has an interdigitated bilayer structure. As the cross-section of the alkyl chain is smaller than that of the trimethylammonium group, this amphiphilic compound acquires stable molecular packing by inserting its alkyl chains from both sides of the bilayer. However, the reversed bilayer structure does not allow such interdigitation. If the alkyl chains in an all-*trans* conformation are closely packed in the reversed bilayer, they need to be highly tilted. However, such a molecular arrangement necessarily leads to many defects. We estimated the degree of conformational disorder of the alkyl chains from the FTIR spectra. Alkyl chains that have an all-*trans* conformation in the crystalline state give CH_2 stretching vibration bands near 2918 (ν_{as}) and 2848 cm^{-1} (ν_s). These bands are known to shift up to near 2927 (ν_{as}) and 2856 cm^{-1} (ν_s), respectively, when conformational disorder is induced in the alkyl chains.[22] The dried foam films of DTAB give absorption peaks at 2924.7 (ν_{as}) and 2855.3 cm^{-1} (ν_s). These peaks are significantly shifted to higher wavenumbers from the bands of ordered alkyl chains, thereby indicating that the alkyl chains in the DTAB film are very disordered at room temperature. Similar large shifts to higher wavenumbers were observed for all the dried foam films derived from charged amphiphilic compounds (see the Supporting Information), meaning that the alkyl chains in the films are never closely packed. We have shown that dried foam films are self-standing and that if the alkyl chains are disordered, the hydrophilic moieties have to contribute to the structural stabilization. As observed in the crystallographic analysis of CTAB, the trimethylammonium groups and bromide ions form into two-dimensional ionic sheets.[23] Such a structure might be what makes it possible to keep the film in suspension. The importance of hydrophilic moieties was supported by the following phenomenological facts: C18-N-Si gives films that are very stable against a focused electron beam, and zwitterionic D-PC forms uniform dried foam films. In contrast, nonionic Brij-35 and related surfactants give highly tattered films.

The thermal stability of dried foam films was analyzed statistically by monitoring the change of the surface coverage on a 150-mesh microgrid with increasing temperature. As shown in Figure 5, the coverage of DTAB films lies in a range from 93 to 98 % from room temperature to 150 °C. However, the coverage drastically decreases to 10 % when the grid is heated at 160 °C. That this change occurs at a temperature well above the boiling point of water strongly indicates that no water is present in the dried foam films. A bulk crystal of DTAB, in which the alkyl chains have an interdigitated structure, has a melting point of 246 °C. The dried foam films that have loosely packed alkyl chains show a transition temperature about 90 °C lower than this melting point. These temperatures are considerably higher than the phase transition temperatures of biolipids as the head-groups of biolipids are fully hydrated and their phase transition is generally caused by the disordering of the alkyl chains. What is important is that the coverage in Figure 5 declines sharply. This means that the dried foam films have high molecular cooperativity: if the alkyl chains are disordered, the hydrophilic moieties have to be in the crystalline state. This is probably the reason why the films have high thermal stability.

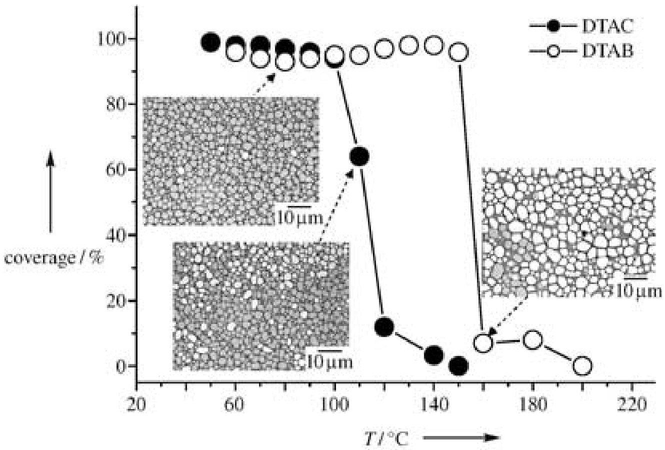

Figure 5. Temperature dependence of the coverage of DTAB and DTAC films.

The coverage of DTAC, which has a chloride ion as the counteranion of a trimethylammonium group, decreases greatly at a temperature about 40°C lower than that of DTAB, thus showing that the thermal stability is very sensitive to the size of the counterion.[24]

Foam films have been known for more than three centuries and water has always been thought to be an essential component. However, we have found that water is not always indispensable on the micrometer scale as dried foam films are quite stable in the air, under vacuum, and even at high temperature.[25] These findings have immense potential for the design of nanoscale architectures. In fact, we have made it possible to combine a wet process for film formation and a dry process for metal coating. It is also possible to form free-standing films composed of metal oxides and polymers. These artificially organized thin films will contribute widely to various fields of chemistry.

Experimental Section

Materials. The 150-mesh microgrid and 2000-mesh copper grid were purchased from Oken, Japan. The former grid has a perforated polymer membrane, with the surface of the polymer membrane coated with thin glassy carbon to reinforce the pores of a few micrometers. The latter grid is made of pure copper and has regularly arranged square holes of 7 μm at an interval of 2000 per inch. The porous alumina membrane (Anodisc-25) with a pore size of 0.2 μm was purchased from Whatman and used as the substrate for FTIR measurements.

Pt Coating. TEM and FE-SEM specimens were often coated with a 2-nm-thick platinum layer by using a Hitachi E-1030 ion sputter. The coating was performed with a current density of 10 mA at room temperature under an argon pressure of 10 Pa or lower. The thickness was calibrated by using the quartz crystal microbalance technique. Under our experimental conditions, platinum nanoparticles of about 0.8 nm were uniformly deposited on the surfaces of any kind of dried foam film. The deposition did not have any effect on the film morphology. However, deposition of more than 10 nm of platinum was prone to disrupt the films, probably resulting from the high surface tension of the platinum layer.

Characterizations. TEM observations were made with a JEM-1010 (JEOL) instrument at an acceleration voltage of 100 kV. FE-SEM images were obtained with a Hitachi S-4800. The cross-sectional specimen was prepared by carefully tearing a 2000-mesh copper grid covered with dried foam films, followed by Pt coating in a vertical sample holder. FTIR spectra were obtained with a Bio-Rad Win-IR spectrometer. The sample was set in a chamber filled with dried nitrogen gas. Confocal laser microscopy images were obtained with an instrument from Lasertec (VL2000D). The coverage of dried foam films was calculated by counting the films remaining after heating for 15 min at a given temperature. The number of holes examined was higher than 600.

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[24] The thermal stability of dried foam films is sensitive to the molecular structure of amphiphilic compounds, too. The dried foam films of D-PC and C18-N-Si disappeared near 160 and 180°C, respectively. The higher thermal stability of the latter film must be because of the covalent bonding between the hydrophilic groups.

[25] We also found that C18-Si gave very stable films from the ethanol solution. Formation of dried foam films may not, therefore, be restricted to a dehydration mechanism. The molecular design of amphiphilic compounds will provide new types of self-standing films.