Two-Dimensional Piezochromism and Orientational Modulations in Polysilane Monolayer

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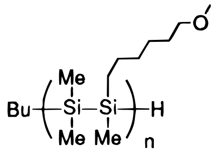
Polysilanes possessing a catenated silicon backbone exhibit a variety of interesting physical properties, mostly derived from their σ-conjugated electronic structure, and hence are of potential technological importance.[1] As for the optical properties of bulk polysilanes, preparations of several polysilanes bearing functional groups and their Langmuir−Blodgett (LB) films have been investigated.[2] However, the characteristic behavior of such a functional polysilane monolayer at the air/water interface has not been explored in detail. Recently, we reported the synthesis of a new functional polysilane (**1**) by the anionic polymerization of masked disilene and the observation of a "surface-mediated chromism" in this polysilane LB film as a novel chromic behavior of polysilanes.[3,4] UV absorption of the monolayer of **1** showed a significant bathochromic shift only on a *hydrophilic* surface, whereas a *hydrophobic* substrate surface gave an absorption band analogous to that of a cast film. Thus, the chromism reflects the *hydrophilic/hydrophobic* nature of the substrate surface, and the bathochromic shift should be mediated by a hydrogen bond interaction between the silica surface and the ethereal part in the substituent of **1** that could preserve the thermally unstable on-water conformation of **1**.



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We now report a particular piezochromic behavior of the monolayer of **1** on a water surface, which is observed during the process of monolayer compression. In addition, it was also found that this piezochromism is accompanied by a significant change of the in-plane orientation of the monolayer on a water surface.

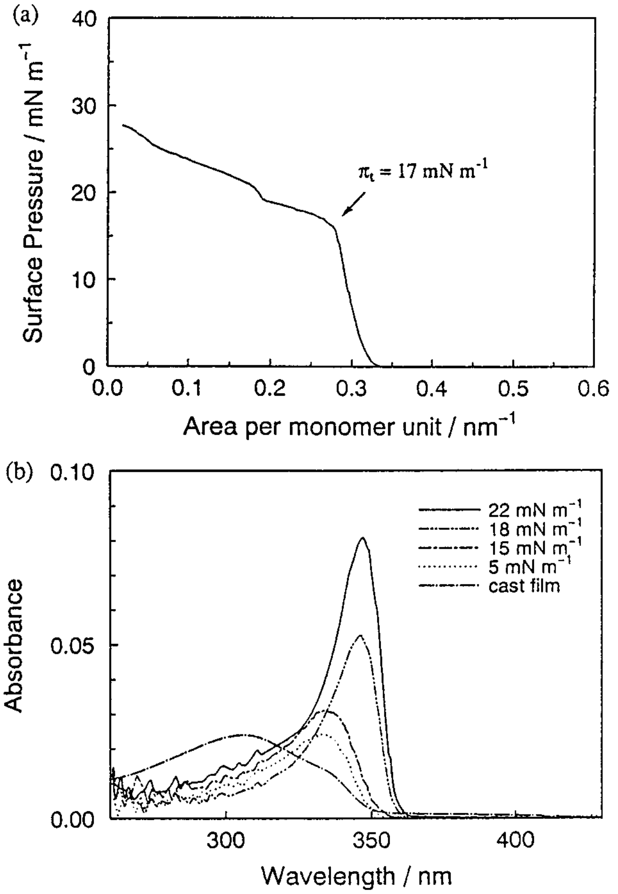

Figure 1. (a) Surface pressure−area isotherm of polysilane **1** on distilled water at room temperature. (b) UV spectrum of the cast film of polysilane **1** and surface-pressure-dependent UV spectra of the monolayer of **1** on a water surface. Absorbance of the cast film is normalized to that of the monolayer observed at 5 mN m^{-1}.

LB experiments were performed with a Lauda MGW film balance, and the absorption spectra of the monolayer on a water subphase were measured by using a photodiode array spectrometer with optical fibers (MCPD-1000, Otsuka Electronics). Figure 1 indicates the pressure−area isotherm at room temperature and the UV absorption spectra of the monolayer of **1** (M_n = 7.2 × 10^3, M_w/M_n = 1.5) on the water subphase. It was found that there was an obvious inflection at 17 mN m^{-1} in the pressure−area isotherm. As we reported in the previous study,[3] an absorption band peaking at 334 nm was observed on a water surface below 17 mN m^{-1}, which was red-shifted and narrower than that of the cast film. However, above a surface pressure of 17 mN m^{-1}, the intensity of the absorption suddenly increased, and the absorption maximum was shifted to 347 nm. This remarkable change was completely reversible, and the critical pressure exhibiting this piezochromism corresponded exactly to that of the inflection point of the surface pressure−area isotherm of **1**. The large absorption changes around 17 mN m^{-1} are not due to increases of monolayer density but should be attributed to the inherent conformational change of polysilane **1**, because the absorbance enhancement was not proportional to the area change. Similar abrupt piezochromism of polysilanes has been observed in high-pressure measurements of bulk films.[5] Although Seki *et al.* have already reported the small hypsochromic shift of polysilane absorptions depending on the surface area,[2b] the present observation can be regarded as the first example of abrupt piezochromism of a polysilane monolayer observed on a water surface.[6] This result shows that the abrupt piezochromism of polysilane still occurs without three-dimensional packing effects of

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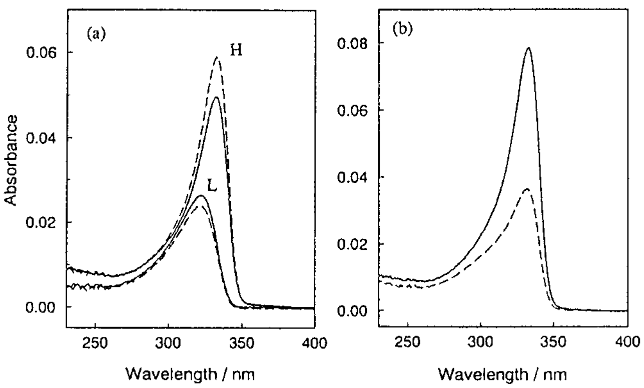

Figure 2. (a) Polarized UV absorption spectra of the monolayer of polysilane **1** on a *hydrophilic* quartz plate prepared at 13 and at 18 mN m^{-1}, labeled L and H, respectively. (b) Polarized UV absorption spectra of the monolayer of polysilane **1** on a *hydrophilic* quartz plate prepared in the different deposition manner, as illustrated in Figure 3, at 21 mN m^{-1}. Absorption spectra were taken at normal incidence with the linearly polarized light set parallel (solid line) and orthogonal (dotted line) to the dipping direction.

polysilane rods and that a two-dimensional compressive force is strong enough to stabilize the *all-trans* conformation of polysilane **1**.[7]

For the monolayers transferred onto a *hydrophilic* quartz plate by the conventional vertical dipping method, the position of the absorption peak was qualitatively in agreement with that on the water surface (Figure 2a). The wavelengths of the absorption peaks for the LB films deposited at 13 and 18 mN m^{-1} were 322 and 333 nm, respectively, which were significantly shifted to longer wavelengths from that for a cast film ($\lambda_{\max} = 306$ nm). Although these values showed some hypsochromic shifts from those obtained on the water surface, the spectral shapes were precisely maintained (*cf.* Figures 1b and 2a).[9] On the other hand, the monolayers deposited on a *hydrophobic* quartz surface at any surface pressure conditions gave blue-shifted absorption spectra identical to those observed for the cast film. This should show that the compression-induced conformational change of **1** on water is preserved on a *hydrophilic* surface but is randomized on a *hydrophobic* surface.

The most striking pressure-dependent feature of the monolayer of **1** was the facile change of the direction of two-dimensional orientation on a quartz plate. The dichroic ratio of the monolayer of **1** prepared at 13 mN m^{-1} was 1.11, indicating that the polysilane backbone is aligned parallel to the dipping direction to some extent. The dichroic ratio of the monolayer prepared at a relatively high pressure of 18 mN m^{-1}, in contrast, became less than 1, *i.e.*, 0.84. This result signifies that, under the higher pressure condition, the backbone orientation is inverted and aligned perpendicular to the dipping direction. Both the shift of absorption and the change of dichroic ratio are completely reversible *via* surface pressure changes, and thus it is apparent that the conformational and orientational changes occur concomitantly. This unique switching of the direction of orientation on a quartz plate due to the increase of surface pressure is explained not by a flow orientation mechanism adopted for all previous polysilane LB films[2,10] but by a compression-induced orientation mechanism. It is envisioned that polysilane chains are forced to align parallel to the compression bar of the rectangular Langmuir trough at the higher surface pressure condition. Similar compressive in-plane orientation under static conditions has been observed in other monolayers of rigid and hairy rodlike polymers, *i.e.*, polyimides,[11] polydiacetylenes,[12] and so on.[13] Therefore, it is suggested that the rigidity and viscoelasticity of **1** are likely to be increased by the compression-induced transformation of backbone to the *all-trans* conformation.[14] Consequently, at higher pressures, the changes of the physical properties are considerable enough to allow the compression-induced orientation and to overcome the flow-induced orientation.

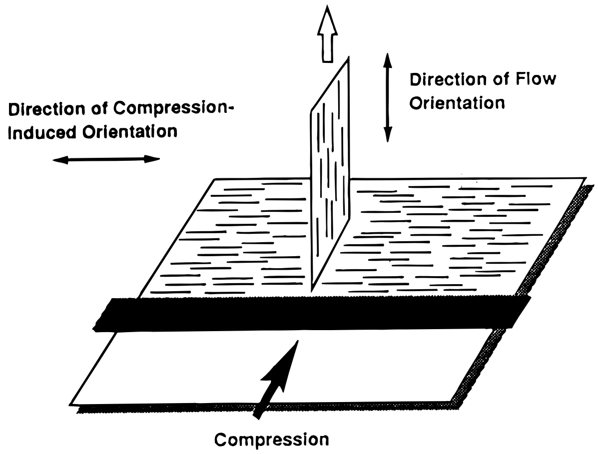

Figure 3. Brief illustration of the deposition manner of the monolayer of **1**, in which a cooperative orienting effect by both flow and compression is attained.

To confirm the in-plane orientation of **1** on a water surface, the direction of the quartz plate was just arranged from perpendicular to parallel to a compressive direction during the process of LB deposition, as illustrated in Figure 3. The highest value of the dichroic ratio, 2.17, was obtained from this measurement, as we expected (Figure 2b). It is thus concluded that, in this deposition manner, the flow orientation and the compression-induced orientation mechanisms are cooperated to give high backbone orientation on a *hydrophilic* quartz surface. It is noteworthy that this significant dependency of dichroic ratio on the configuration used is not observed below the surface pressure of 17 mN m^{-1}, indicating that compression-induced orientation does not occur at lower surface pressure conditions.

In summary, we have demonstrated a novel piezochromism and switching behavior of in-plane surface orientation of functional polysilane **1** at the air/water interface. These results disclose that the combination of a hydrogen bond interaction and a surface pressure will considerably affect not only the conformation of the individual polysilane chain but also the two-dimensional structure of aggregates at the air/water interface. Detailed studies on the behavior of other functional polysilane monolayers are in progress.

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(6) There appeared to be a small but reproducible kink, where the collapse of the monolayer could occur, at *ca*. 20 mN m^{-1} in the pressure−area isotherm. The details of compressive deformation process of the monolayer of **1** above this pressure will be reported elsewhere.

(7) The absorption maximum of **1** at 347 nm is *ca*. 15 nm shorter than that of poly(dihexylsilane), which is regarded as a typical *all-trans* polysilane. However, it has been demonstrated that there is a substituent effect on the absorption maximum wavelength of *all-trans*-poly(dialkylsilane); poly(dimethylsilane) (PDMS) shows an absorption maximum at 340 nm in the solid state, although the *all-trans* conformation of PDMS has been confirmed by X-ray diffraction.[8] Since the absorption maximum wavelength of polysilane **1** is sufficiently comparable to that of PDMS, the *all-trans* conformation of **1** at the high surface pressure region is supposed.

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(9) As for the wavelengths of the absorption maxima, there was not an exact coincidence between the monolayers on a water and on a *hydrophilic* quartz plate; hypsochromic shifts (*ca*. 12 nm) of absorption maxima were commonly observed on a *hydrophilic* quartz surface compared with that of a water surface. It could be explained that a slight conformational disordering of the main chain due to release from the surface pressure should occur even on a *hydrophilic* quartz plate, resulting in the small blue shift of the absorption maximum.

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