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Preparation of Oriented Langmuir–Blodgett Films of Polysilanes Bearing Hydroxyalkyl or Alkoxyalkyl Groups

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ABSTRACT: Polysilane polymers bearing hydroxyalkyl or alkoxyalkyl groups form monolayers (L films) at an air–water interface. It is possible to transfer all of the L films to hydrophobic substituents to provide Langmuir–Blodgett films. Among these polymers, polysilanes having more than three alkyl carbons have provided oriented polysilane thin films in which the silicon main chains align with each other in the direction parallel to the dipping direction of the substrates. The orientations were evaluated by their polarized UV absorptions. The dichroic ratios increase when Ca^{2+} ions were added to the water. Polysilane films with alkoxyalkyl groups show abrupt thermochromic transitions, while polysilanes with hydroxyalkyl groups show no thermochromism.

Introduction

Ever since soluble polysilanes were synthesized,[1,2] polysilanes have been extensively studied because of their unusual electronic and photochemical properties,[3–12] as well as potential applications in future electronic devices[13–24] such as in microlithiography, photoconductivity, and nonlinear optics. These properties have been attributed to the extensive delocalization of σ electrons, which is strongly coupled with the polymer conformation.[11,12]

Because the σ electrons are delocalized along the silicon main chains, it would be useful to obtain thin films in which the silicon chains align in one direction in order to evaluate the polysilane properties (Figure 1b). The Langmuir–Blodgett (LB) technique is an excellent method for preparing ultrathin films with a well-defined molecular order.[25–30]

Suitable LB films can be formed either from amphiphilic polymers[26,27] or from polymers with rigid chains.[28,29] The authors have already synthesized amphiphilic polysilanes with hydroxyphenyl groups and have revealed that these polymers provide monolayers at the air–water interface.[31] Seki et al. have independently reported LB films formed by amphiphilic polysilanes bearing ammonium ion groups.[32] Duda et al. have reported that rodlike polymers where the rods are modified by attachment of side groups with conformational flexibility and minimal polarity become a new class of layer-forming materials.[28,29] Applying this idea to polysilanes, Embs et al. succeeded in preparing stable monolayers by using poly(diphenylsilane)s whose main chains are made rigid by the two phenyl groups.[33]

All polymers which provide stable monolayers (L films) at the air–water interface do not necessarily yield oriented polymer films in a plane when the monolayers are transferred to substrates, because if L films are transferred to substrates in the same states as they are at the air–water interface, orientations of polysilanes in a plane would not be observed (Figure 1a). Poly(diphenylsilane)s and polysilanes bearing hydroxyphenyl groups have been reported to provide oriented LB films in a plane (Figure 1b).[31,33] These polysilanes always had phenyl groups directly bonded to the silicon chains, which has been considered to be necessary to endow the polymers with rigidity, leading to oriented films in a plane.[39]

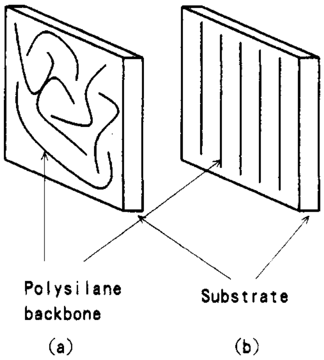

Figure 1. Two possibilities for polysilane orientations obtained by the LB technique.

We now report oriented thin films formed from polysilanes bearing all alkyl groups such as hydroxyalkyl groups and alkoxyalkyl groups, which have been described as a flexible coil.[34]

Experimental Section

Synthesis. The polysilanes investigated in this work are summarized in Table 1. The polymers were synthesized by a Wurtz-type coupling reaction starting from the corresponding dichlorosilanes as described elsewhere.[35,36]

Film Preparation. The quartz plate was treated with a mixture of sulfuric acid and a hydrogen peroxide aqueous solution and rinsed again with deionized water. The procedure was repeated three times. After baking, the plate was treated with hexamethyldisilazane for 12 h at room temperature in order to render the surface hydrophobic. LB films were prepared by a vertical deposition method on a Kyowa Kaimen Kagaku Model HBM Langmuir trough. A solution of 0.4 g of polysilane in 1 L of cyclohexanone was spread at the air–water interface. The monolayers were compressed at 15 mN/m and a transferred step by step onto a quartz plate under a compression rate of 20 mm/min and a dipping speed of 5 mm/min at 15 °C. The surface pressure–area isotherms were monitored with a Wilhelmy plate.

Spectroscopy. The absorption spectra of the LB films were recorded with a Shimadzu Model UV-260 visible recording spectrometer. All measurements were made in transmission geometry using quartz as the substrate. The incident beam was polarized with a Melles Griot Glan–Taylor polarizing prism or polarizing film (Polaroid technical filters 605215) to measure the anisotropy of the UV absorption. The dichroic ratio (R) was defined by UV absorption in the direction parallel to the dipping

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Table 1. Polysilanes Applied for Fabricating LB Films

abbrev	R_1	R_2	mol wt ($\times 10^{-3}$)[a]
1	$-(CH_2)_4OH$	$-(CH_2)_3CH_3$	210
2	$-(CH_2)_6OH$	$-(CH_2)_5CH_3$	420
3	$-(CH_2)_5OC_2H_5$	ethyl	660
4	$-(CH_2)_5OC_2H_5$	propyl	900[b]
5	$-(CH_2)_5OC_2H_5$	butyl	860
6	$-(CH_2)_5OC_2H_5$	hexyl	980[b]
7	$-(CH_2)_5OC_2H_5$	Octyl	1050
8	$-(CH_2)_5OC_2H_5$	$-(CH_2)_5OC_2H_5$	1010

[a] Molecular weights were determined by gel permeation chromatography. [b] Reference 35.

Table 2. Dichroic Ratios and Order Parameters for Polysilanes

polymer	dichroic ratio (*R*)	order para(*S*)	polymer	dichroic ratio (*R*)	order para(*S*)
1	1.75	0.20	6	1.81	0.21
2	2.08	0.26	7	2.10	0.27
3	1.04	0.01	8	2.86	0.38
4	2.90	0.38	2[a]	2.63	0.35
5	2.24	0.29			

[a] Water containing Ca^{2+} ion. Concentration: $CaCl_2$, 4×10^{-4} M; $NaHCO_3$, 5×10^{-5} M. *S* and *R* are the mean values of four samples.

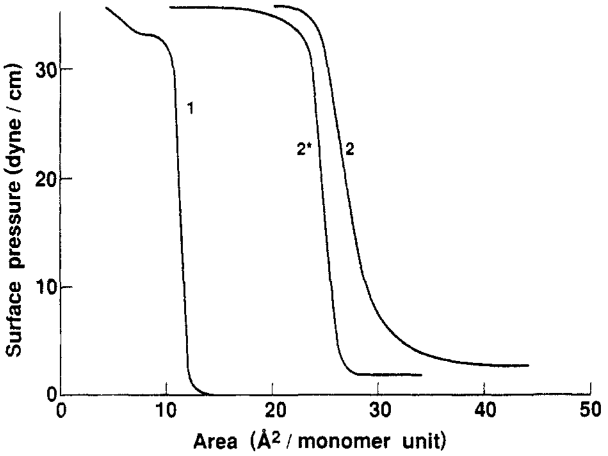

Figure 2. Relation between the surface area and surface pressure for various polysilanes bearing alkyl and hydroxyalkyl groups. 2*: 4×10^{-4} mol of $CaCl_2$ and 5×10^{-5} mol of $NaHCO_3$ were added in 1000 mL of water.

direction (A_a)/UV absorption in the direction perpendicular to the dipping direction (A_e). The order parameter (*S*) was defined by $(A_a/A_e - 1)/(A_a/A_e + 2)$. Dichroic ratios and order parameters in Table 2 are the mean values for four samples.

Results and Discussion

Behavior at the Air–Water Interface. Surface pressure–area diagrams of eight polysilanes are summarized in Figures 2 and 3. The surface pressure for polysilanes bearing hydroxyalkyl groups increased and leveled off when the molecules on the water were compressed (Figure 2). It has been believed that molecules provide monolayers at the air–water interface at the region between the point where the surface pressure appears (point A) and the point where the surface pressure levels off (point B).[25] The diagrams indicate that polysilanes bearing hydroxyl groups gave stable L films (monolayers at the air–water interface). Polysilanes having alkyl ether groups instead of hydroxy groups also provide stable L films, which shows that hydroxy groups are not necessarily needed to provide L films (Figure 3). For comparison, a surface pressure–area diagram of poly(dibutylsilane) is included in Figure 3. The level-off point (point B) was not observed in the diagram.

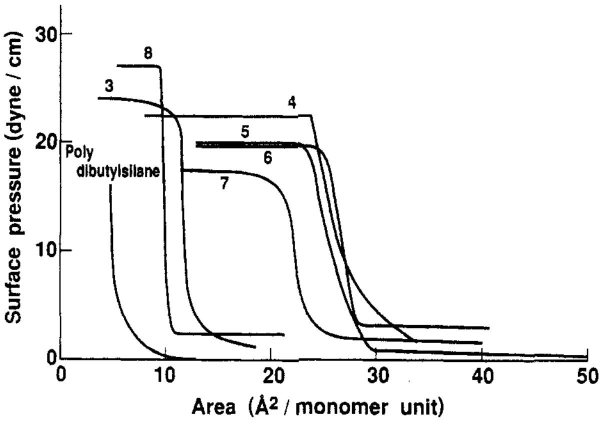

Figure 3. Relation between surface area and surface pressure for various polysilanes bearing alkyl and ethoxypentyl groups.

The experimental values of the area per unit where the pressure begins to increase steeply were about 10–15 Å²/unit for **1**, **3**, and **8** and around 25–30 Å²/unit for **2** and **4**–**7**. Supposing that these alkyl groups are perpendicular to the substrate, the area should be around 20–25 Å²/unit from the models. The areas of polysilanes **1**, **3**, and **8** are rather lower than that calculated. Considering that the L films were not destroyed at all when the pressure were kept at 15 dyn/cm, it seems likely that monolayers are actually being made at the air–water surface but that a part of the polymer chains is bent and lies under the surface of water. The surface areas at point A increased to values close to the calculated ones as the number of carbons in the side chain increases from two (polysilane **3**) to three (polysilane **4**). The same trend was observed for polysilanes bearing hydroxyalkyl groups; namely, the surface area for polymer **2** at point A is larger than that for polymer **1**.

The surface area at point A for polysilane **2** decreased from 30 to 23 Å²/unit when Ca^{2+} ions were added to the water as shown in Figure 2. This may be because the interaction between hydroxy groups and the water surface is strengthened in the presence of Ca^{2+} ions so that the packing of the polysilanes at the air–water interface becomes better. Salt effects were not observed for polysilanes bearing phenol groups or an ethoxypentyl group.

LB Multilayers. L films (monolayers at the air–water interface) of **1**–**8** were transferred to a quartz plate at 15 °C and at a surface pressure of 15 dyn/cm. The transfer ratio was from 0.9 to 1.0 for polysilanes **1**, **2**, and **5**–**8**. The film was not transferred perfectly for polysilanes **3** and **4**, where the transfer ratios were 0.7 and 0.4, respectively.

Polarized UV Spectroscopy. Polarized transmission UV spectra of the LB films were measured to determine the orientation. The dichroic ratios (*R*) and order parameters (*S*) are listed in Table 2. The meanings of *R* and *S* are described in the Experimental Section. Two polysilanes bearing hydroxy groups gave oriented LB films in a plane. Polymer **2** bearing a hexyl chain gave a better dichroic ratio, 2.08, than that bearing a butyl group. The dichroic ratio increased and reached 2.63 when Ca^{2+} ions were added in the water.

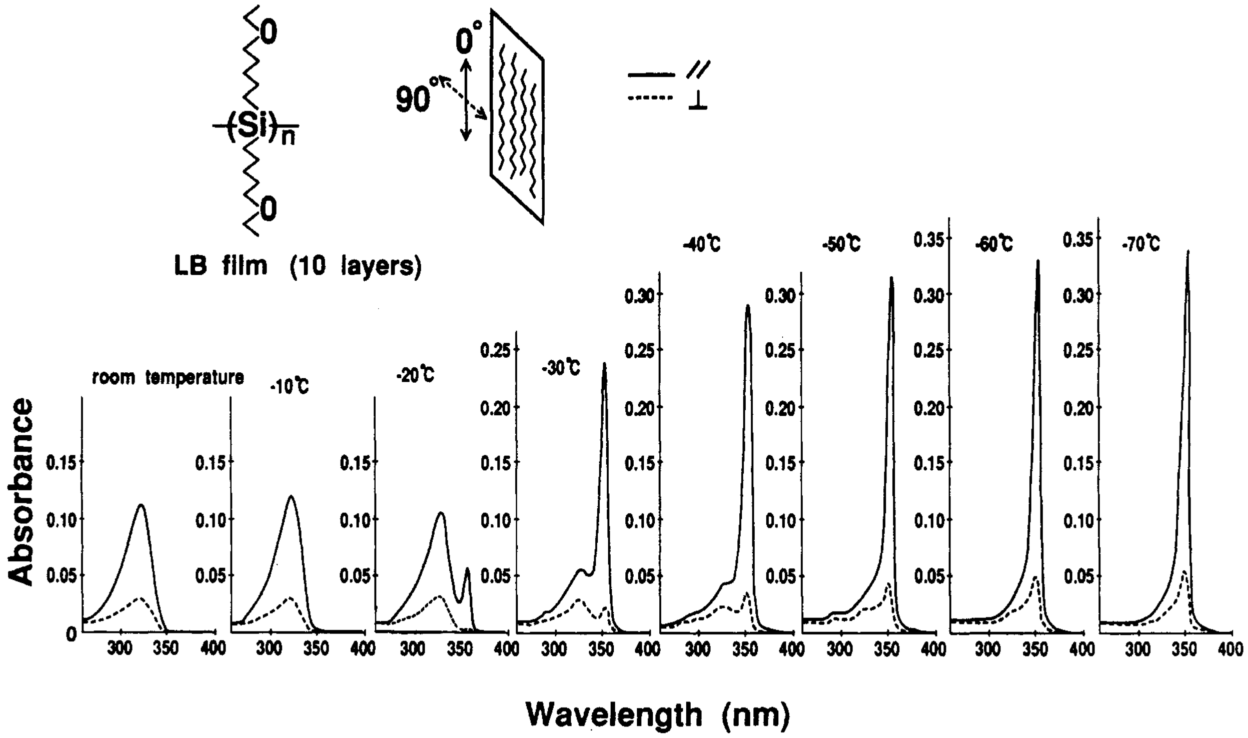

Figure 4. Polarized UV absorptions at various temperatures for polymer 8. Film thickness: 10 layers.

In the polysilane series bearing an ethoxypentyl group, the polysilanes having more than three carbons (polymer 4–7) gave oriented LB films in a plane, except for the polysilane bearing an ethyl group. More than three alkyl carbons were needed to provide the oriented films in a plane. The dichroic ratios varied from 1.81 to 2.90 and decreased roughly with an increase in the number of alkyl carbons.

The polysilane bearing two ethoxypentyl groups, 8, also gave an oriented film in a plane, which contrasts with the poly[bis(alkoxyphenyl)silanes] reported by Embs et al.[33] They introduced two phenyl groups to make the polymer chain rigid, which is favorable for fabricating oriented LB films. Our results showed that oriented LB films can be provided even when the polymers are poly(dialkylsilanes) which have been reported to be rather flexible coils.[34]

A large difference between the LB films mentioned so far and the LB film prepared with poly[bis(*m*-butoxyphenyl)silane] is that the latter has all-trans structures in the LB films[33] but the former does not, even if both polymers provided oriented polysilane films. The conformation of the former polymer seems like random coils, as is suggested by UV spectroscopy. However, polysilane LB films with a regular structure closely approaching an all-trans conformation were obtained when the film was cooled as shown in the next section.

Thermochromism. Polysilanes bearing a hexyl group, such as poly(butylhexylsilane), poly(dihexylsilane), and poly(octylhexylsilane), show thermochromism in both solution and film, even if the two groups are not substituted symmetrically.[37] The two polysilanes bearing a hydroxy group did not show the thermochromism in the LB films, but thermochromism was observed for polymer 1 in an ethyl alcohol solution at −70 °C from 312 to 352 nm and for polymer 2 at −40 °C from 312 to 352 nm.

In contrast to polysilanes with hydroxy groups, polysilanes bearing ethoxypentyl groups showed thermochromism even in LB films. Figure 4 shows the polarized UV absorptions for polymer 8 at various temperatures. At room temperature, a UV absorption with shorter wavelength (absorption A) was observed. The dichronic ratio was 3.9. This value is higher than that seen in Table 2, because the dichroic ratios in Table 2 are mean values of four samples. At −20 °C, abruptly, a UV absorption with longer wavelength (absorption B) was observed only in the direction parallel to the dipping direction. The absorption B appeared in the direction perpendicular to the dipping direction at −30 °C. The UV absorption A disappeared at −70 °C in both directions.

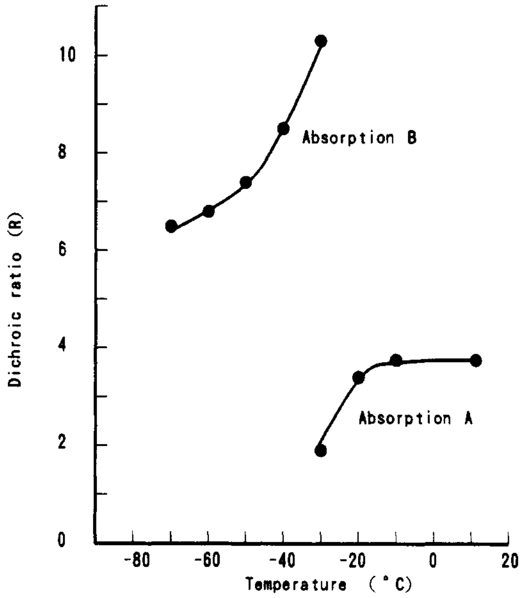

Figure 5. Dichroic ratios at various temperatures for polymer 8.

The order parameters obtained by measuring the UV absorptions for both directions are summarized in Figure 5. The dichroic ratios (*R*) were constant from room temperature to −10 °C. The dichroic ratio (*R*) for the absorption A decreased rapidly at −20 °C, and the UV absorption B appeared with a rather high dichroic ratio of more than 10.0. On cooling, the dichroic ratio (*R*) decreased and was 6.5 at −70 °C.

Much attention should be paid to the fact that the dichroic ration (*R*) for the UV absorption A began to decrease steeply, immediately after the UV absorption B appeared (Figure 5). Polarized UV absorption at -20 °C in Figure 4 indicates that the conformation assigned to the UV absorption B appears first in the direction parallel to the dipping direction. The polymer chains are most likely aligned with each other in the dipping direction, where conformational changes would take place easily probably because of the better polymer packing. Disordered (or less ordered) chains, which have much UV absorption in the direction perpendicular to the dipping direction, would be left with their conformations unchanged. Because of this, the dichroic ratio (R) for the UV absorption A would decrease. On cooling, the order parameter for the UV absorption B decreased gradually, because the less ordered polymer chains, which incline to the dipping direction, start to change their conformations at lower temperature to form the conformation having UV absorption B. Namely, the conformational changes at the regions where the polymers pack better start at a higher temperature than those at the regions where the polymers pack worse. Similar phenomena have recently been reported for poly(dihexylsilane) aligned by rubbing.[38]

Conclusion

Oriented polysilane LB films in a plane with all alkyl groups were provided with polysilanes bearing ethoxypentyl or hydroxyalkyl groups for the first time. More than three alkyl carbons were needed on the other side of the alkyl ether or hydroxyalkyl group. The orientation became better for the polysilanes bearing a hydroxyalkyl group when Ca^{2+} ions were added in the water. The precise experiment on the thermochromism for the polysilane films suggested an explanation of how the thermochromism in LB film took place.

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