

Langmuir-Blodgett Study of a Cationic Polysilane Amphiphile

Takahiro Seki,* Takashi Tamaki, and Katsuhiko Ueno

Research Institute for Polymers and Textiles, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

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In the past decade much attention has been directed toward soluble linear polysilanes, catenated Si polymers bearing two organic substituents at each Si unit.¹ This new class of polymers exhibits photosensitive properties attributed to the delocalization of σ -orbitals of the Si backbone, which leads to UV absorption, light emission, photodegradation, nonlinear optical effects, photoconductivity, etc.^{1,2} To date, evaluation of these properties has been pursued with bulk materials.^{1,2} On the other hand, much recent effort has been devoted to Langmuir-Blodgett (LB) films of preformed polymers, and data on these films are now rapidly being accumulated.³ LB films of preformed polymers have such advantageous features as increased stability, domain-free structures, and the possibility to impose an in-plane anisotropic nature.³ From the above standpoints, the application of the LB technique to polysilanes should be of both scientific and technological importance. Difficulty in direct syntheses of amphiphilic polymers by Wurtz-type coupling⁴ seems to have prevented LB work with polysilanes. Recently, the first LB study of polysilanes was reported by Embs et al.⁵ They succeeded in preparing well-defined LB films for a couple of particular polysilanes; however, they also showed poor applicability of the LB method for most of the existing polysilanes that bear no hydrophilic moiety. This communication presents a facile synthetic method for a polysilane amphiphile starting from a conventional polysilane. We report herein that the UV absorption properties of the polysilane molecular film are effectively controlled by interfacial procedures of the LB process.

Scheme I indicates the synthetic route for the polysilane derivative in this work. Poly(β -phenethylmethylsilane) (1) was synthesized by conventional Wurtz-type coupling.⁶ The molecular weight (M_w) of this polymer determined by gel permeation chromatography (GPC, polystyrene standards) was 21 400 ($M_w/M_n = 1.23$). The phenyl group of 1 was then chloromethylated using chloromethyl methyl ether and SnCl_4 essentially by the method of Ban et al.⁷ The GPC measurement revealed that the molecular weight was virtually unaffected by the chloromethylation: M_w after chloromethylation was 28 000 ($M_w/M_n = 1.30$). In the $^1\text{H-NMR}$ spectrum the chloromethylene protons showed a broad peak ranging from 4.2 to 4.7 ppm in CDCl_3 . The percentage of chloromethylation determined from the $^1\text{H-NMR}$ spectrum was more than 95% of the total Si units. The chloromethylated polysilanes were finally quaternized with N,N -dimethyloctadecylamine at 70 °C for 20 h to obtain the amphiphilic polysilane 2. From the $^1\text{H-NMR}$ measurement, the quaternization proceeded completely; i.e., the peak due to the chloromethylene protons was completely replaced by ammoniomethylene signals at 4.6–5.6 ppm. The final product 2 was purified twice by sedimentation from tetrahydrofuran to n -hexane.

* To whom correspondence should be addressed.

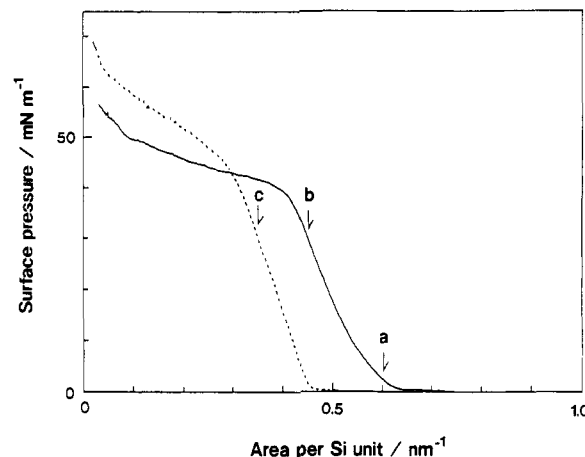
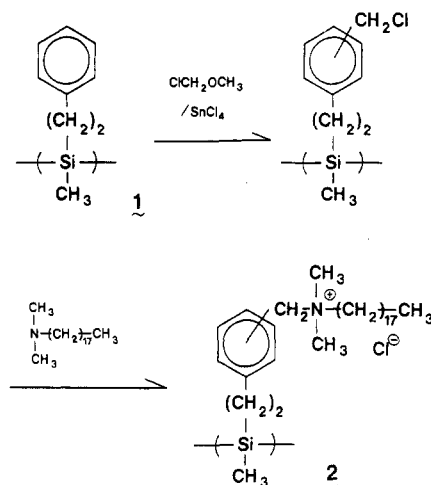


Figure 1. Surface pressure-area isotherm of 2 per Si unit on pure water (solid curve) and on NaClO_4 aqueous solution (dotted line, $5 \times 10^{-4} \text{ mol dm}^{-3}$) at 20 °C. The letters a–c refer to the conditions of the LB deposition.

Scheme I



LB experiments were performed with a Lauda MGW film balance. The amphiphilic polysilane 2 was spread from freshly prepared chloroform solution⁸ (ca. $1 \times 10^{-3} \text{ mol dm}^{-3}$) in dim red light. Figure 1 indicates surface pressure-area isotherms per Si unit of 2 on distilled water (solid curve) and NaClO_4 aqueous solution (dotted curve, $5 \times 10^{-4} \text{ mol dm}^{-3}$) at 20 °C. On the NaClO_4 aqueous subphase, 2 formed a more condensed monolayer than on pure water as the result of anion exchange from Cl^- to more hydrophobic ClO_4^- at the air/water interface. In both cases the limiting area per Si unit, estimated by extrapolation of the steepest region to zero surface pressure (0.57 and 0.45 nm^2), was much larger for the cross section of a vertically oriented long hydrocarbon chain (ca. 0.2 nm^2). This indicates that the molecular dimension of the condensed surface monolayers is determined by the bulky β -phenethylmethylsilane unit and not by the hydrocarbon chain.

The monolayers of 2 could be transferred to quartz substrates at good transfer ratios (>0.95) by the conventional vertical dipping method. The surface pressures selected for deposition were 2 and 30 mN m^{-1} on pure water and 30 mN m^{-1} on NaClO_4 aqueous solution. These transfer conditions are indicated by the three arrows in Figure 1. They correspond to the area per Si unit of (a) 0.6, (b) 0.45 , and (c) 0.35 nm^2 , respectively. Figure 2 illustrates the UV spectra of transferred monolayers on both sides measured on a JASCO HSSP-3 spectropho-

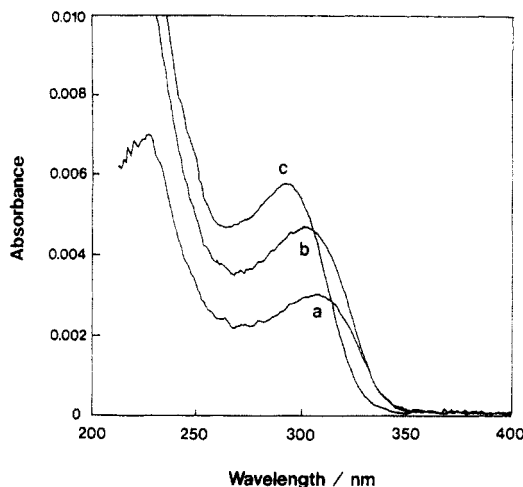


Figure 2. UV absorption spectra of monolayers of **2** on both sides of a quartz substrate. Monolayers were transferred under conditions corresponding to a–c in Figure 1.

tometer. The absorption band of the Si backbone around 300 nm showed clear blue shifts: the band peaked at 310, 301, and 290 nm for the most loosely packed (spectrum a, 0.6 nm^2 per Si unit), the intermediate (spectrum b, 0.45 nm^2), and the most densely packed (spectrum c, 0.35 nm^2) monolayer films, respectively. The apparent spectral shift should be attributed to conformational changes of the σ -conjugated Si backbone from an expanded state to a more condensed state at the two-dimensional interface, which is attained by the compression force of the moving bar and the anion exchange. This phenomenon resembles the size effect of substituents of polysilanes in solution.⁶ It is noteworthy that this finding provides the first direct evidence for shrinking behavior of a flexible polymer backbone induced by surface pressure and ion exchange at an air/water interface. Information on the conformation of flexible backbones is not available with carbon-based polymers hitherto investigated in LB research.

Figure 3 displays polarized UV absorption spectra of an 18-layer film (9 layers on each side) of **2** deposited at 25 mN m^{-1} in the Y mode on the NaClO_4 aqueous subphase. The electric vector of the polarized light was set parallel (solid spectrum) and perpendicular (dotted spectrum) to the dipping direction in the normal incidence. The absorptivity of the σ -conjugated band was larger when the polarization plane was set parallel to the dipping direction, indicating the polymer backbone preferentially aligns parallel to the dipping direction. The dichroic ratio (ca. 1.13) was much smaller than the datum of Embs et al.⁵ for stiff poly[bis(*m*-butoxyphenyl)silane] having an all-trans planar zigzag conformation (≈ 2.9). The difference can be ascribed to the high flexibility and lack of stereoregularity of the backbone of **2**.

Polysilanes are widely known to show thermochromism in solutions⁹ and films,¹⁰ solvatochromism,¹¹ and pie-

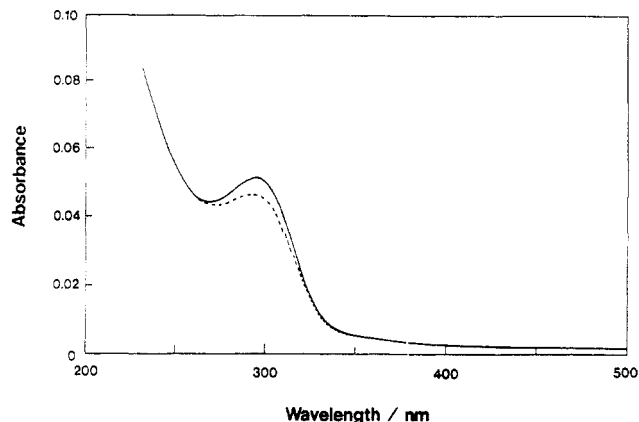


Figure 3. Polarized absorption spectra of a 9-layered LB film of **2** on both sides of a quartz substrate. Absorption spectra were measured in normal incidence with the linearly polarized light set parallel (solid line) and perpendicular (dotted line) to the dipping direction.

zochromism.¹² This work presents a new type of chromism based on mechanical and chemical effects at the air/water interface. In conclusion, the amphiphilic polysilane provides useful information on interfacial phenomena of polymeric molecular films by means of direct spectroscopic observations.

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References and Notes

- (1) For reviews, see: (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (b) Zeigler, J. M.; Fearson, F. W. G., Eds. *Silicon-Based Polymer Science*; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990. (c) West, R. J. *Organomet. Chem.* **1988**, *300*, 327. See also references cited in these reviews.
- (2) Miller, R. D. *Angew. Chem., Int. Ed. Engl., Adv. Mater.* **1989**, *28*, 1733.
- (3) Embs, F. W.; Funhoff, D.; Laschewsky, A.; Licht, U.; Ohst, H.; Prass, W.; Ringsdorf, H.; Wegner, G.; Wehrmann, R. *Adv. Mater.* **1991**, *3*, 25 and references cited therein.
- (4) The phenol group has been successfully introduced into polysilanes by protecting the functional group during the Wurtz-type condensation: Horiguchi, R.; Onishi, Y.; Hayase, S. *Macromolecules* **1988**, *21*, 304.
- (5) Embs, F. W.; Wegner, G.; Neher, D.; Albouy, P.; Miller, R. D.; Willson, C. G.; Schrepp, W. *Macromolecules* **1991**, *24*, 5068.
- (6) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601.
- (7) Ban, H.; Sukegawa, K.; Tagawa, S. *Macromolecules* **1987**, *20*, 1775.
- (8) The polysilane gradually decomposes in chloroform also in the dark to lower molecular mass polymers: ref 5 and our unpublished results.
- (9) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 209.
- (10) Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611.
- (11) Miller, R. D.; Sooriyakumaran, R. *Macromolecules* **1988**, *21*, 3122.
- (12) Song, K.; Miller, R. D.; Wallraff, G. M.; Rabolt, J. F. *Macromolecules* **1991**, *24*, 4084.