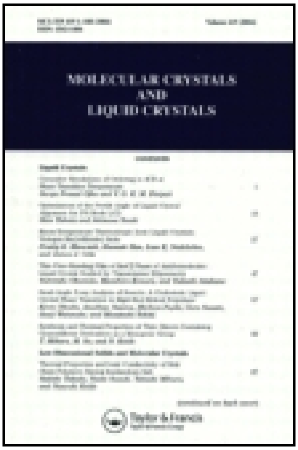

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Langmuir-Blodgett Films of Functional Polysilanes. Modification of Optical Properties in Polysilane Monolayer at the Air/Water Interface

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Langmuir-Blodgett Films of Functional Polysilanes. Modification of Optical Properties in Polysilane Monolayer at the Air/Water Interface

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Novel functional polysilanes bearing ethereal groups were prepared and the interfacial behavior of the polysilanes was investigated by using the LB method. It was found that the polysilane monolayers demonstrated a unique chromic effect induced by a specific conformational and orientational change of polymer backbones at the air/water interface.

Keywords: polysilane; functional group; LB film; monolayer; UV absorption; self-organization

INTRODUCTION

Recently, considerable interest has been focused on organic conjugated polymers due to their unique electronic structure, being expected of the industrial applications for organic semiconductors, light-emitting materials and so on. The polysilane, which is a organometallic σ-conjugated polymers, exhibits a distinct UV absorption and fluorescence due to the strong σconjugation effect derived from Si-Si catenations.[1] It has been known that the absorption of polysilanes highly depends on the conformational change of the main chain similar to the other π-conjugated polymers. So far, thermochromism, piezochromism and solvatochromism have been observed for several polysilane derivatives. Recently, we have reported the synthesis of a new functional polysilane with an ordered alternating structure by masked disilene method[2] and the observation of a novel 'surface-mediated chromism' for the LB film of this material.[3] In addition, a significant change of in-plane orientation on a water surface has been also observed for the monolayer of the functional polysilane.[4] In this paper, the detail of the unique chromic and orientational phenomena of the functional polysilane thin film is described. Similar interfacial phenomena and self-organization behavior of novel helical polysilanes are also investigated.

EXPERIMENTAL

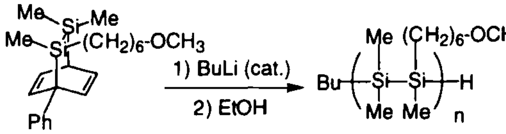
LB experiments were performed with a Lauda MGW film balance, and the absorption spectra of the monolayer on a water subphase were measured by using a photodiode array spectrometer with or without a polarizer. (MCPD-1000, Otsuka Electronics). Optical microscopy study was conducted using a OLYMPUS BH-2 polarized light microscope. Atomic force microscopy (AFM) was performed by using a Digital Instruments Nanoscope IIIa atomic force microscope in a contact mode.

RESULTS AND DISCUSSION

1) Preparation of the Functional Polysilanes with an Alternating Structure by

the Anionic Polymerization of Masked Disilene

Polysilane **1** was prepared from the corresponding masked disilene monomer. (eq. 1) The molecular weight of **1** was determined by gel permeation chromatography with THF as eluent; Mn = 7.2 x 10^3, Mw/Mn = 1.5.



(1)

1

The formation of a stable monolayer of **1** at the air/water interface was confirmed by a surface pressure-area isotherm measurement. Figure 1 illustrates the UV absorption spectra of the monolayer measured on a water subphase. In the lower surface pressure region, the absorption band peaking at 334 nm was observed on a water surface. This band was red-shifted and much narrower than that of cast film and thus a strong hydrogen bond interaction between ethereal substituents and the water surface should cause the bathochromic shift of absorption. In addition, it was also found that a particular piezochromic behavior of the monolayer. The intensity of the absorption dramatically increased above the critical surface pressure of 17 mN m^{-1}, and the absorption maximum was markedly red-shifted to 347 nm. In this situation, a compression-

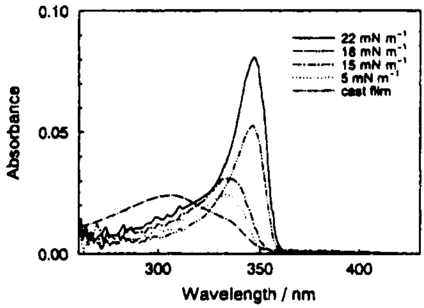
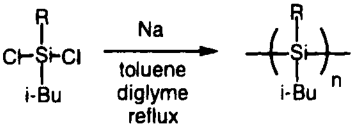


FIGURE 1. UV spectrum of the cast film of polysilane **1** and surface pressure-dependent UV spectra of the monolayer of **1** on a water surface

induced orientation simultaneously occurred and an ordered alignment of polysilane chains on a water surface was detected by polarized absorption spectroscopy. It is noteworthy that this significant orientation is not observed below the surface pressure of 17 mN m^{-1}, indicating that the compression-induced orientation occurs only at the higher surface pressure condition. 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.

2) Preparation of Helical Polysilanes with Functional Group and the Interfacial Behavior of the Polysilanes

Recently, unusual helical polysilanes have been prepared by Fujiki in the chiral polysilane study.[5] Even in a solution, the helical polysilanes sustain a rigid rod-like structure induced by the steric hindrance of a branched substituent on silicon, and shows a distinct circular dichroism derived from a sole screw-sense of the main chain when the chiral substituents connected with the backbone. In order to investigate the specific conformational behavior of such helical polysilanes, a new helical polysilane **2** bearing ethereal group was prepared by Wurtz coupling method (eq. 2). As a reference compound, the known helical polysilane without a functional group **3** was also prepared. On the basis of their surface pressure-isotherm



(2)

2: R = $-(CH_2)_6-OCH_3$
3: R = $-(CH_2)_6-CH_2CH_3$

measurements, only polysilane **2** was found to form a stable monolayer on a water surface. Therefore, it is obvious that the functional groups are always necessary to prepare a polysilane monolayer even for the highly stiff, rod-like helical polysilanes. Polysilane **2**, however, did not show any chromic effect at the interface, indicating too high stability of the helical backbone conformation to change. The polysilane **2** nevertheless demonstrated a characteristic compression-induced orientation at the air/water interface. Figure 2 shows a polarized UV spectra of the monolayer of **2** 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 **2** had an enough high rigidity to take place a molecular alignment on a water surface by a two-dimensional compression. Furthermore, during the course of the study on that helical polysilane property, it was unexpectedly found that one of the helical polysilanes showed a somewhat unique self-organization phenomenon. Figure 3 demonstrates the optical texture of the cast film of polysilane **3** observed by using a polarized light microscope. Obviously, a two-dimensional mesh-like structure is indicated. Although the columnar mesophase[6] and spherulite[7] of polysilanes have been reported, the present

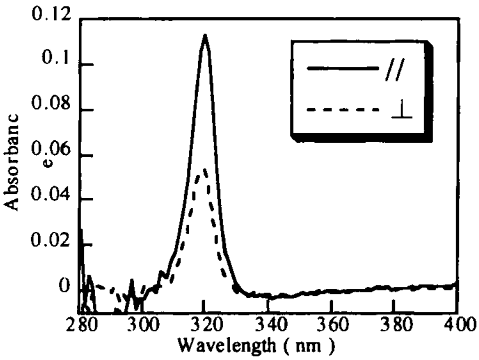


FIGURE 2. Polarized UV spectra of the monolayer of polysilane **2** floated on a water surface at 25 mN/m. (solid line: parallel, dotted line: orthogonal to the direction of a compression bar)

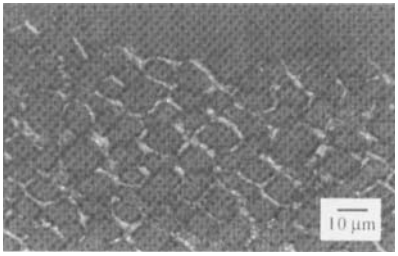


FIGURE 3. Optical texture of the polysilane 3 thin film taken by polarized light microscope.

observation is regarded as a quite new type of self-organization behavior of polysilanes. This mesh-like structure was also confirmed by AFM measure-ment, and the specific formation of micro-crystalline domain was strongly suggested as the origin of the two-dimensional structure of **3** by the AFM images. Further detailed study on this phenomenon is under investigation.

Acknowledgments

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