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Characterization of Poly(silane) Thin Films Oriented by the Langmuir–Blodgett Technique

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ABSTRACT: Characteristic properties of order parameters and layer structures of highly oriented poly[(*m*-hydroxyphenyl)butylsilane] (PPBS), poly[[(*m*-potassiooxy)phenyl]butylsilane] (PPBS-K), and poly[(6-hydroxyhexyl)hexylsilane] (PHHS) were studied by polarized fluorescence measurement and small-angle X-ray diffraction. Samples were prepared by the Langmuir–Blodgett (LB) technique. The temperature dependence of the order parameter ($\bar{P}_2$, $\bar{P}_4$) in PPBS and PHHS can be determined by the fluorescence depolarization ratios (r_1 and r_2). The order–disorder conformational transitions of PPBS and PHHS occur at $T_c = 130.0$ and 100.0 °C, respectively. $\bar{P}_2$'s and $\bar{P}_4$'s of PPBS are higher than those of PHHS. $\bar{P}_2$'s of PPBS and PHHS depend clearly on the temperature, while the $\bar{P}_4$'s show steady negative values which increase slightly near T_c. X-ray diffraction patterns taken at room temperature show that the steroregularities of PPBS, PPBS-K, and PHHS thin films are completely different. PPBS shows a long and a short period peak. This long period peak is observed for the first time in oriented thin films for poly(silane)s. That is, the oriented PPBS film is constituted as a bilayer structure with one hydrogen bond and one hydrophobic bond in view of facts that the temperature dependence of intensity, peak shift, and full width at half maximum in two X-ray diffraction peaks are clearly different. One layer spacing and amorphous states are found in PPBS-K, and PHHS does not have a regular layer but indicates a broad amorphous feature. The amorphous states of PPBS-K and PHHS are considered to be of different origin because the amorphous X-ray diffraction feature of PPBS-K differs clearly from that of PHHS. The sharp peak of PPBS-K cannot originate from the same layer spacing of PPBS since hydrogen bonding is stereochemically hindered by the potassium atoms of PPBS-K. The disappearance of two layer spacings in PPBS is in accordance with the Lindeman's criterion of melting, when the temperature approaches $T^+ \sim 1.0$ where T^+ means a reduced temperature. It can be also found that deviations of the second-order parameters around their equilibrium values in PPBS and PHHS approach ~1/5, as the temperature is raised near $T^* = 1.0$ where $T^*(= T/T_c)$ is a reduced temperature.

I. Introduction

Up to the present, many poly(silane)s possessing various kinds of functional side groups have been synthesized[1–3] because characteristic optical[4–6] and electrical properties[7,8] have been observed, and potential applications in the field of electrooptics, nonlinear optics, etc. have been expected. The characteristic properties for poly(silane)s, which show an intense UV absorption,[9] sharp fluorescence spectra,[10] and a large third-harmonic generation[11] originate from the σ–σ^* transition moment[12,13] along the successive silicon backbone. In fact, the thermochromic nature of the absorption spectra[14–17] is regarded as a showing the conformational change of this polymer backbone induced from an order–disorder transformation.

Uniaxial alignment of the silicon main chain may enable us to realize more potential applications of poly(silane)s. The rubbing/stretching method or the Langmuir–Blodgett(LB) technique,[18–20] therefore, has been attempted to obtain uniaxial oriented polymers. The LB method, in particular, is excellent for preparing ultrathin films with a well-defined molecular order as well as oriented thin films, but only a few poly(silane)s for which highly oriented thin films can be prepared by the LB technique have been reported.[21–23]

Recently we reported that not only the second- but also the forth-order parameters ($\bar{P}_2$ and $\bar{P}_4$) for poly[(*m*-hydroxyphenyl)butylsilane] (PPBS), oriented to the in-plane dipping direction by the LB technique, were determinable on the supposition that the oriented PPBS would be uniaxial.[22,23] This paper reports that the temperature dependence of $\bar{P}_2$ and $\bar{P}_4$ in PPBS and poly[(6-hydroxyhexyl)hexylsilane] (PHHS) can be determined on the basis of polarized fluorescence spectroscopy.[22] The molecular orientations of PPBS and PHHS disappear at $T_c = 130.0$ and 100.0 °C, respectively. The $\bar{P}_2$'s and the $\bar{P}_4$'s of PPBS were larger than those of PHHS over the range of observed temperatures.

The stereoregularities of PPBS, PHHS, and PPBS-K have been investigated by small-angle X-ray diffraction (SAXD) at room temperature. PPBS shows two sharp peaks corresponding to (A) 25.4 Å (3.48°/2θ) and (B) 12.9 Å (6.84°/2θ) layer spacing. The intensity of A layer is about 10 times that of B layer. PPBS-K, in which the hydrogen atoms of hydroxy groups in PPBS are substituted for potassium atoms, displays one sharp peak at B′ 12.6 Å (7.02°/2θ) and a broad amorphous signal C′ at the peak position of ~3.76 Å (23.6°/2θ). Compared with that of PPBS, this result suggests that the potassium atoms considerably hinder the stereoregularity of PPBS-K because PPBS-K is barely able to form the hydrogen bonds within the layers. In fact, the intensity of ν_{O-H} stretching mode in PPBS-K observed from IR spectrum, compared with that of PPBS, is remarkably decreased by the potassium atoms. This fact may suggest that the layer structure of B in PPBS differs from that of B′ in PPBS-K. PHHS never displays any regular structure and shows a wide amorphous patter C″ at peak position of ~3.11 Å (28.7°/2θ). The amorphous states of PPBS-K and PHHS have clearly different origins because of their different diffraction features.

A 25.4 Å layer spacing for oriented poly(silane)s has not yet been reported, therefore, thermal behavior of A

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and B layers in PPBS has been examined by means of SAXD so as to clarify the stereoregularity of PPBS. The intensity of A decreases rapidly, while that of B shows a gradual decrease when the temperature is raised. Comparing the thermal behavior of relative intensities of A and that of B, the former shows a continuous decrease, whereas the latter clearly shows a discontinuity near $T^{+}(= T/T_m) \sim 1.0$ where T^{+} is a reduced temperature, and T_m is a temperature at which the layer spacing disappears. Discrepancies in the properties of the A and the B layer are also observed from the temperature dependence of the layer spacing and the full width at half maximum (FWHM/$\Delta 2\theta$). It is found that the layer spacing and FWHM of the A layer are only slightly dependent on the temperature, whereas those of the B layer are significantly dependent on the temperature showing the expansion of the layer spacing as the temperature is raised. These results suggest that the structures of A and B layer have different properties, leading to the conclusion that PPBS has a bilayer structure as is well known in some kinds of smectic phases of liquid crystals,[24,25] consisting of one hydrogen bond and one hydrophobic bond.

Values of the mean square displacements of Si atoms at a temperature from the equilibrium position divided by the square distances of A layer and B layer at 20.0 °C, which can be evaluated by relative intensities of A and B against the reduced temperature, approach the value empirically predicted by F. Lindenman when the temperature is raised near $T^{+} = 1.0$. This behavior is also observed from deviations of the second-order parameters around their equilibrium values in PPBS and PHHS, which can be evaluated by the order parameters ($\bar{P}_2$ and $\bar{P}_4$). That is, the deviations of PPBS and PHHS approach $^1/_5$ as the temperature is raised near $T^* = 1.0$, where $T^*(= T/T_c)$ stands for the reduced temperature. In addition, this behavior of order parameters has been also observed from the nematic ↔ isotropic phase transition of liquid crystals.[26] These facts leads to the conclusion that the stereoregularity of the A and B layer in PPBS is definitely correlated with the order parameters.

II. Experimental Section

The method of synthesis of poly[(*m*-hydroxyphenyl)butylsilane] (PPBS) and poly[(6-hydroxyhexyl)hexylsilane] (PHHS), and the fabrication processes of these thin films oriented by the LB technique have been reported in previous papers.[3,22,23] Poly[[(*m*-potassiooxy)phenyl]butylsilane] (PPBS-K), in which the hydrogen atoms of hydroxy groups in PPBS were substituted for potassium atoms, was prepared by spreading PPBS/cyclohexanone solution on surface of a 0.05 mol/L KOH solution. PPBS and PHHS samples of 100 monolayers deposited on quartz substrates were prepared by the LB technique for polarized fluorescence measurements. PPBS, PPBS-K, and PHHS samples having 30, 100, and 86 monolayers, respectively, deposited on glass substrates, were also provided by the LB method for use in X-ray diffraction measurements. All samples used in this work were found, from absorption dichroic ratios, to have uniaxial orientation in plane of the dipping direction.

Polarized fluorescence measurement was performed by using an Hitachi F-3000 fluorescence spectrophotometer. The specimens of PPBS and PHHS were heated by a custom-built temperature controller, the temperature of which was controlled within ±0.5 °C. The temperature dependence of depolarization ratios (r_1, r_2) in the oriented PPBS and PHHS was measured in a right angle arrangement as shown in Figure 1. Order parameters ($\bar{P}_2$, $\bar{P}_4$) of PPBS and PHHS were determined by r_1 and r_2. During the experiments, a small volume of N_2 gas was constantly diffused into the sample box to avoid the oxidation of these specimens.

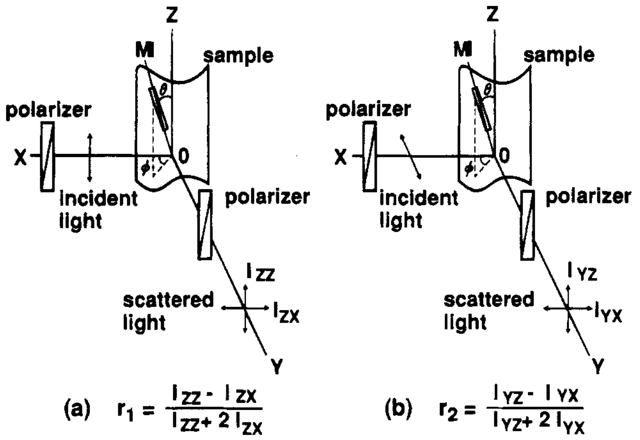


Figure 1. Experimental geometries for measuring the depolarizations ratios (a) r_1 and (b) r_2 in right angle arrangement. Arrows indicate the polarization direction of incident and scattered light.

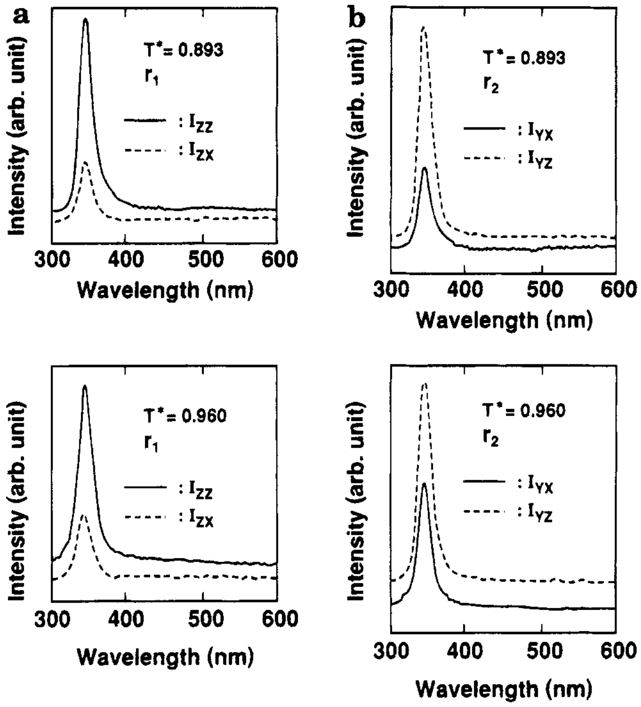


Figure 2. Comparison of the fluorescence depolarization ratios of (a) r_1 and (b) r_2 geometry at the reduced temperatures of $T^* = 0.893$ and $T^* = 0.960$.

Small-angle X-ray measurement for PPBS was carried out, in the range from room temperature to 130.0 °C, using a Rigaku RU-200 X-ray diffractometer equipped with a temperature controller. PPBS was irradiated by the Ni-filtered Cu Kα line (λ = 1.54 Å), at a settingh of 150 mA and 30 kV. Rigaku RINT X-ray Diffractometer was used, at room temperature, for measuring small-angle X-ray diffractions of PPBS-K and PHHS. The experiments were performed with the Cu Kα radiation line and at setting of 40 mA and 40 kV.

III. Results and Discussion

a. Polarized Fluorescence Measurement. Figure 2, parts a and b, show the temperature dependence of the depolarization ratios (r_1 and r_2) in the oriented PHHS. These spectra were obtained from polarized fluorescence measurements in right angle geometry as seen in Figure 1, where T_c is the order–disorder transition temperature of PHHS and $T^* = T/T_c$ is the reduced temperature. The T_c's for PHHS and PPBS are

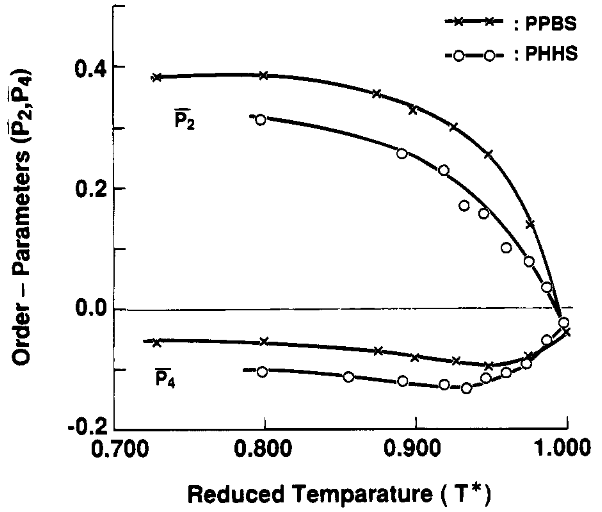


Figure 3. Temperature dependence of $\bar{P}_2$ and $\bar{P}_4$ on PPBS and PHHS: (×) PPBS and (○) PHHS.

found at 100.0 and 130.0 °C, respectively. r_1 and r_2 are significantly dependent on temperature. Both the intense spectra of r_1 (I_{zz}) and r_2 (I_{yz}) are mainly emitted from the σ–σ^* transition moment parallel to the silicon backbone, suggesting that the intramolecular energy transfer of poly(silane)s can occur in several picoseconds.[27] The fluorescence spectra do not show another peak at ~450 nm and it has been discussed whether this peak originates from excimers or contaminations.[28,29] Measurement was also carried out in the oriented PPBS.

The order parameters of PPBS and PHHS are determinable by making the same assumptions as Yoshida et al.[22] Then, not only the second- but also the forth-order parameters can be simultaneously determined from r_1 and r_2 as follows:[22,30–32]

$$\bar{P}_2 = \frac{-2r_1r_2 + 5r_1 + 8r_2 - 2}{4r_1r_2 - 10r_1 + 2r_2 + 13} \tag{1-a}$$

$$\bar{P}_4 = \frac{19r_1r_2 + 5r_1 - 13r_2 - 2}{4r_1r_2 - 10r_1 + 2r_2 + 13} \tag{1-b}$$

where $\bar{P}_2$ and $\bar{P}_4$ are the second and the fourth Legendre polynomials. The $\bar{P}_2$'s and the $\bar{P}_4$'s of PPBS are larger than those of PHHS as shown in Figure 3. The $\bar{P}_2$'s of PPBS and PHHS depend clearly on the reduced temperature, i.e. the $\bar{P}_2$'s decrease steeply as the temperature increases to $T^* = 1.0$. This result suggests that a uniaxial orientation for PPBS and PHHS gives rise to order–disorder configurational transformation at $T^* = 1.0$. The $\bar{P}_4$'s, however, do not show this behavior, and remain negative, displaying a slight increase near $T^* = 1.0$. It should be noted that this behavior near T_c has been also observed from liquid crystals near the nematic ↔ isotropic phase transition.[32] Physically $\bar{P}_4$ is correlated with a variance of the second-order parameter around its equilibrium value; that is, $\bar{P}_4$ appears at $\overline{P_2^2} = (1/35)(18\bar{P}_4 + 10\bar{P}_2 + 7)$.[26] This behavior near $T^* = 1.0$ will be investigated in detail latter in this paper.

b. Small-Angle X-ray Diffraction. Figure 4 shows small-angle X-ray diffraction patterns of PPBS, PPBS-K, and PHHS at room temperature. The diffraction patterns of these samples appear completely different.

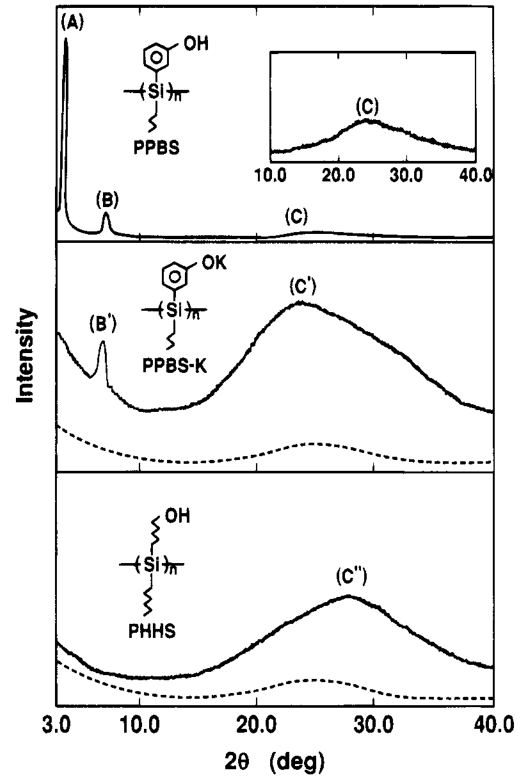
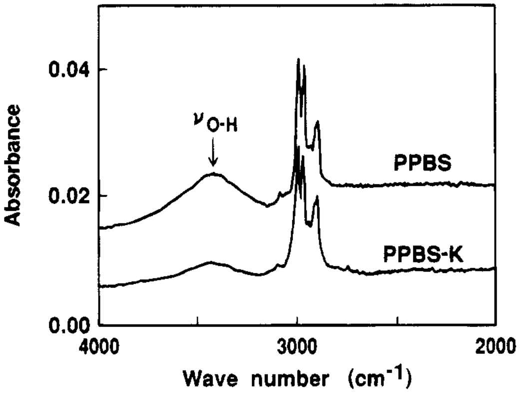


Figure 4. Small-angle X-ray diffraction patterns of the oriented (a) PPBS, (b) PPBS-K, and (c) PHHS thin films at room temperature.

PPBS clearly shows two sharp peaks: (A) corresponding to 25.4 Å (3.48°/2θ) layer spacing, and (B) corresponding to 12.9 Å (6.48°/2θ) layer spacing. A broad pattern, C, at peak of ~3.66 Å (24.3°/2θ) is also seen. Reported fine diffraction peaks from poly(di-*n*-hexylsilane)[33] at about this region cannot be found. The broad signal for PPBS is caused by the reflection of glass substrate itself, not the amorphous states of PPBS. The long period layer A has been observed for the first time in this sample, although the short period layer B has been previously reported.[21] This result suggests that a PPBS thin film oriented by the LB technique may be consist of complex layer structures. The diffraction patterns of PPBS-K, however, show one sharp peak B′ at 12.6 Å (7.02°/2θ) and a broad pattern C′ at peak of ~3.76 Å (23.6°/2θ). The broad peak C′ clearly stems from amorphous states of PPBS-K, considering the fact that the intensity of C′ is significantly greater than the intensity of glass substrate (shown as the broken line). This leads to the conclusion that formation of hydrogen bonds and a regular layer structure in PPBS-K are stereochemically hindered by the presence of potassium atoms that are much larger than the hydrogen atoms of PPBS. Therefore, the sharp peak B′ of PPBS-K cannot have the same origin as B of PPBS. In fact, the IR intensity of $\nu_{\text{O-H}}$ stretching mode in PPBS-K shows a noticeable decrease as shown in Figure 5a. Figure 5b shows a differential spectrum for PPBS obtained from polarized IR measurement, where the symbols ∥ and ⊥ stand for the polarization directions parallel and perpendicular to the silicon main chain, respectively, and $\nu_{\text{C-H}}$ means the phenyl out-of-plane mode in PPBS. Assignments of other signals were seen in ref 21. Figure 5b suggests that the phenol substituents are perpendicular to the Si main chain, but the *n*-butyl groups are in low orientational states. PPBS and PPBS-K of 100 monolayers deposited on (001) silicon substrates using

(a) IR spectra



(b) Differential spectrum for PPBS

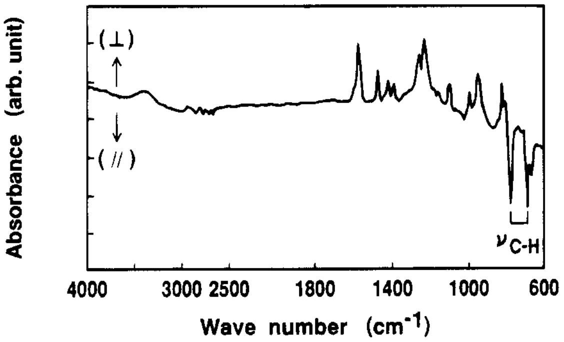


Figure 5. (a) Comparison of IR spectra in PPBS and PPBS-K at room temperature and (b) differential spectrum for PPBS at room temperature. The symbols || and ⊥ stand for parallel and perpendicular polarization directions to the silicon main chain, respectively.

the LB technique were used for these IR measurements. X-ray diffractions of PHHS show no sharp peaks, and only a broad amorphous pattern C″ at peak of ~3.11 Å (28.7°/2θ). This result suggests that the stereoregularity does not exist in PHHS although the orientational order is found to be considerably high. The amorphous states of PHHS are clearly different from those of PPBS-K, as can be seen from the distinction in the features observed in X-ray diffraction as seen in Figure 4.

Then, the thermal properties of X-ray diffractions in the A and B layers were studied. The temperature dependence of X-ray diffraction intensities on the A and B layers is shown in Figure 6. The diffraction peak of the A layer disappears at 80.0 °C, while that of the B layer persists at 100.0 °C. The intensity of the A layer peak rapidly decreases, but that of the B layer gradually decreases when the temperature is raised as shown in Figure 7. This behavior becomes clearer when the relative intensities of the A and B layer peaks, evaluated by $I(T)/I(20)$, are plotted against the reduced temperature, as seen in Figure 8, where $I(T)$ is the intensity at an absolute temperature (T) and I (20) the intensity at 293.2 K. T_m = 353.2 and 373.2 K are the temperatures at which the A layer spacing and the B layer spacing, respectively, disappear. The relative intensity of the A layer peak indicates a continuous decrease, while that of the B layer clearly displays a discontinuity near T/T_m = 1.0. This thermal behavior of the relative intensities is consistent with that of the relative intensities observed from bilayer structures of the smectic-A and mesophases by X-ray diffraction.[34] These results can suggest that X-ray diffractions observed from the A and the B layers stems from different layer spacing, not from the first and the second reflection of X-ray diffraction.

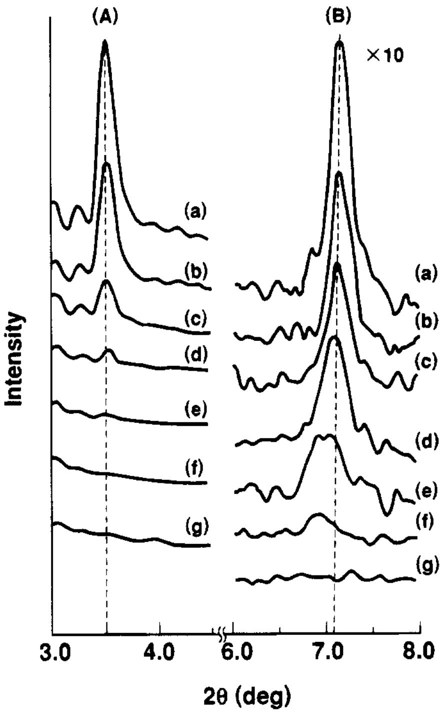


Figure 6. Temperature dependence of the (A) and (B) X-ray diffraction peaks on PPBS: (a) 20.0, (b) 50.0, (c) 70.0, (d) 75.0, (e) 80.0, (f) 90.0, (g) 100.0 °C.

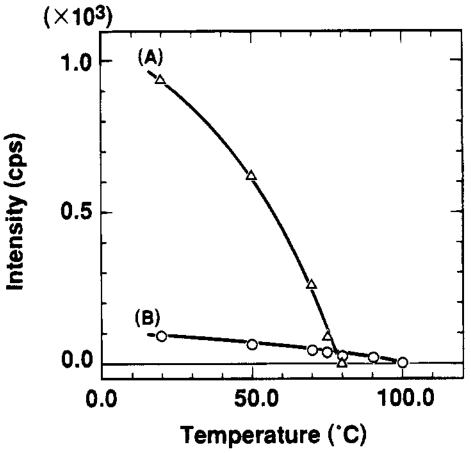


Figure 7. Plots of X-ray diffraction intensities in PPBS as a function of temperature: (△) A layer and (○) B layer.

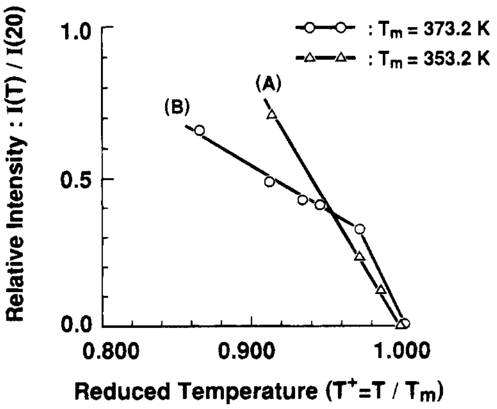


Figure 8. Plots of relative intensities in PPBS versus reduced temperature: (△) A layer and (○) B layer.

The discrepancy in the properties of the A and the B layers becomes clearer when the temperature dependence of layer spacing and full width at half maximum

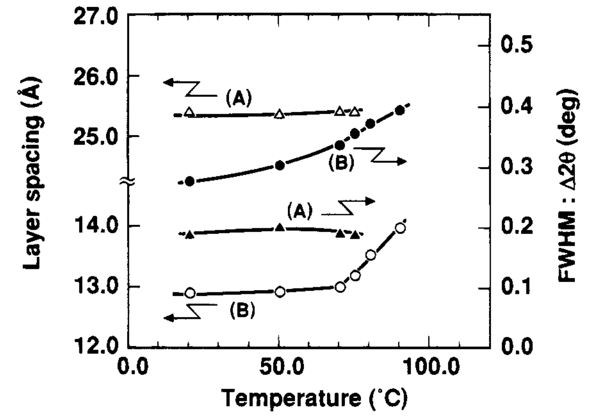


Figure 9. Temperature dependence of layer spacing and full width at half maximum (FWHM; /Δ2θ) on PPBS. Layer spacing: (△) A layer, and (○) B layer. FWHM: (▲) A layer, and (●) B layer.

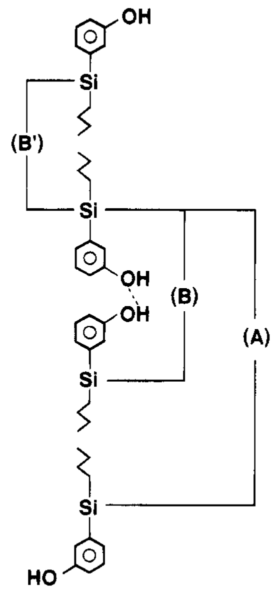


Figure 10. Bilayer structure of A and B in PPBS. Monolayer structure of B′ in PPBS-K.

(FWHM/Δ2θ) in the A and the B layer peaks are compared as shown in Figure 9. The layer spacing and FWHM of the A layer depend slightly on the temperature, whereas those of the B layer are considerably dependent of the temperature. These findings lead to the conclusion that the layer structure of PPBS is an asymmetric bilayer structure, consisting of (A) one hydrogen bonded and one hydrophobic bonded region and (B) one hydrogen bonded region as shown in Figure 10. Then, assuming that n-butyl chain has an all-trans conformation, the hydrogen bond length is ~3.0 Å and the hydrophobic bond length ~1.5 Å, we can roughly calculate spacings of the A and the B layers (l_A, l_B). That is, $l_A = 29.2$ Å × cos 30° ~ 25.3 Å, and $l_B = 12.8$ Å × cos 30° ~ 11.1 Å. These values are roughly consistent with the X-ray results. The bilayer structure of smectic-A$_2$ phase shows two sharp X-ray diffraction peaks.[25] This is attributed to a preferential up–down ordering of the dipolar heads within each layer, alternating from layer to layer to produce a periodicity equal to twice the molecular length. The bilayer structure of PPBS has asymmetric side groups, i.e. the hydrophobic and hydrophilic substituents. Various distinctions in the temperature dependence of the A and B layer can be explained by this bilayer model. Since both the hydrogen bond and the phenol group forming the B layer are tighter and stiffer than the hydrophobic bond and the *n*-butyl side group constituting the A layer, the A layer is strongly affected by thermal vibrations so that the intensity of the A layer can be rapidly decreased as compared with the intensity of the B layer, and the soft *n*-butyl chain of the A layer can relax thermal stress so that the layer spacing and FWHM depend slightly on the temperature. The above conclusion may be supported by the finding that PPBS-K, showing only one sharp peak, is barely able to form hydrogen bonds since their formation is stereochemically hindered by potassium atoms. Hence, the layer structure of B′ in PPBS-K is probably different from that of B in PPBS as shown in Figure 10. Furthermore, the results provides interesting similarities in view of the facts that some kinds of poly(silane)s display smectic mesophases,[35,36] and the smectic phases are bilayer structures.[25]

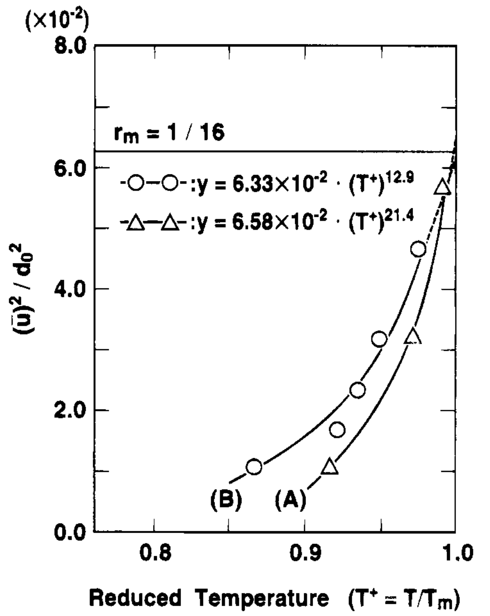


Figure 11. Plots of mean square displacements of Si atoms at a temperature per square distances of A layer and B layer at 20.0 °C as a function of reduced temperature: (△) A layer and (○) B layer.

If we assume that the decrement in the intensity observed from X-ray diffraction is mainly caused by thermal vibrations, the displacement from the equilibrium position of atom can be evaluated by using a thermal factor. Then, the decrease in the intensity is given as follows:

$$I = I_0 \exp(-2M) \tag{2}$$

where I and I_0 are the intensities of X-ray diffractions observed at a temperature (T) and at room temperature (20.0 °C), respectively. M stands for the thermal factor. The thermal factor can be written

$$M = 2\pi^2[(\bar{u})^2/d_0^{\,2}] \tag{3}$$

where $\bar{u}$ is a mean displacement of an atom from equilibrium position at a temperature (T), d_0 being lattice constant at equilibrium position. Assuming that d_0's are equal to the layer spacing of A and B at 20.0 °C, we can estimate the mean square displacements of silicon atoms in the A and B layers at a temperature (T) by using eq 2 and 3. Figure 11 shows that the values of $(\bar{u})^2/d_0^{\,2}$ in the A and B layers are plotted against the reduced temperature. The solid lines for A and B are

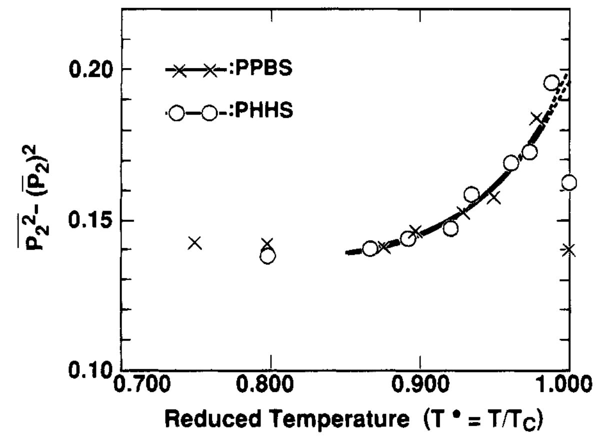


Figure 12. Plots of deviation of the second-order parameter around its equilibrium value as a function of reduced temperature: (×) PPBS and (○) PHHS.

determined by exponent recurrence fits. Both lines seem to approach a constant value ($r_m = 1/16$) when the temperature is increased to near $T^+ = 1.0$. As pointed out by F. Lindeman, solids begin melting at $r_m \sim \overline{(\delta R)^2}/R_0^{\,2} \sim 1/16$, where $\overline{(\delta R)^2}$ and R_0 corresponding to $(\bar{u})^2$ and d_0, respectively, are the mean square displacement of the atom and a lattice constant. This result may suggest that both the layer structure A and B disappear near r_m, in accordance with the Lindeman's criterion of melting. It is also found that the deviation of the second-order parameter around its equilibrium value increasingly approaches $\sim 1/5$ as the temperature is raised near to $T^* = 1.0$. The deviation of $\bar{P}_2$ is defined by

$$\overline{(P_2^{\,2} - \bar{P}_2)^2} = \overline{P_2^{\,2}} - (\bar{P}_2)^2 = (1/35)(18\bar{P}_4 + 10\bar{P}_2 + 7) \qquad (4)$$

where $\overline{P_2^{\,2}}$ stands for the variance of the second-order parameter around its equilibrium value, which can be evaluated from the polarized fluorescence results. The results of PPBS and PHHS vs reduced temperature are shown in Figure 12. The deviations of PPBS and PHHS approach $\sim 1/5$ when the temperature approaches $T^* = 1.0$, although these values just at $T^* = 1.0$ show clearly discontinuities because order–disorder first-order transitions occur at $T^* = 1.0$. This result may support the fact that the disappearance of layer structure is in accord with the Lindeman's criterion of melting, considering that order parameters which enable us to universally describe phase transitions are some of the most fundamental physical values and that the structure of smectic bilayer phases is very similar to that of this oriented thin film.

IV. Conclusion

Characterization of order parameters ($\bar{P}_2$, $\bar{P}_4$) and layer structures of oriented PPBS, PPBS-K, and PHHS thin films prepared by the LB technique have been studied by means of polarized fluorescence spectroscopy and small-angle X-ray diffraction. The order parameters of PPBS and PHHS can be determined by using fluorescence depolarization ratios (r_1, r_2). It is found from the order parameters that the molecular alignments for PHHS and PPBS disappear at $T_c = 100.0$ and 130.0 °C, respectively. $\bar{P}_2$'s of PPBS and PHHS show significantly high values, while $\bar{P}_4$'s are constantly negative and show a slight increase near T_c. $\bar{P}_2$'s and $\bar{P}_4$'s of PPBS are higher than those of PHHS in the region of observed temperatures. $\bar{P}_2$'s of PPBS and PHHS rapidly decrease when the temperature approaches $T^* = 1.0$, where $T^*(= T/T_c)$ is the reduced temperature. This result clearly shows that order–disorder conformational transformations for PPBS and PHHS occur at $T^* = 1.0$.

The layer structures of PPBS, PPBS-K, and PHHS thin films have been investigated by small-angle X-ray diffraction at room temperature. Two sharp peaks for PPBS corresponding to (A) 25.4 Å (3.48°/2θ) and (B) 12.9 Å (6.48°/2θ) layer spacings and a broad amorphous pattern at peak of ~3.66 Å (24.3°/2θ) originating from the glass substrate itself have been observed. This long period diffraction peak is found, for the first time, in these oriented films. Hence, the thermal properties of the A and the B layers have been investigated to clear the stereoregularity of PPBS thin films. The intensity of the A layer decreases more rapidly than that of the B layer. And the former disappears at 80.0 °C, but the latter persists at 100.0 °C. The layer spacing and FWHM of the A layer peak are barely independent of the temperature, while those of the B layer peak significantly depend on the temperature, indicating the expansion of the layer spacing as the temperature is increased. These results are very similar to X-ray diffraction patterns and the behaviors observed from smectic bilayer phases.[32,33] The above findings lead to the conclusion that PPBS is constituted from a bilayer structure containing (A) one hydrogen bond and one hydrophobic bond and (B) one hydrogen bond. The diffraction patterns of PPBS-K show one sharp peak corresponding to B′, 12.6 Å layer spacing, and a wide amorphous signal C′ about at 3.76 Å (23.6°/2θ), which is clearly due to the amorphous parts of PPBS-K. This result suggests that the formations of a regular structure and hydrogen bonding in PPBS-K are considerably hindered by potassium atoms as compared with PPBS. This fact is supported by the IR intensity of $\nu_{\mathrm{O-H}}$ stretching mode in PPBS-K, which shows a considerable decrease compared with that of PPBS. Regular spacing of PHHS has not been observed although the molecular alignment shows a significant degree of orientation. And a broad amorphous feature induced from the random states of PHHS has been found at a peak of ~3.11 Å (28.7°/θ) by X-ray diffraction. This result may be due to the flexible *n*-hexyl side chains. The amorphous states of PHHS are clearly different from those of PPBS-K because of their discrepancies in X-ray diffraction patterns.

The mean square displacements of silicon atoms at a temperature (T) per the square distances of A layer and B layer at 20.0 °C can be evaluated by X-ray diffraction intensities. These values increasingly approach $r_m(= 1/16)$, when the temperature is raised to near $T^+ = 1.0$, according with the Lindeman's criterion of melting. It is also observed that the deviations of the second-order parameters around their equilibrium values in PPBS and PHHS approach $\sim 1/5$ when the temperature is increased to near $T^* = 1.0$. This result clearly correlates with the disappearance of regular spacings in PPBS.

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References and Notes

(1) West, R.; David, L. D.; Djurovitch, P. I.; Steareley, K. L.; Srinivasan, K. S. V.; Yu, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 1352.

(2) Trujillo, R. E. *J. Organomet.* **1980**, *198*, C27.

(3) Nakano, Y.; Murai, S.; Kani, R.; Hayase, S. *J. Polym. Sci.* **1993**, *31*, 3361.

(4) Harrah, L. A.; Zeigler, J. M. *J. Polym. Sci. Lett. Ed.* **1985**, *23*, 209.

(5) Trefonas, P.; Damewood, J. R.; West, R.; Miller, R. D. *Organometallics* **1985**, *4*, 1318.

(6) Miller, R. D.; Hofer, D.; Rabolt, J.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2712.

(7) Kepler, R. G.; Zeigler, J. M.; Harrah, L. A.; Kurtz, S. R. *Phys. Rev.* **1987**, *B35*, 2818.

(8) Sawodny, M.; Stumre, J.; Knoll, W. *J. Appl. Phys.* **1991**, *69*, 1927.

(9) West, R. *J. Organomet.* **1986**, *300*, 327. Niller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(10) Tilgner, A.; Trommsdorff, H. P.; Zeigler, J. M.; Hochstrasser, R. M. *J. Chem. Phys.* **1992**, *96*, 781.

(11) Neher, D.; Wolf, A.; Bukeck, D.; Wegner, G.; *Chem. Phys. Lett.* **1989**, *163*, 116.

(12) *The Chemistry of Organic Silicon Compounds*; Patai, S., Rapport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; p 1207.

(13) Miller, R. D. *Chem. Rev.* **1989**, *89*, 1359.

(14) Itoh, T.; Mita, I. *Macromolecules* **1992**, *25*, 479.

(15) Yuan, C. H.; West, R. *Macromolecules* **1994**, *27*, 629.

(16) Kodaira, T.; Tanahashi, H. *Macromolecules* **1989**, *22*, 4645.

(17) Schilling, F. C.; Lovinger, A. J.; Zeigler, J. M.; Davis, D. D.; Bovery, F. A. *Macromolecules* **1989**, *22*, 3055.

(18) Kuzmany, H.; Rabolt, J. F.; Farmer, B. L.; Miller, R. D. *J. Chem. Phys.* **1986**, *85*, 7413.

(19) Tachibana, H.; Kawabata, Y.; Yamaguchi, A.; Moritomo, Y.; Soshihara, S.; Tokura, Y. *Phys. Rev.* **1992**, *B45*, 8752.

(20) Seki, T.; Tamaki, T.; Ueno, K. *Macromolecules* **1992**, *25*, 3825.

(21) Embs, F. W.; Wegner, G.; Neher, D.; Albouy, P.; Miller, R. D.; Wilson, C. G.; Schrepp, W. *Macromolecules* **1991**, *24*, 5068.

(22) Yoshida, H.; Kani, R.; Hayase, S.; Horie, K. *J. Phys. Chem.* **1993**, *97*, 5370. Note: We assumed in the text that relaxation times of poly(silane)s are several picoseconds so that order parameters (P_2,P_4) are independent on time.

(23) Kani, R.; Yoshida, H.; Nakano, Y.; Murai, S.; Mori, Y.; Kawata, Y.; Hayase, S. *Langmuir* **1993**, *9*, 3045.

(24) Galli, G.; Chiellini, E.; Lans, M.; Angeloni, A. S.; Francescacgeli, O.; Yang, B. *Macromolecules* **1994**, *27*, 303.

(25) Chan, K. K.; Pershan, P. S.; Sorensen, L. B.; Hardouin, F. *Phys. Rev.* **1986**, *A34*, 1420.

(26) Kobinata, S.; Nakajima, Y.; Yoshida, H.; Maeda, S. *Mol. Cryst. Liq. Cryst.* **1981**, *66*, 67.

(27) Kim, Y. R.; Lee, M.; Thorne, J. R. G.; Hochstrasser, R. M. *Chem. Phys. Lett.* **1988**, *145*, 75.

(28) Kagawa, T.; Fujino, M.; Takeda, K.; Matsumoto, N. *Solid State Commun.* **1986**, *57*, 635.

(29) Thore, J. R. G.; Hochstrasser, R. M.; Zeigler, J. M. *J. Phys. Chem.* **1988**, *92*, 4275.

(30) *Introduction to Liquid Crystals*; Priestley, E. B., Wojtowicz, P. J., Eds.; Plenum: New York, 1975; p 72.

(31) Zannoni, C. *Mol. Phys.* **1979**, *38*, 1813.

(32) Chapoy, L. L.; Dupre, D. B. *J. Chem. Phys.* **1978**, *69*, 519; **1979**, *70*, 2550.

(33) Lovinger, A. T.; Schilling, F. C.; Bovey, F. A. *Macromolecules* **1986**, *19*, 2657.

(34) Galli, G.; Chiellini, E.; Laus, M.; Angeloni, A. S.; Francescangel, O.; Yang, B. *Macromolecules* **1994**, *27*, 303.

(35) West, R.; Menescal, R.; Asuke, T.; Fveland, J. *J. Inorg. Org. Polym.* **1992**, *2*, 29.

(36) Weber, P.; Guillon, D.; Skonlios, A.; Miller, R. D. *J. Phys. (France)* **1989**, *50*, 793.

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