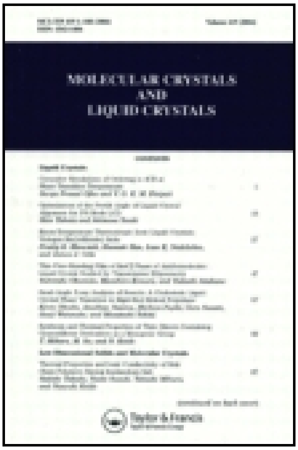

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Novel Surface-Mediated Chromism of Polysilane at the Air/Water Interface

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NOVEL SURFACE-MEDIATED CHROMISM OF POLYSILANE AT THE AIR/WATER INTERFACE

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Abstract A novel ethereal group-substituted polysilane with an ordered structure exhibits an unusual chromism induced by the hydrophilic nature of the substrate surface. Compression-induced chromism and the in-plane orientation of the polysilane monolayer were also observed at the air/water interface.

INTRODUCTION

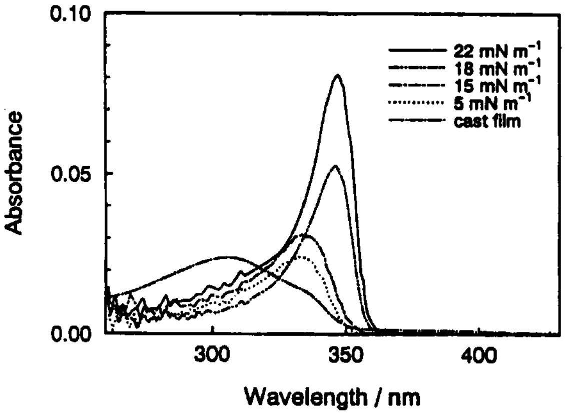
Polysilanes that consist of a catenated silicon backbone exhibit a variety of interesting physical properties due to their σ conjugated electronic structure, and hence have technological importance.[1] In connection with the optical properties of bulk polysilane films, preparation of several functional groups-substituted polysilanes and their Langmuir-Blodgett (LB) films have been investigated.[2] Recently, we have reported the synthesis of a new functional polysilane (**1**) with an ordered structure by the anionic polymerization of a masked disilene and the observation of a novel 'surface-mediated chromism' for the LB film of this material.[3] In this study, we have investigated the detail of the unique chromic effect at the air/water interface and found that an additional compression-induced chromism and the in-plane orientation of the polysilane monolayer also take place at a relatively high surface pressure region.

EXPERIMENTAL

LB experiments were performed with a Lauda MGW film balance, and the absorption spectra of the monolayer on a water subphase were measured using a photodiode array spectrometer with optical fibers (MCPD-1000, Otsuka Electronics). Polarized absorption spectra of the monolayers transferred onto quartz plates were measured on a JASCO HSSP-3 spectrophotometer.

RESULTS AND DISCUSSION

As we have already reported,[3] polysilane **1** indicates a characteristic surface pressure-area isotherm with a large inflection at 17 mN m^{-1} on a water surface. Fig.1 illustrates the UV absorption spectra of the monolayer of **1** (Mn = 7.2 x 10^3, Mw/Mn = 1.5) measured on the water subphase. In the lower surface pressure region, the absorption band with a λ_{max} of 334 nm was observed on a water surface. This band was red-shifted and narrower than that of cast film due to a strong hydrogen bond interaction between ethereal substituents and the water surface. However, above the critical surface pressure of 17 mN m^{-1}, the intensity of the absorption dramatically increased, and the absorption maximum was markedly red-shifted to 347 nm.



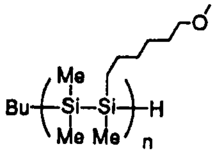


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FIGURE 1. UV spectrum of the cast film of polysilane 1 and surface-pressure dependent UV spectra of the monolayer of 1 on a water surface. Absorbance of the cast film is normalized to that of the monolayer observed at 5 mN m^{-1}.

This remarkable change was completely reversible, and the critical pressure exhibiting this piezochromism was identical with that of the surface pressure-area isotherm of **1**. Therefore, it is concluded that a compressive force applied in two dimensions at the interface is strong enough to induce the abrupt conformational change of polysilane **1**.

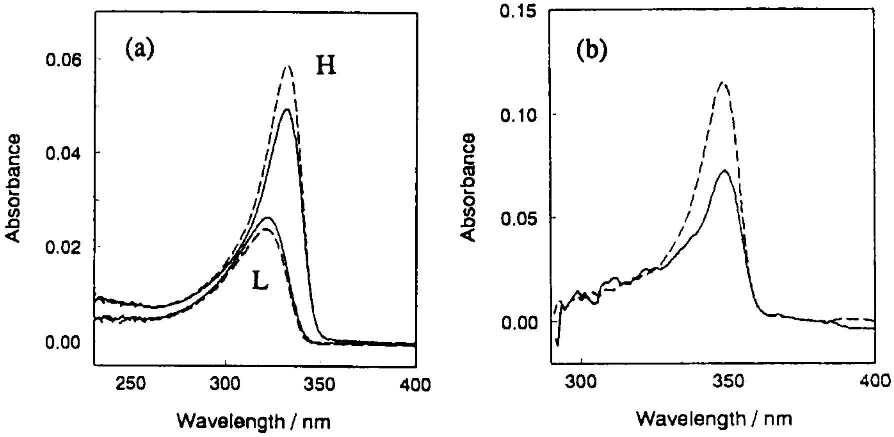

FIGURE 2. (a) Polarized UV spectra of polysilane **1** on a *hydrophilic* quartz plate prepared at 13 mN m^{-1} and at 18 mN m^{-1}, labeled 'L' and 'H', respectively. (b) Polarized UV spectra of the monolayer of polysilane **1** floated on a water surface at 21 mN m^{-1}. Absorption spectra were taken in normal incidence with the linearly polarized light set parallel (solid line) and orthogonal (dotted line); (a) to the dipping direction; (b) to the direction of a compression.

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). However, 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** transferred at 13 mN m^{-1} was 1.11, indicating that the polysilanes are roughly aligned parallel to the dipping direction. In contrast, the dichroic ratio of the monolayer prepared at a relatively high pressure of 18 mN m^{-1}, 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. This unique direction switching of orientation on a quartz plate induced by an increase in surface pressure is not explained by a flow orientation mechanism adopted for all of previous polysilane LB films,[2] but by a compression-induced orientation mechanism. It is envisioned that polysilane chains are forced to align parallel to the compression bar of the Langmuir trough at the higher surface pressure condition.

The in-plane orientation of **1** on a water surface was successfully confirmed from the polarized UV absorption spectra of the monolayer directly measured on a water subphase. As shown in Figure 2b, a large dichroic ratio, *i.e.*, 0.63 was observed even on a water surface. Thus it is obvious that polysilane rods already align parallel to the compression bar at the interface. It is noteworthy that this significant orientation is not observed below the surface pressure of 17 mN m^{-1}, indicating that a compression-induced orientation occurs only at the higher surface pressure condition.

In summary, we have demonstrated the novel chromic and orientational phenomena of functional polysilane **1** at the air/water interface. From these results, it is evident that the combination of hydrogen bond interactions and surface pressure will considerably affect both the conformation of the individual polysilane chain and the two dimensional structure of the monolayer at the air/water interface.

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