Surface-mediated chromism in a polysilane Langmuir–Blodgett film

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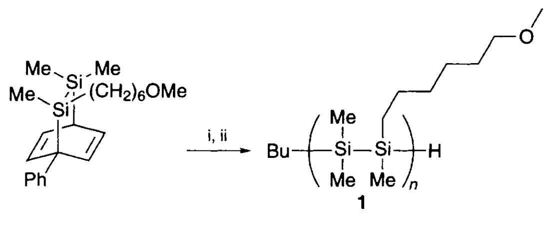
A novel functional polysilane with an alternating structure is synthesized by anionic polymerization of a masked disilene monomer; the monolayer of the polysilane shows a unique chromism that reflects the hydrophilic/hydrophobic nature of the substrate surface.

Polysilanes are a new class of polymers which have a strong electronic conjugation effect due to linear Si–Si catenations.[1] In order to control the optical properties of bulk polysilane films, preparation of several polysilanes containing functional groups and their Langmuir–Blodgett (LB) films have been investigated.[2] The preparation method of the functional polysilanes, however, has been limited to a conventional Wurtz coupling method. We have recently established the anionic polymerization of masked disilenes as an entirely new synthetic route to polysilanes of highly ordered structure.[3] Herein, we report the synthesis and LB film preparation of a novel functional polysilane bearing an ethereal group,[4] poly[1-(6-methoxyhexyl)-1,2,2-trimethyldisilanylene] **1**, by the masked disilene method. In this study, it was found that a new type of chromism in the polysilane LB film was induced by the difference in the surface properties of substrates. We propose that this phenomenon could be termed as a 'surface-mediated chromism'.

Polysilane **1** was prepared from a corresponding masked disilene monomer (Scheme 1). The molecular mass of **1** was determined by gel permeation chromatography with THF as eluent: $M_n = 7.2 \times 10^3$, $M_w/M_n = 1.5$. The structure was also confirmed by ^{1}H and ^{13}C NMR spectral analyses.† The ratio of head-to-tail : head-to-head was estimated to be 65 : 35 by ^{13}C NMR analysis. Altough the order of regioselectivity was not high compared with the results of our previous study,[3] **1** exhibited a well defined thermochromism which is characteristic of polysilanes with an alternating structure. As shown in Fig. 1, a cast film of **1** gave an absorption maximum at 306 nm at 23 °C, but below 15 °C a new band peaking at 328 nm started to grow.

LB experiments were performed with a Lauda MGW film balance. Fig. 2 shows the surface pressure–area isotherm per monomer unit of **1** on distilled water. The characteristic curve obtained clearly shows the formation of a stable monolayer at the air/water interface. The monolayer could be transferred onto both a clean hydrophilic quartz plate and a hydrophobic one treated with hexamethyldisilazane at 10 mN m^{-1} by the conventional vertical dipping method.



Scheme 1 *Reagents and conditions*: i, BuLi (cat.), −78 °C to room temp.; ii, EtOH

Fig. 3 indicates polarized UV spectra of the monolayers transferred onto these quartz substrates. A considerable difference was observed in these spectra depending on the surface properties of the quartz plate used.

The monolayer of **1** deposited on a *hydrophobic* quartz plate showed a broad UV absorption at 306 nm, which was in agreement with the value obtained for the cast film at room temperature. On the other hand, the absorption maximum of **1** on a *hydrophilic* quartz plate shifted to 322 nm and the width of absorption became substantially narrower. The dichroic ratio obtained at the absorption peak was 1.11, indicating that the polysilane backbone aligned parallel to the dipping direction to some extent. The absorption spectrum of the monolayer of **1** was also measured on the water subphase at 10 mN m^{-1} by using a photodiode array spectrometer. The shape of the UV absorption spectrum obtained on the water surface resembled

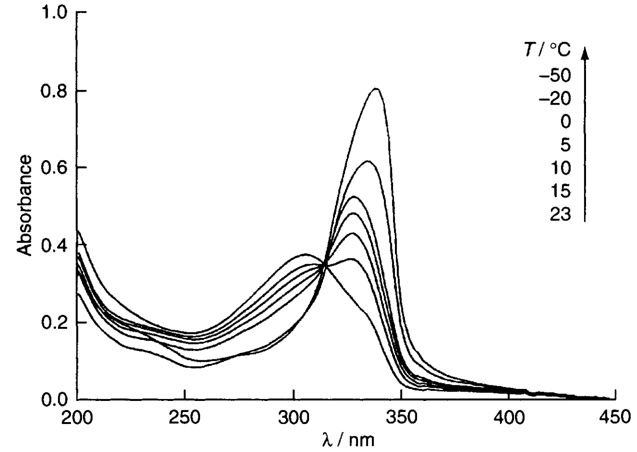


Fig. 1 Temperature dependent UV spectra of the cast film of polysilane **1**

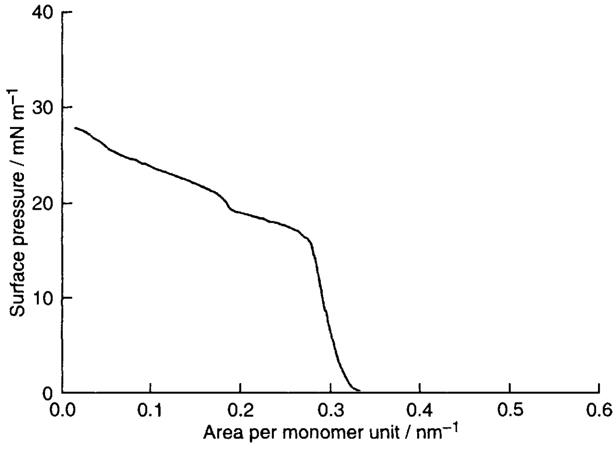


Fig. 2 Surface pressure–area isotherm per monomer unit of the monolayer of polysilane **1** on distilled water

that observed for the hydrophilic surface giving a maximum at 334 nm. The above results indicate that the conformations of the transferred monolayer of **1** on the hydrophobic and hydrophilic surfaces correspond to those in the cast film and on the water surface, respectively. We consider that this is a new type of chromism, which is essentially similar to the thermochromism in Fig. 1, but induced by hydrophilic surface properties.

The phenomenon can be explained as follows. The conformation of **1** on the water surface is preserved by the hydrogen bonding between the silica surface and the ethereal part in the substituent of **1** on the hydrophilic quartz plate. On the other hand, the monolayer of **1** is attached to the hydrophobic surface only by van der Waals forces, and this weaker interaction would not sustain the thermodynamically unstable conformational state that is attained on the water surface. This should lead to a conformational change to a stable conformation with a short-wavelength absorption as observed in the cast film at room temperature.

Although several chromic phenomena, *i.e.* thermochromism,[5] piezochromism[6] and solvatochromism,[7] have been well known for many polysilanes, such a 'surface-mediated chromism' has not been reported in previous studies. The present results imply the fixation of a thermally unstable backbone conformation *via* hydrogen bonding between functional groups of polysilane and hydrophilic surfaces. We also assume that the marked modulation effect on the backbone conformation may be derived from the ordered alternating structure of **1**.

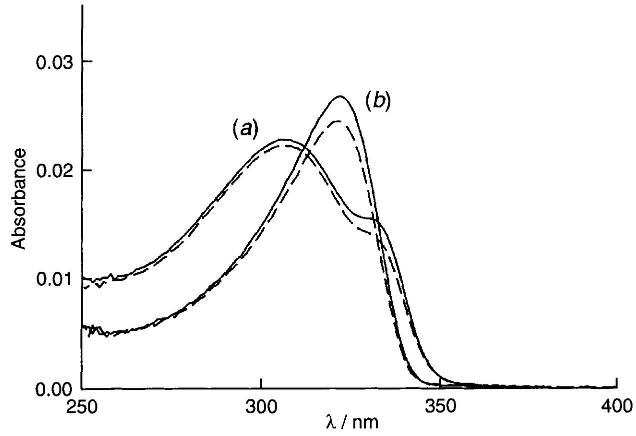


Fig. 3 Polarized UV absorption spectra of the monolayer of polysilane **1** on both sides of (*a*) a hydrophobic quartz plate and (*b*) a hydrophilic quartz plate. Absorption spectra were taken in normal incidence with the linearly polarized light set parallel (—) or orthogonal (---) to the dipping direction.

In summary, a new type of chromic behaviour of a polysilane is observed through interfacial interactions with substrate surfaces. The present work provides a unique technique far controlling the conformation of the backbone through intermolecular interactions. The effect of the surface pressure and metal ions dissolved in the subphase on the absorption and orientation of this polysilane LB film monolayer is now under investigation.

Footnote

† **1**: colourless sticky gel, 32%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.51 (s. 9 H), 1.10 (m, 2 H), 1.30–1.75 (m, 8 H), 3.17 (s, 3 H), 3.28 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ −4.9 [Si*Me*R, head-to-tail (HT)], −4.4 [Si*Me*R, head-to-head (HH)], −2.3 (Si*Me*$_2$, HH), −1.8 (Si*Me*$_2$, HT), 15.1 ($SiCH_2$, HT), 15.4 ($SiCH_2$, HH), 26.5, 27.7, 30.3, 34.6, 58.4, 72.96; ^{29}Si NMR (59 MHz, $CDCl_3$) δ −36.3 (m, $SiMe_2$), −32.2 (m, SiMeR).

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