

Carbonate Crystal Growth Controlled by Interfacial Interactions of Artificial Cell Membranes

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Morphology of carbonate crystals grown on the surface of artificial cell membranes was controlled by changing the interfacial chemistry. For octadecyltriethoxysilane (OTE) films with terminal methyl groups interacting little with an aqueous calcium carbonate solution, calcite (104) crystals were formed. Polymerized pentacosadiynoic acid (PDA) films with terminal carboxylic acid groups induced deposition of calcite (012) crystals aligned along with each other within a polymer domain. On the other hand, stearyl alcohol (StOH) films with terminal hydroxyl groups induced deposition of aragonite crystals. When PDA was mixed with StOH, the 8:1 PDA:StOH (molar ratio) film produced dominating calcite (012) crystals without any crystal alignment, and the 4:1 mixture film produced minor calcite (012) crystals and major aragonite crystals. For the 2:1, 1:1, 1:2, and 1:4 mixture films, aragonite crystals were dominating. Hence, it is found that the chemical composition at the interface plays a very important role in controlling the morphology of deposited carbonate crystals.

Key words: carbonate crystals, interfaces, artificial cell membranes

INTRODUCTION

Biological systems are capable of controlling inorganic crystal growth to a remarkable degree [1]. This oriented crystal growth has inspired numerous studies of template-directed crystallization at condensed surfactant thin films, which are often called artificial cell membranes due to their structural resemblance to natural cell membranes. Such attempts have been tried for the template systems like Langmuir monolayers and Langmuir-Blodgett films [2-4]. Owing to these works, calcite crystals with peculiar morphology were found to deposit preferentially at highly acidic interfaces where strong ionic interactions with solution containing calcium carbonate are present. Absence of such interaction results in natural calcite (104) crystals. However, the crystal morphology on the corresponding template films remained unchanged and could not be controlled.

In the present study, for the first time to the authors' knowledge, we try to control the morphology of the crystals by varying the composition of the template films, hence changing the interfacial chemistry and interaction with the solution. We chose template systems of polymerized pentacosadiynoic acid and stearyl alcohol because these two systems produce different crystal morphology due to different interfacial chemistry. The results show that the mixing of the two components influences strongly the crystal form and arrangement. Implications of this study will be very important both in understanding biomineralization processes and in developing related technologies like new nanocomposite materials and anti-calcium biomaterials or medical implants.

MATERIALS AND METHODS

Materials

Octadecyltrichloroethoxysilane (OTE, 99%) and 10, 12-pentacosadiynoic acid (PDA, 99%) were purchased from Huls America and Farchan Laboratories. Stearyl alcohol (StOH, 99%) and calcium carbonate (CaCO_3 , 99%) were from Aldrich. Distilled water was purified with a Millipore water purifier and the initial resistivity was $18.2\text{M}\Omega$. Spreading solvents used for PDA and StOH were chloroform of reagent grade (Aldrich). The solutions of PDA and StOH were 1 mM and kept at a temperature of 4°C in the dark. The solutions were allowed to equilibrate at room temperature before use.

Surface Isotherms

Surface isotherms of pure and mixture monolayers of PDA and StOH were obtained by using a standard Langmuir trough (KSV minitrough, Finland). The solutions were spread on the pure water ($\text{pH}=5.5$, 25°C) from microsyringes. About 20 min was waited until the solvent evaporated completely. The air/surfactant/water interface was compressed symmetrically by two teflon-coated barriers at a speed of 10 mm/min. The surface isotherms were acquired until the surface pressure reaches 30 mN/m.

Film Formation

OTE film was formed on a cleaned glass plate by following the reported self assembly technique [5]. Measured advancing contact angle of water ($\text{pH}=5.5$) at 110° confirmed formation of a typical hydrophobic OTE film on the glass surface. StOH films at the air/water interface ($\Pi=30$ mN/m) were deposited on the OTE coated glass substrate, by using a horizontal

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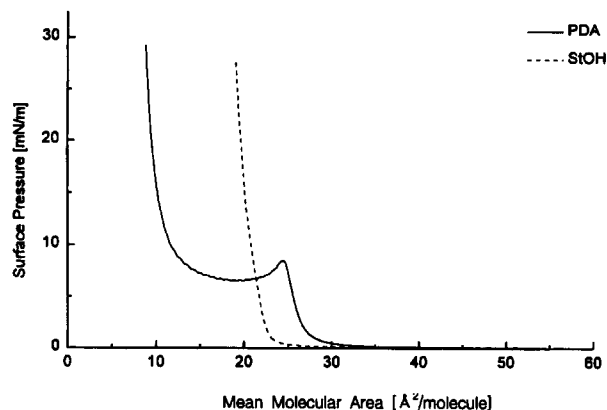


Fig. 1. Surface isotherms of pure PDA and StOH monolayers.

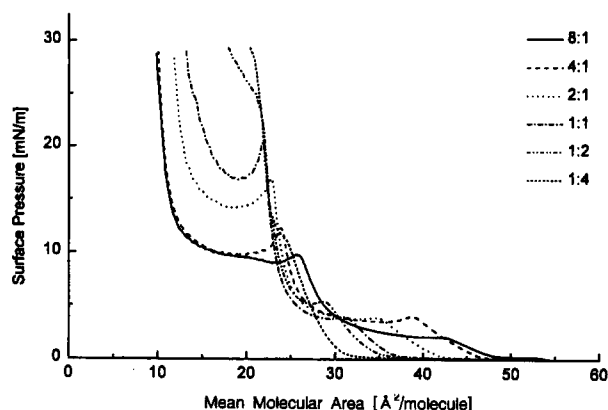


Fig. 2. Surface isotherms of mixture monolayers of PDA and StOH. Molar ratio of PDA to StOH is indicated.

touch method (Langmuir-Schaefer method) in order for hydroxyl head groups to be exposed. For PDA films, photopolymerization was executed at the air/water interface by exposure to UV light of 254 nm wavelength for 1min. The film turned blue upon photopolymerization. Then, by using the horizontal touch method the PDA film with carboxylic acid groups exposed was deposited on the OTE coated glass substrate. The mixture films of 8:1, 4:1, 2:1, 1:1, 1:2, and 1:4 PDA:StOH (molar ratio) were fabricated by following the procedure done for the pure PDA film.

Crystal Growth

Supersaturated calcium carbonate solution was prepared by bubbling carbon dioxide gas through a stirred aqueous suspension of calcium carbonate for ca. 30 min. Thus prepared solution was filtered by membranes of 0.22 μm pore size to remove residual crystals. The total concentration of calcium ion in the final solution was ca. 8 mM as measured by a calcium electrode. An aliquot of supersaturated solution was placed on the various film surfaces. After 30 min were allowed for carbon dioxide gas to evaporate from the solution, the films were rinsed with running pure water. Crystals formed on the film surface were observed under an optical microscope.

RESULTS AND DISCUSSION

Surface Isotherms

Surface isotherms of pure PDA and pure StOH Langmuir monolayers on the water (pH=5.5) surface are given in Fig. 1. The isotherm for the StOH monolayer shows no collapse and is similar to that for stearic acid monolayer, which is in solid-like state above the surface pressure of 15 mN/m. The mean molecular area (MMA) is ca. $19\text{\AA}^2/\text{molecule}$ at $\Pi=30$ mN/m. By contrast, the PDA monolayer undergoes the monolayer collapse at ca. $24\text{\AA}^2/\text{molecule}$ ($\Pi=8$ mN/m) and thereafter as the surface area is reduced increases to 30 mN/m. The MMA at this surface pressure is ca. $8\text{\AA}^2/\text{molecule}$, indicating that a fairly compact trilayer film is formed at the air/water interface.

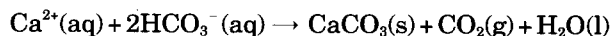
In Fig. 2, surface isotherms for mixture films are shown. As the amount of StOH in the mixture increases, the surface isotherm gradually changes from that of pure PDA to that of pure StOH. For the 8:1 PDA:

StOH mixture, the monolayer is collapsed at ca. $26\text{\AA}^2/\text{molecule}$ ($\Pi=10$ mN/m) and reaches 30 mN/m at ca. $9\text{\AA}^2/\text{molecule}$, indicating again that a stable trilayer is formed. As the StOH content increases to 4:1, 2:1, 1:1, 1:2, and 1:4, the collapse pressure gradually increases to ca. 12.5, 17, 21, 25, and 30 mN/m. If PDA and StOH molecules in the mixture monolayers are not well-mixed, the collapse pressure of PDA molecules does not change and maintains its value at 8 mN/m. Hence, we can infer that the StOH and PDA molecules are well-mixed in the monolayer.

In the meantime, there appears a transition at ca. $43\text{\AA}^2/\text{molecule}$ ($\Pi=2$ mN/m) for the 8:1 PDA:StOH mixture monolayer, which is not observable in the pure PDA case. This transition pressure becomes enhanced as the StOH content increases: 4-3 mN/m for the 4:1, 2:1, and 1:1 mixtures, 6 mN/m for the 1:2 mixture, and 12 mN/m for the 1:4 mixture. The reason for this transition is not clear at present. Most probably it will result from chain reorientation of the PDA molecules in the PDA/StOH mixture monolayer. Since molecular chain orientation of the PDA molecules is different from that of the StOH molecules at the air/water interface, surface compression will result in formation of a more compact monolayer at the cost of the chain reorientation of the PDA molecules that are less stable compared to the StOH molecules.

Crystal Formation on Pure Films

Carbonate crystals were formed at the various film surfaces by exposing the film to the supersaturated calcium carbonate solutions containing ca. 8 mM calcium ions. Upon exposure, carbonate crystals are formed at the film interface as carbon dioxide gas diffuses out of the solution, according to the following reaction:



The crystals grown on pure OTE, PDA, and StOH films are shown in Fig. 3. For the OTE films, the natural phase, calcite (104) is formed. Since the OTE film exposes terminal methyl group, the film surface is hydrophobic and the surface interacts weakly with the solution. Thereby the natural calcite (104) morphology results. For the PDA films, calcite (012) face is nucleated at the film surface. The crystallographic a-axis (long axis of the crystals) of (012) face is aligned along with the linearly polymerized PDA backbone [4]. The lattice spacing in this direction is 4.99\AA that matches

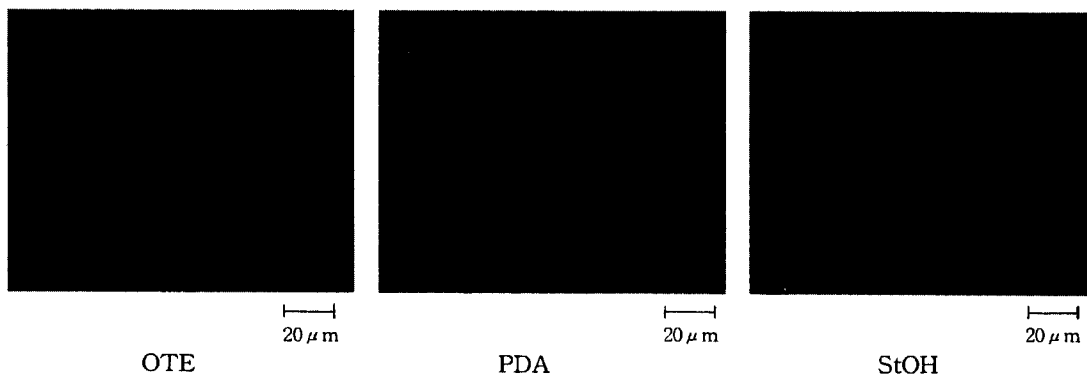


Fig. 3. Carbonate crystal formation on pure film surfaces.

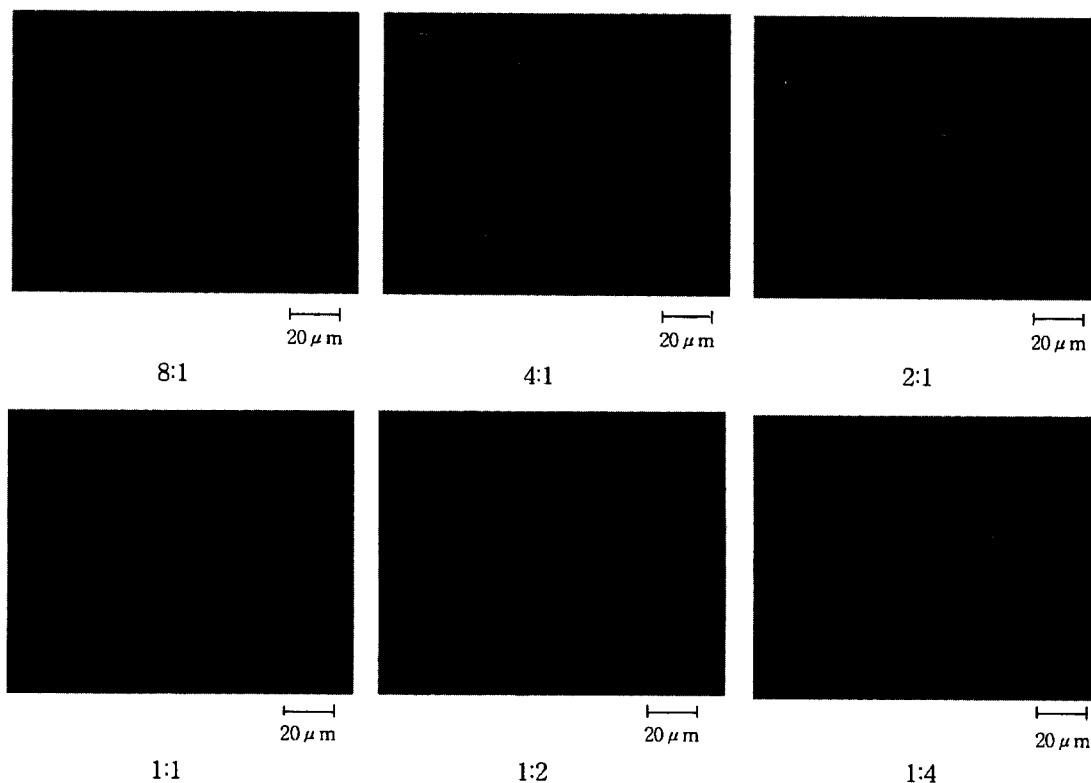


Fig. 4. Carbonate crystal formation on PDA/StOH mixture film surfaces. Molar ratio of PDA to StOH is indicated.

very well with $4.9 \pm 0.3 \text{ \AA}$ lattice spacing of the exposed carboxylic acid group at the film surface. Macroscopically, such (012) crystals are aligned along with each other within a polymer domain. By contrast to the above cases, aragonite phase of calcium carbonate is found to deposit at the StOH film surface, where the exposed hydroxyl group has no ionic interaction with the solution. In addition, aragonite crystals do not show such alignment as calcite (012) crystals do.

The morphology of the carbonate crystals is found to be controlled by the interfacial chemistry of the film surface. Thus, different crystal morphology is an indicative of different interfacial properties.

Crystal Formation on Mixture Films

When mixture films of PDA and StOH are exposed to the supersaturated calcium carbonate solution, interesting crystal morphology is observed as given in Fig. 4. For the 8:1 PDA:StOH mixture film, calcite (012) crystals are found. Interestingly, no such crystal align-

ment is observed as was seen in the case of pure PDA films. Adding ca. 11% of StOH into the PDA monolayer forms a well-mixed two component film, as analyzed from the surface isotherm behavior. As a result, the domain size of the polymer is significantly reduced. Hence, although the calcite (012) crystals are still formed at the surface, their long-range alignment is now forbidden. For the 4:1 films in which PDA is still major, the number density of the calcite (012) crystal becomes small and the aragonite is unexpectedly the major crystal structure. Considering the collapse of the PDA monolayer and the trilayer formation, the film surface is roughly the 1.3:1 PDA:StOH mixture. However, the number density ratio of calcite (012) to aragonite crystals is only about 0.5, as given in Table 1. Therefore, it can be concluded that a minimum polymer domain size is required to facilitate the growth of calcite (012) crystals. As the amount of StOH increases to 2:1, 1:1, 1:2, and 1:4, the aragonite is the major crystal phase. For every film composition studied, calcite (104) and vaterite crystals are very minor. This indicates that sim-

Table 1. Number density of crystals grown on various film surfaces

Film (PDA:StOH)	Number density of crystals (%)			
	Calcite (012)	Calcite (104)	Aragonite	Vaterite
OTE	0	98	2	0
PDA	89	11	0	0
StOH	0	6	94	0
8:1	88	10	2	0
4:1	30	13	57	0
2:1	11	6	76	7
1:1	0	7	90	3
1:2	0	8	88	4
1:4	0	6	92	2

ply mixing two chemical components, hence changing domain size and interfacial chemistry, do not induce the crystallization of less interacted phases such as calcite (104) or vaterite.

CONCLUSIONS

Morphology of calcium carbonate crystals was examined on various template films. For pure films, peculiar crystal morphology was found to the corresponding film surfaces: calcite (104) crystals for OTE films, aligned calcite (012) crystals for PDA films, and aragonite crystals for StOH films. When PDA and StOH molecules are mixed, calcite (012) crystals without alignment were present along with aragonite crystals. Mixing StOH molecules into PDA films made

the polymer domain size reduced and the growth of calcite (012) was suppressed. Chemical composition of the interface is found to strongly influence the crystal form and arrangement.

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