

Langmuir–Blodgett Films of a Water-soluble Polysilane based on Interfacial Polyion Complexation

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Langmuir–Blodgett (LB) films of a water soluble cationic polysilane are successfully prepared by ion-complexation with an arachidic acid monolayer at the air–water interface; UV absorption characteristics of the LB films are dependent on the pH of the water subphase on transfer.

Polysilanes are important photofunctional polymers with unique photosensitive properties attributed to σ -electron delocalisation along the Si–Si main chain.¹ Langmuir–Blodgett (LB) films comprised of various types of polysilanes have recently been prepared.^{2–4} Development of a molecular handling technique for polysilanes by the LB method should be of importance for future applications on molecular electronics and photonics. To date, polysilanes explored for the monolayer studies at the air–water interface have been designed to have minimal polar² or amphiphilic^{3,4} structures. In this communication, we present a novel approach to LB film preparation of a polysilane based on polyion complexation. This method involves dissolving a water-soluble ionic polysilane in the aqueous subphase, ion-complexation with an oppositely charged amphiphile at the air–water interface, and deposition of the interfacial polyion-complex by the LB technique. While this technique has been applied for ordinary polyelectrolytes,^{5–7} ion-complexation of the polysilane at the air–water interface and its LB deposition are explored for the first time.

The water-soluble polysilane **1** used in this study was obtained by chloromethylation of poly(β -phenethylmethylsilane) ($M_w = 21000$) followed by quaternization with trimethylamine. The details on synthesis and spectroscopic

properties in aqueous solutions of this compound will be reported elsewhere.⁸ A Lauda film balance was filled with an aqueous solution containing **1** (1×10^{-5} unit mol dm⁻³) under dimmed red light. A chloroform solution of arachidic acid (1×10^{-3} mol dm⁻³) was then spread (1.20×10^{-4} dm³) on this subphase; in this procedure, the subphase contains *ca.* 50-fold excess amount of the Si unit to the arachidic acid molecule at the interface.

Fig. 1 indicates spreading behaviour of arachidic acid at 20 °C on the aqueous subphase in the absence (*a*) and presence (*b*) of polysilane **1** at pH 2.0–8.0. The presence of the cationic polysilane **1** in the water subphase brought about a large expansion of the monolayer in lower surface pressure regions. The shape change in the isotherms induced by addition of the polymer indicates polyion-complex formation between arachidic acid and the cationic polysilane at the interface. The change was most profound at pH 8, suggestive of the most effective ion-complexation in the pH regions under investigation. At this pH the lift-off area expanded to *ca.* 0.6 nm². This area is comparable to that of the monolayer of the formerly explored amphiphilic polysilane **2** having the identical backbone structure.⁴ This consistency can be well understood by assuming formation of the 1:1 ion-complex of polysilane **1** with the fully charged arachidic acid. In the high surface pressure regions, the limiting area agreed exactly with those of the pure arachidic acid monolayers, *ca.* 0.2 nm², which corresponds to the packed long chains oriented normal to the water surface.

The polyion-complexed monolayers could be readily transferred onto a quartz plate by the vertical dipping method at

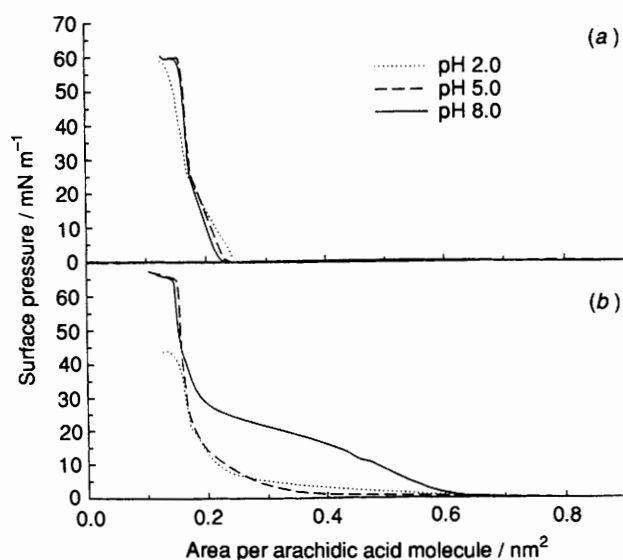
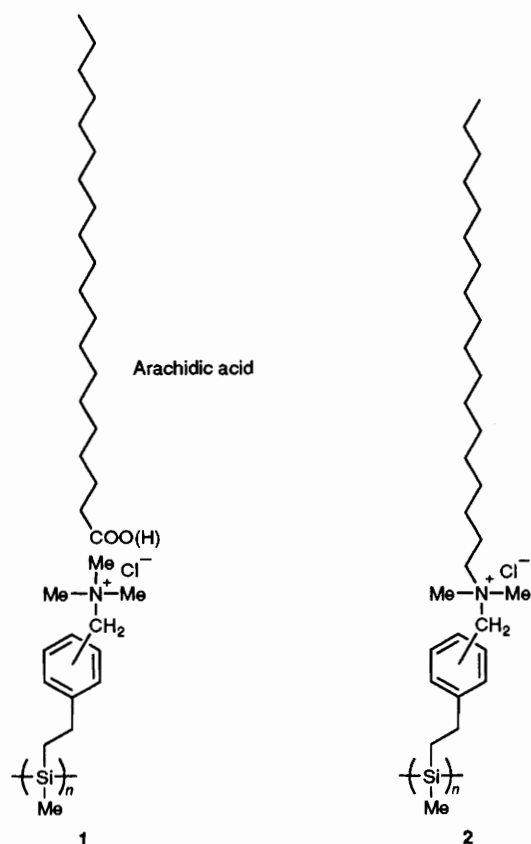


Fig. 1 Surface pressure–area isotherms of arachidic acid at 20 °C on aqueous subphase containing NaCl (1×10^{-2} mol dm⁻³) in the absence (*a*) and presence (*b*) of polysilane **1**. The compression speed was 50 cm² min⁻¹. pH of the subphase was adjusted by adding appropriate amount of concentrated HCl or NaOH aqueous solutions.

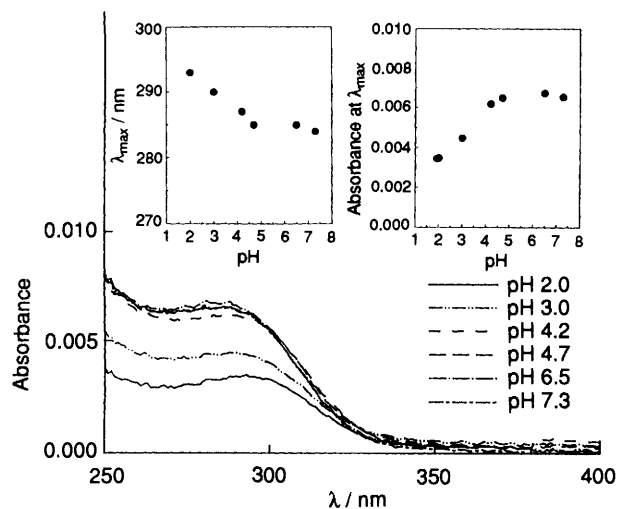


Fig. 2 UV absorption spectra of single LB monolayers on a quartz plate on both sides transferred at 5 mN m^{-1} at various pHs. The inset figures on the left and right hand sides show the pH profiles of λ_{max} of $\sigma\text{-}\sigma^*$ band of the Si backbone and the absorbance at λ_{max} , respectively.

good transfer ratios (> 0.95). The UV absorption spectra of LB monolayers transferred at various pH are depicted in Fig. 2. As shown in the figure, the spectral peak (λ_{max}) attributed to the $\sigma\text{-}\sigma^*$ band and the absorbance at these wavelengths exhibited clear pH dependence. The pH-profiles of these two parameters are indicated as the insets of Fig. 2. These profiles imply that the spectral changes are correlated to the dissociation state of the arachidic acid monolayer: dissociation constants ($\text{p}K_{\text{a}}$) of *n*-alkyl carboxylic acids are approximately 4.8 at room temperature.

The UV absorption of polysilanes are sensitive to their backbone conformation, namely, the *trans*:*gauche* population in the main chain.¹ Therefore, the changes in λ_{max} observed here can be ascribed to pH dependent conformational changes of ion-complexed **1** at the interface. The following model can be presented. At lower pH, the Si backbone takes a more expanded (more *trans*-abundant) state from the requirement of ion-complexation with the interfacial arachidic acid monolayer having the lower anionic charge density. At higher pH, in contrast, the polysilane backbone is more folded (more *gauche*-abundant) to form the 1:1

complex at the fully charged monolayer interface. It is to be noted that λ_{max} in the LB film prepared at higher pH was comparable to that obtained in aqueous solution of the identical ionic strength. In the aqueous solution, however, the spectrum was apparently broadened, suggestive of the existence of more dispersed conformational states. We have reported previously obvious area dependent spectral shifts of $\sigma\text{-}\sigma^*$ band of LB films of the amphiphilic polysilane **2**.⁴ In the present system, on the contrary, the spectral shifts were observed solely by the difference in the charge density of the monolayer, but not by the area changes controlled by the moving bar. This is suggestive of the ready occurrence of ion exchanges between arachidic acid and polysilane **1** at the interface upon compression, which differs from the monolayer behaviour of **2** in which the backbone conformation is directly modulated by the monolayer area.

In regard to the pH profile of absorbance of the LB films, it is revealed that the amount of the transferred **1** is smaller in the LB film when prepared at lower pH. This is plainly explained by the lower charge density for ion-complexation. The absorbance at λ_{max} above pH 5 ($\approx ca. 0.006$) is identical to that of the authentic monolayer of **2**,⁴ which justifies an assumption that **1** is transferred monomolecularly by the present ion-complexing LB technique.

In conclusion, a new preparation method for polysilane LB films is presented. Use of the photosensitive polysilane-electrolyte provides intriguing knowledge on the interfacial ion-complexation, in particular, on the conformational state and the complexed and transferred amounts of the poly-electrolyte.

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