

Permethylhexasilane Assembly fabricated by the Langmuir–Blodgett Method

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A Langmuir–Blodgett film of a new amphiphilic permethylhexasilane, tridecamethylhexasilanylacetic acid, has been fabricated.

The increasing interest in polysilanes¹ is due to their σ -conjugation that provides a narrow band gap and is perturbed by changes in skeletal conformation. Their electric and optical properties have been studied mainly in solution² or in amorphous films³ with little attempt at ordering or assembling their structures. Our strategy is to build up a highly ordered polysilane assembly by the Langmuir–Blodgett (LB) technique and to explore electric and optical properties specific to the designed polysilane structure. Already, the LB technique has been applied to amphiphilic polysilanes with a long alkyl chain as a hydrophobic component.⁴ In such films, the polysilane skeleton is in the plane parallel to the substrate. Our aim is, however, to fabricate thin films in which the polysilane skeleton is oriented normal to the surface of the substrate. Here, we report the first fabrication of such polysilane LB films.

The new polysilane amphiphile, tridecamethylhexasilanylacetic acid† (MSi6AA), was synthesized as follows: (i) chlorinative cleavage⁵ of dodecamethylcyclohexasilane (Shinetsu Chemicals) with PCl_5 ; (ii) methylation⁶ of one terminus of the resulting 1,6-dichlorododecamethylhexasilane; (iii) coupling of the resulting 1-chlorotridecamethylhexasilane with acetate α -anion ($-\text{CH}_2\text{CO}_2^-$) which was independently prepared by the reaction of acetic acid with butyllithium.⁷

† Details of the synthesis will be reported elsewhere. Spectral data of MSi6AA: ^1H NMR (δ in CDCl_3): 0.09–0.22 (s, 39H, CH_3), 1.96 (s, 2H, CH_2) and 11.0 (br, CO_2H); ^{13}C NMR (δ in CDCl_3): –5.73 to –1.12 (m, CH_3), 25.4 (s, CH_2) and 180.0 (s, CO_2H); IR (KBr tablet): ν/cm^{-1} 2952 ($\nu_{\text{as}} \text{CH}_3$), 2894 ($\nu_s \text{CH}_3$), 1675 ($\nu \text{C}=\text{O}$ of CO_2H), 1397 ($\delta_{\text{as}} \text{CH}_3$), 1245 ($\delta_s \text{CH}_3$), 836, 747 (ρSiMe_2), 691 ($\nu_{\text{as}} \text{Si}-\text{CH}_3$) and 634 ($\nu_s \text{Si}-\text{CH}_3$); UV (in hexane): λ_{max} 261 nm (ϵ $2.7 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The synthetic route adopted here has potential in the design of various polysilane-based amphiphiles including a sequence-defined copolymer of silylene and methylene units.

Fig. 1 shows a typical surface pressure–area isotherm of MSi6AA on an aqueous subphase containing Cd^{2+} ions. Over a relatively wide temperature range (10–35 °C), MSi6AA by itself formed a stable monolayer with a sufficiently high

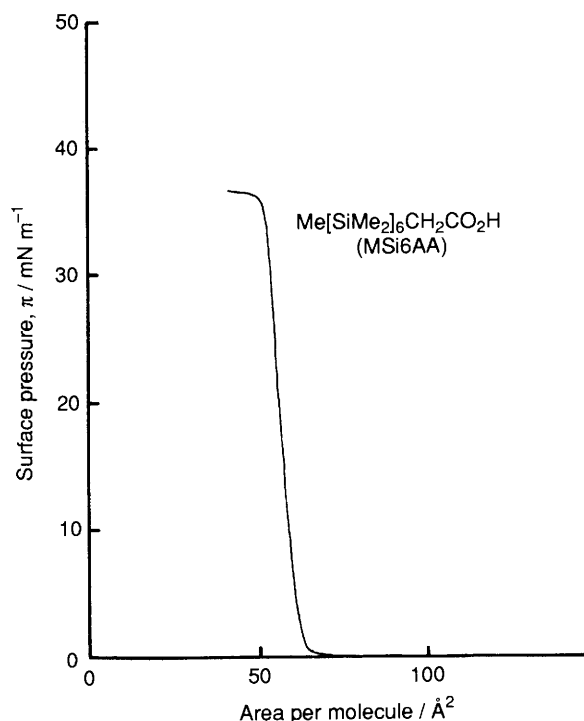


Fig. 1 π -A curve of MSi6AA on an aqueous subphase containing CdCl_2 ($1 \times 10^{-3} \text{ mol dm}^{-3}$) and KHCO_3 ($1.7 \times 10^{-4} \text{ mol dm}^{-3}$) at 15 °C, pH about 6.3

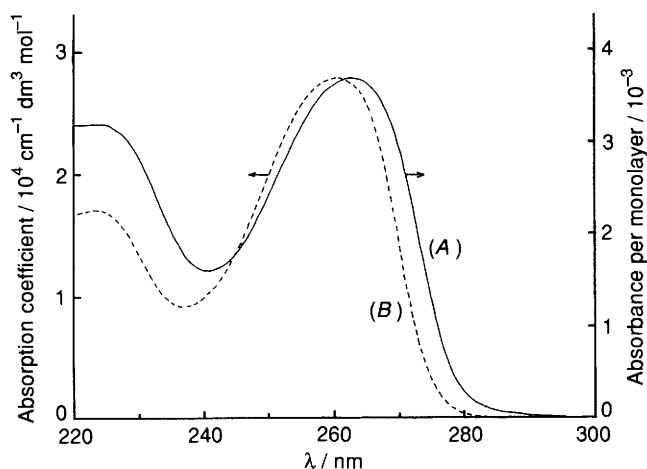


Fig. 2 UV absorption spectra of (A) the LB film of MSi6AA (60 layers on silanised quartz substrate) and (B) a n-hexane solution ($3 \times 10^{-5} \text{ mol dm}^{-3}$)

collapse pressure (about 40 mN m^{-1}) for it to be transferred. The limiting molecular area ($59\text{--}61 \text{ \AA}^2$ per molecule) was in good agreement with the cross section (58 \AA^2) of the all-*trans* conformation[‡] of permethylpolysilane, so that the condensed MSi6AA monolayer on the subphase should have a close-packed structure. On a pure water subphase or on a solution containing K^+ ions, the monolayer showed a low collapse pressure (20 mN m^{-1}) with an identical limiting area. Judging from the 8.8 \AA interchain distance calculated from the limiting area, the present monolayer might be regarded as a σ -conjugation assembly with little side-by-side interaction.⁹

The monolayer was transferred onto various hydrophobic substrates (*e.g.* silanised glass, silanised quartz and CaF_2) by the vertical dipping method at 33 mN m^{-1} surface pressure. The transfer ratio (1.0 for the up stroke and 0.8 for the down stroke) was kept constant throughout more than 100 layers of accumulation. Thus, the resulting film was a Y-type multilayer. The X-ray diffraction patterns of the resulting LB films indicated a fine layered structure with 24.4 \AA bilayer d spacing. Considering the long axis length of MSi6AA (19 \AA , estimated from molecular model), the amphiphile on the substrate is possibly tilted at 50° from the surface normal.

Fig. 2 shows the UV absorption spectra of the LB film and of MSi6AA in hexane. Both absorption bands were assigned to the $\sigma\text{--}\sigma^*$ transition of the hexasilane skeleton.¹⁰ Since the change of the absorption maximum from the solution to the

LB film was slight and to a longer wavelength, the major conformation of the hexasilane involves a more expanded form, possibly all-*trans*.[‡]

To estimate the tilting angle of MSi6AA in the LB films, the dependence of the incident angle to the film on the absorbance was analysed under the assumption that the $\sigma\text{--}\sigma^*$ transition moment is parallel to the long axis of the expanded hexasilane skeleton. The average tilting angle of the long axis of the amphiphile was about 50° , which is consistent with that estimated from the XRD measurement.

The present approach should provide a correlation between polysilane properties and the structure of designed assemblies. In addition, this polysilane LB film is of great value to test functionalization¹¹ of the hydrophobic part, differing from conventional amphiphiles having a long alkyl chain.

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‡ Our expectation that the conformation of the tridecamethylhexasilanyl group is all-*trans* is partly supported by the structure of the solid crystalline permethylpolysilane deduced from X-ray and electron diffraction.⁸