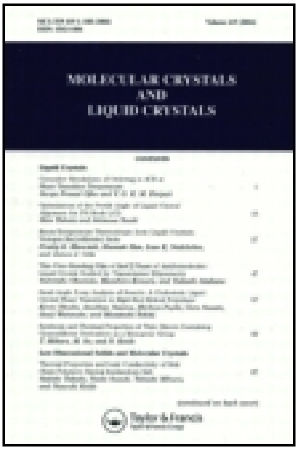

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Abstract Novel functional polysilane homopolymers bearing ethereal groups were prepared by Wurtz coupling method. The polysilane monolayers demonstrated a unique chromic effect induced by a specific conformational and orientational change of polymer backbones at the air/water interface.

Key Words: polysilane, LB films, monolayer, UV absorption, orientation

INTRODUCTION

Recently polysilane has been received considerable attention as a novel candidate for an organic conjugated polymer.[1] The polymer exhibits a strong UV absorption due to the σ-conjugated electronic structure, and it has been known that the spectrum highly depends on the conformational change of the polysilane backbone. Recently, we have reported the synthesis of a new functional polysilane with an ordered alternating structure and the observation of a novel 'surface-mediated chromism' for the LB film of this material.[2] The chromism observed reflects the *hydrophilic/hydrophobic* nature of the substrate surface, and the specific bathochromic shift of the absorption was mediated by a hydrogen bond interaction between the *hydrophilic* surface and the ethereal substituent of the polysilane. In addition, it was also found that a particular piezochromic behavior of the monolayer accompanied by a significant change of in-plane orientation on a water surface. In this report, novel functional polysilane homopolymers were prepared, and their conformational and orientational behavior at the air/water interface were investigated. We found that the new polysilanes also demonstrated a unique chromic effect at the interface as observed in our previous study.

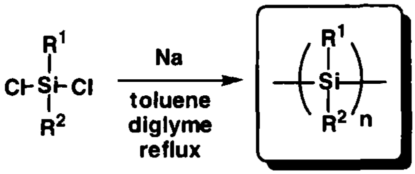
EXPERIMENTAL

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 or without a polarizer. (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

1) Preparation of the functional polysilanes

It has been known that the substituents on a backbone play a very important role in the conformational change of polysilanes. Hence new functional polysilane homopolymers **1-3** having different substitution patterns were prepared as described in the following scheme.



1a: $R^1 = (CH_2)_6\text{-}OCH_3$, $R^2 = CH_3$
1b: $R^1 = (CH_2)_{10}\text{-}OCH_3$, $R^2 = CH_3$
2a: $R^1 = R^2 = (CH_2)_6\text{-}OCH_3$
2b: $R^1 = R^2 = (CH_2)_{10}\text{-}OCH_3$
3a: $R^1 = (CH_2)_6\text{-}OCH_3$, $R^2 = i\text{-}C_4H_9$
3b: $R^1 = (CH_2)_{10}\text{-}OCH_3$, $R^2 = i\text{-}C_4H_9$

Polysilanes **1** and **2** are unsymmetrically and symmetrically substituted, respectively. Polysilanes **3** adopt not only an unsymmetrical substitution system but also have a rigid helical structure induced by the steric hindrance of a branched substituent. Such helical polysilanes have been originally found by Fujiki in a recent chiral polysilane study.[3] The structure of the polymers were confirmed by NMR spectra and the molecular weights were distributed in the range of 10^5 - 10^3 determined by GPC analyses.

2) Monolayer properties

Surface pressure-area isotherms of the polysilanes **1-3** at the air/water interface were measured by means of LB method. (Fig. 1) Polysilanes **1a**, **2a** and **3a** bearing methoxyhexyl group showed a characteristic isotherm with a large inflection and a plateau region, indicating the formation of a stable monolayer. However, in the cases of polysilanes **1b** and **3b** bearing methoxydecyl group, the collapse of monolayer started at a relatively low surface pressure and no plateau region was observed. Resulting from these observation, it should be concluded that the methoxydecyl group reduced a

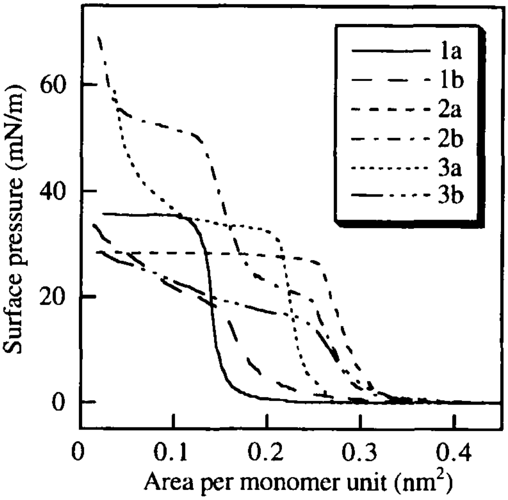


FIGURE 1. Surface-area isotherms of functional polysilanes 1-3 at the air/water interface

stability of the polysilane monolayer probably due to the flexibility of long methylene units in the substituent. Interestingly, a symmetrically substituted polysilane **2b** demonstrated a two-step isotherm and the final surface pressure reached to more than 60 mN/m in spite of the methoxydecyl substitution. It would be considered that a specific bilayer formation could take place in **2b**. Similar explanation for the two-step isotherm was already suggested in the early study of polysilane LB films.[4] Fig. 2 illustrates the comparison of UV absorption spectra of the polysilanes between the cast film and the monolayer transferred onto a hydrophilic quartz plate. In the case of **1a**, the absorption of the monolayer was obviously red-shifted and narrower than that of cast film. This optical behavior was substantially identical with that of the ordered alternating polysilane in our previous study.[2] Moreover, a notable change of absorption was also observed even in polysilane **2a**. This polysilane, however, did not show a *bathochromic shift* but gave a drastic *hypsochromic shift* in the monolayer. Although there were two peaks of **2a** in the cast film, the absorption peaking at 350 nm of the cast film completely disappeared for the monolayer, and only an absorption at a relatively short

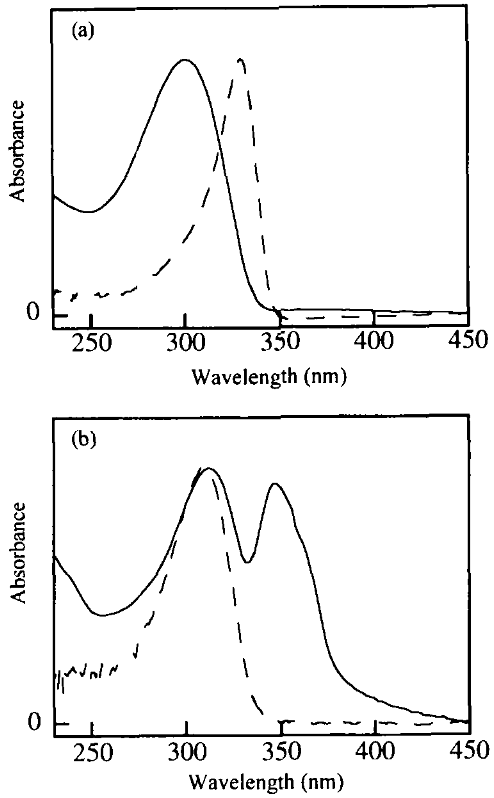


FIGURE 2. UV spectra of (a) polysilane 1a and (b) 2a. (solid line: cast film, dotted line: monolayer on a quartz plate)

wavelength remained. Since the rest of polysilanes **1b** and **2b** also exhibited a spectral change with a bathochromic shift for the monolayer, it was concluded that a 'surface-mediated chromism' induced by a hydrogen bond interaction between substituents and a hydrophilic surface should be very common phenomena among the functional polysilane derivatives, and the most stable conformation induced on a water surface highly depended on the substituents. On the contrary, the helical polysilanes **3** did not show any chromic effect at the interface, indicating too high stability of the helical backbone conformation to move. However, only polysilane **3a** demonstrated a compression-induced orientation at the air/water interface, which have never been observed for the rest of polysilanes **1**, **2** and **3b**. Fig. 3 shows a polarized UV spectra of the monolayer of **3a** directly measured on a water surface at 25 mN/m. The dichroic ratio obtained is 2.1, indicating a specific in-plane orientation of the monolayer. This result clearly manifested that **3a**

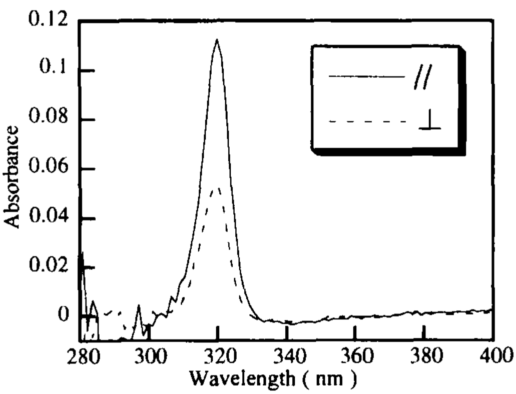


FIGURE 3. Polarized UV spectra of the monolayer of polysilane 3a floated on a water surface at 25 mN/m. (solid line: parallel, dotted line: orthogonal to the direction of a compression bar)

had an enough high rigidity, derived from a helical backbone structure, to attain a molecular alignment on a water surface by a two-dimensional compression. On the other hand, a similar helical polysilane **3b** did not exhibit such an orientation at all. The reason for the disordering would be the methoxydecyl group on **3b** was so flexible, as mentioned above, that the monolayer should be collapsed before the alignment took place.

In summary, we have demonstrated that 'surface-mediated chromism' commonly occurs in a lot of functional polysilanes. It has been also found that a helical polysilane with short ethereal groups has a high rigidity to enable a compression-induced orientation.

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