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Fluorescence Polarization Method for Studying Molecular Orientation of Mono- and Multilayered Polyimide Films Prepared by the Langmuir–Blodgett Technique

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ABSTRACT: Molecular orientation of mono- and multilayered polyimide films has been studied by the fluorescence polarization method. The high sensitivity of the fluorescence method enabled us to measure the orientation of extremely thin films. A perylene pigment was synthesized as a fluorescence probe and was introduced into polyamic acid chains. Layered films of polyamic acid alkylamine salt were prepared by the Langmuir–Blodgett (LB) technique. Even after chemical conversion to polyimide, molecular axes of the polyimide chain retained a 2-dimensional distribution in the substrate plane. The perylene probes in the LB film showed fluorescence anisotropy, and their second moment of orientation, $\langle \cos^2 \omega \rangle$, was determined to be 0.54–0.58 by 2-dimensional analysis. The principal axis of the orientation was in agreement with the dipping direction. These measurements reveal the orientation of a "genuine surface" of molecular dimension. This LB polyimide surface aligns highly liquid-crystal molecules as a rubbed surface of polyimide film does. The ability of LB films to orient a liquid crystal correlated with the surface orientation measured by the fluorescence method.

Introduction

Surface structure is one of the most important factors determining the characteristics and functions of polymeric materials. However, the exact meaning of "surface" is quite vague. Strictly speaking, it refers to the single molecular layer at the boundary, which should play a critical role on the so-called surface properties. The Langmuir–Blodgett (LB) technique enables artificial design and construction of molecular assemblies on the scale of molecular dimensions.[1,2] It may be regarded as producing a monolayer architecture on the water surface. Therefore, it offers some potential abilities for surface technology. Extensive studies have been carried out to exploit the LB method, which has been applied to many amphiphilic materials other than the conventional long-chain fatty acids. Evidence showing that a variety of polymers can be spread at the air–water interface has accumulated during the past several decades,[3] and recently some of them were found to be transferable to solid substrates.[4–13]

Studies on polyimide LB film have been developed by several research groups.[14–16] Aromatic polyimide films have many advantages in practical applications because of their thermal and mechanical stability. Besides such characteristic features, their excellent electrical property has increased the demand for ultrathin films of aromatic polyimides. Kakimoto et al. established a procedure for the preparation of polyimide LB films via polyamic acid alkylamine salt.[14] They also reported that the film obtained has a thickness of only ca. 0.5 nm/layer. Furthermore, a slight preferred orientation of polyimide chain to the dipping direction was confirmed by means of absorption dichroism in the IR and UV regions.

The fluorescence polarization method can be used to study molecular orientation of amorphous polymers.[17] The fluorescence probe is excited photoselectively by absorbing a linearly polarized light along its transition dipole and emits fluorescence from the same transition dipole. The direction is usually parallel to the molecular axes for symmetrical fluorescence probes. By analysis of the polarized components of fluorescence intensity, one can evaluate the pattern and extent of molecular orientation.[18] The greatest advantage of this method is the high sensitivity in detection of fluorescence emission. The sensitivity has been further improved by instrumental developments, e.g., laser and photon-counting systems. Even for the specimen of one molecular layer, the single-photon-counting technique gives sufficient signals for the analysis of orientation.

In the current study, this method has been applied to the measurement of molecular orientation of mono- and multilayered polyimide films. After exploring several dyes for this purpose, we synthesized a suitable perylene pigment as a fluorescence probe. The fluorescence from labeled polyimide LB films gave information on the orientation of the "genuine surface".

Experimental Section

Materials. Fluorescence Probe. 3,4,9,10-Perylenetetracarboxylic diimide pigment (1) was synthesized by the reaction of 3,4,9,10-perylenetetracarboxylic dianhydride (Aldrich) with 4,4′-diaminodiphenyl sulfone (Wako Pure Chemical Industries, Ltd.), according to the method of Rademacher et al.[19] The dye was washed with acetone and hot water three times and recrystallized from DMF. This dye is soluble in DMSO, DMF, and dimethylacetamide and slightly soluble in acetone. This is the most important point for the synthesis of labeled polyimides, since most of the perylene pigments are insoluble in common organic solvents.[19a] ^{1}H NMR ($(CD_3)_2SO$, 100 °C): δ 8.38 (br, 8 H), 7.96 (d, 4 H), 7.66 (d, 4 H), 7.57 (d, 4 H), 6.73 (d, 4 H), 5.93 (s, 4 H). IR (KBr): 3480, 3370, 3230, 1700, 1670, 1620, 1590, 1360, 1260, 1150, 1100, 730, 700, 590 and 560 cm^{-1}. The elemental analysis for oxygen could not be obtained, since the product was hygroscopic. The weights relative to that of carbon are as follows. Calcd for $C_{48}H_{28}N_4O_8S_2$: H/C, 4.89; N/C, 9.72; S/C, 11.13. Found: H/C, 4.72; N/C, 9.52; S/C, 11.20.

Polyamic acid (2) was synthesized by the reaction of tetracarboxylic anhydrides and aromatic diamines.[20–22] To a solution of 2.0 g of 4,4′-diaminodiphenyl ether (3) (Wako) in dried dimethylacetamide was added 2.95 g of 3,4,3′,4′-biphenyltetracarboxylic dianhydride (4) (Wako) in a drybox. The solution became extremely viscous. After it was stirred for 3 h at room temperature, the solution was stored at −15 °C. A fluorescence-labeled polyamic acid was prepared by the addition of the perylene dye (1) together with the diamine 3 (0.5 mol %). A red viscous solution

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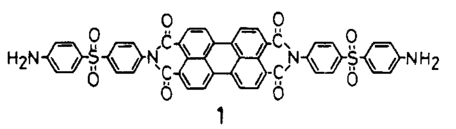

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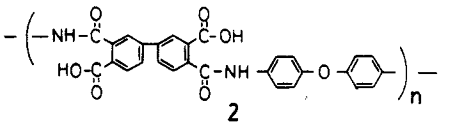

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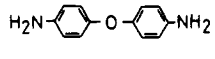

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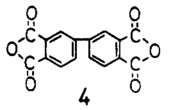

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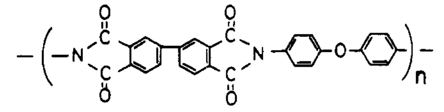

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was obtained as with the unlabeled polyamic acid. Even if the solution was poured into a poor solvent such as acetone, the dye did not dissolve in the solvent; i.e., the perylene dye was covalently attached to the polyamic acid.

Sample Preparation. There are several methods for the preparation of polyimide LB films.[14-16] We adopted the procedure of Kakimoto et al.; the polyamic acid salt with dimethylhexadecylamine was spread on the water from benzene–dimethylacetamide (1:1) solution.[14] The water in the subphase was purified by deionization, distillation, and passing through a filtration system (Barnstead Nanopure II). The LB multilayers were prepared on a trough (Kenkosha Model SI-1) containing a Wilhelmy-type film balance. Quartz plates (10 × 40 mm) used as substrates for the spectroscopic measurements were cleaned in an oxidative sulfuric acid solution and then rinsed with clean water several times. Instead of quartz plates, silicon wafers were used for the measurement of IR spectra. A good transfer ratio (the ratio of the decrease of the surface area on the water to the deposited area on the substrate) was obtained at surface pressures 10–20 mN m^{-1}, at temperatures 5–15 °C, with a dipping speed of 10 mm min^{-1}. Deposition was carried out at the surface pressure of 12.5 mN m^{-1} at 10 °C. The transfer of the monolayer takes place on each downward and upward dip (Y-type) except for the first dip (Z-type). The samples were allowed to dry in the air before the next dip. The LB films were dried overnight in a desiccator and then immersed in a mixed solvent (acetic anhydride–pyridine–benzene (1:1:3)) for 12 h, yielding polyimide LB films **5**.

For the measurements of the orientation of liquid crystals, a sandwich cell from two quartz plates (coated with polyimide LB films) was prepared, in which 4′-ethoxybenzylidene-4-*n*-butylaniline (EBBA) (Tokyo Kasei Kogyo Co., Ltd.) was placed.

Measurements. Fluorescence spectra were measured by a Hitachi 850 fluorescence spectrophotometer. IR spectra were recorded with a Jasco IR-810 infrared spectrophotometer. Absorption spectra were recorded with a Shimadzu UV-200 spectrometer. To observe absorption dichroism, a Glan–Thompson ultraviolet prism polarizer (Karl Lambrecht) was attached to the spectrometer, and the absorbances were measured for the vertically or horizontally polarized light. The apparatus was also used for the determination of whether the molecular axis of the polyimide chains was oriented in a three-dimensional (3D) or two-dimensional (2D) distribution. As shown in Figure 1a, this measurement was carried out by tilting the sample holder with reference to the optical axis.

Fluorescence polarization measurements were performed by the combination of an argon ion laser and a single-photon-counting system. Figure 1b shows the optical system. A vertically polarized excitation beam (514 nm, 10 mW) from an argon ion laser (Spectra Physics, Model 2020) was introduced to a sample box through the Glan–Thompson prism. The film plane was fixed at a right angle to the photon-counting detector but rotatable in a plane. The emission was monitored at two angles with the dipping direction parallel (*Z* axis) or perpendicular (*X* axis) to the vertical excitation light. Vertical and horizontal components of the fluorescence at each angle were detected by a photomultiplier (Hamamatsu Photonics, R3234), through a polarizer (Polaroid, HNP'B type), two sheets of cut-off filter (Toshiba, SC-56), a diffuser, and a monochromator (Ritsu Oyo Kogaku Co., Model MC-10N), which was set at a wavelength of 590 nm and a band width of 20 nm. The signals were treated by conventional single-photon-counting electronics (EG&G Ortec).

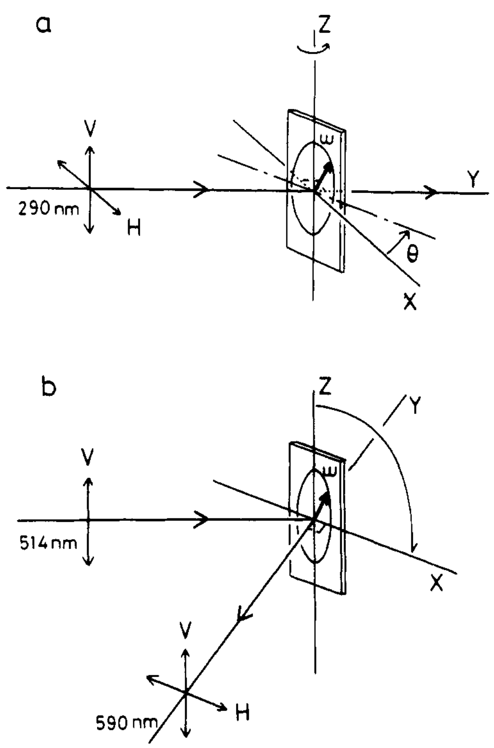

Figure 1. Optical systems for measuring (a) absorption dichroism and tilting angle dependence of UV absorbance and (b) polarized components of fluorescence intensity.

Orientation behavior of the liquid crystal (EBBA) was observed with a polarizing microscope (Nikon OPTIPHOTO). To evaluate the orientation quantitatively, the liquid-crystalline cell was placed on a rotatable hot plate, and the transmittance under the crossed polarizers was measured as a function of the rotation angle (see Figure 10a).

Results and Discussion

Fluorescence Probe. The perylene pigment (**1**) was dissolved in dimethylacetamide. Figure 2 shows the absorption and fluorescence spectra. The absorption peaks appear at 526 nm (molar extinction coefficient, $\epsilon = 8.2 \times 10^4$ L mol^{-1} cm^{-1}), 490 nm (5.1×10^4), and 459 nm (1.9×10^4). These values are similar to those reported for the soluble perylenedicarboximide dyes.[19] The fluorescence spectrum is also quite similar to the reported one. Unfortunately, the fluorescence quantum yield was found to be low (0.03), but the emission from the monolayer is still detectable by our apparatus with a sufficient signal-to-noise ratio. To elucidate fluorescence polarization characteristics in polymer matrices, this dye was doped in a polycarbonate film at a concentration of 1×10^{-3} mol L^{-1}. The upper side of Figure 2 shows the excitation polarization and emission polarization spectra. The excitation spectrum is almost constant in the wavelength range from 460 to 530 nm. The emission polarization spectrum is independent of wavelength in the range of 550–600 nm. The anisotropy ratio was found to be 0.33 in these wavelength ranges. This value is fairly high and

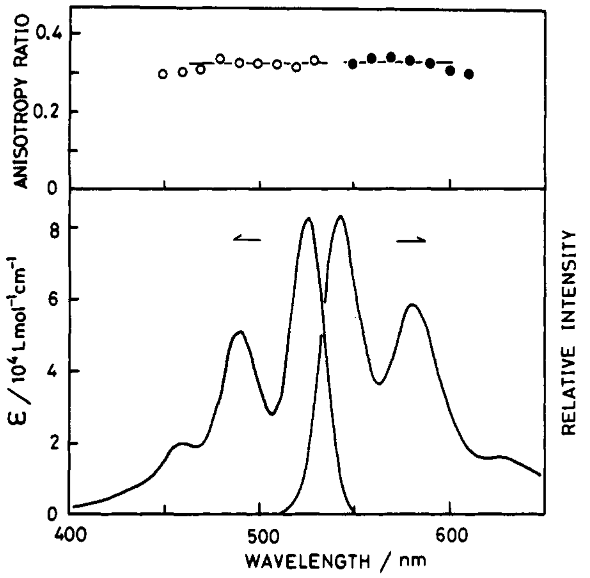

Figure 2. Absorption and fluorescence spectra of perylene probe (1) in dimethylacetamide. The upper figure shows (○) excitation polarization spectrum detected at 590 nm and (●) emission polarization spectrum excited at 490 nm.

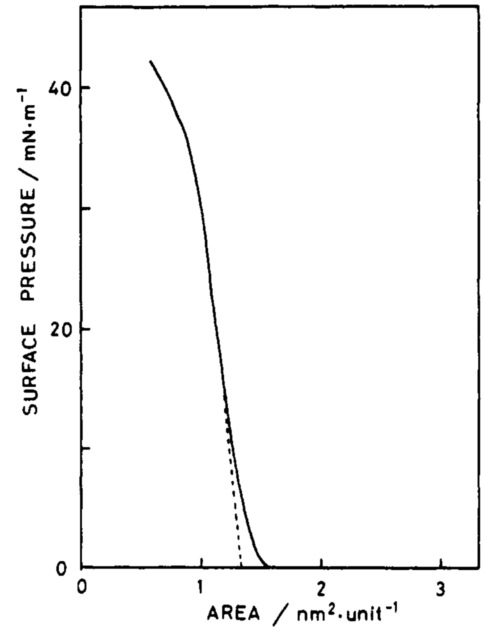

Figure 3. Surface pressure–area isotherm of polyamic acid dimethylhexadecylamine salt at 10 °C. The broken line shows the limiting area: 1.35 nm^2 unit^{-1}.

close to the limiting value, 0.4. This means that the absorption and emission dipoles nearly coincide with each other. These results indicate that the perylene pigment has the characteristics desirable for the fluorescence polarization experiments.

Deposition and Imidization of LB Film. Figure 3 shows the surface pressure–area isotherm for the polyamic acid dimethylhexadecylamine salt. The limiting area at 10 °C was found to be 1.35 nm^2/polymer repeat. The profile of the isotherm and the value of limiting area are similar to data previously reported for the polyamic acid from pyromellitic anhydride and diamine 3, but the collapse pressure is lower than the value reported by Kakimoto et al.[14] Deposition was carried out at the surface pressure of 12.5 mN m^{-1} at 10 °C. Since the substrate was hydrophilic, the transfer at the first dip takes place as Z-type deposition, but in the following dips, the monolayer is transferable at each downward and upward stroke.

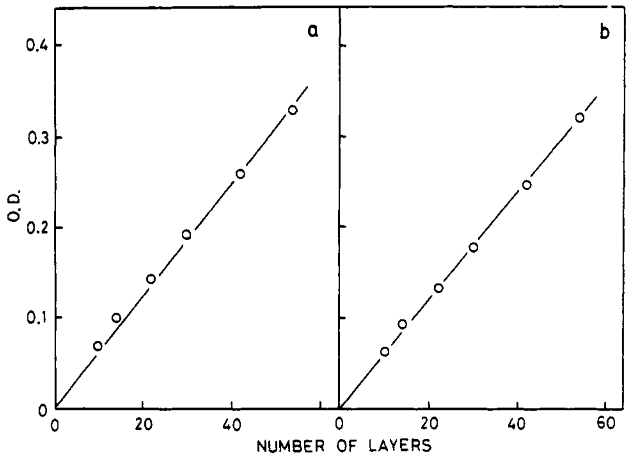

Figure 4. Absorbance of built-up films at 290 nm as a function of number of layers: (a) polyamic acid alkylamine salt LB film and (b) polyimide LB film.

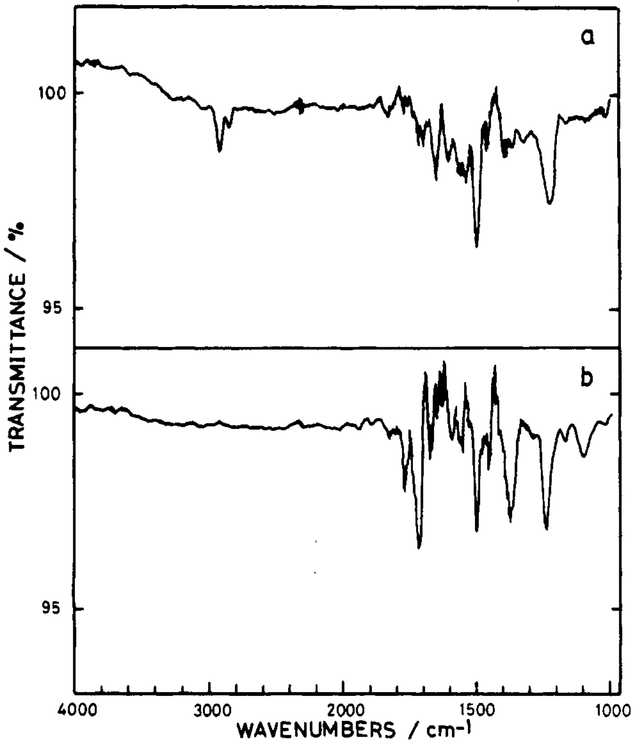

Figure 5. IR spectra of 98-layer LB films on a silicon wafer: (a) polyamic acid alkylamine salt LB film and (b) polyimide LB film.

Thus, the prepared film has an odd number of layers. Figure 4 shows the relation between absorbance at 290 nm and the number of layers, before and after the chemical treatment for imidization. The absorbance increases proportionally with the number of layers, and there is no significant change with the chemical treatment. This shows that the LB film was not peeled off by this treatment. The reaction was monitored by IR spectra for the LB films deposited on silicon wafers. Figure 5 shows the spectral change of the 98-layer films before and after the treatment. The absorption bands of the alkyl chains (2920 and 2850 cm^{-1}) disappeared, and in place of them, the absorption due to the imide group (1720 cm^{-1}) appeared.

Evaluation of Molecular Orientation. (a) Absorption Method. Absorption dichroism can be used for measuring molecular orientation of polyimide LB film. The absorption band at 290 nm is probably due to the transition dipole of biphenyl groups. Kakimoto et al. reported that the UV absorption band gives the same di-

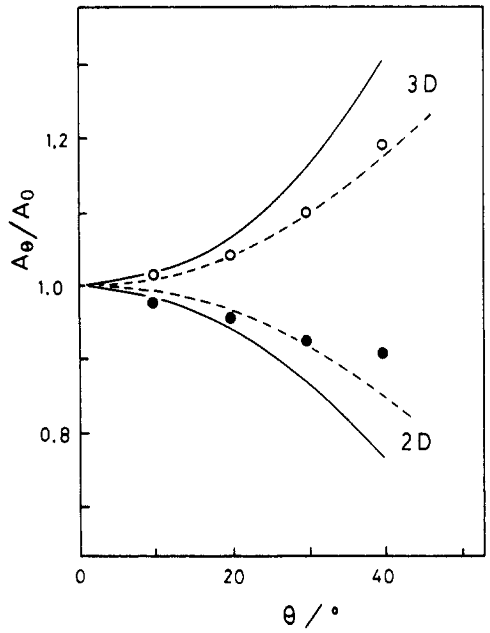

Figure 6. Tilting angle dependence of UV absorbance at 290 nm: (○) vertical light and (●) horizontal light. The upward and downward lines are the curves for eqs 1 and 2, respectively, and the broken lines are their corrected ones according to eq 3.

chroic ratio as the IR band at 1720 cm^{-1}, which is assigned to the carbonyl groups of imide units.[14] This means that the transition dipole of the UV absorption band is parallel to the axis of polyimide chain. The UV absorption dichroism can be measured for the samples thicker than 11 layers.

The dimensionality should be determined: whether the molecular orientation of our system corresponds to a 3-dimensional or a 2-dimensional distribution. This was done by measuring the absorption for the vertically and horizontally polarized light as a function of tilting angle, as shown in Figure 1a. The absorbance at an angle θ for vertical light, $A_{\theta V}$, is independent of the distribution of molecules and changes by the increase of optical path length, as

$$A_{\theta V}/A_{0V} = (\cos\theta)^{-1} \tag{1}$$

where A_{0V} is the absorbance at 0°. On the other hand, the absorbance for horizontal light, $A_{\theta H}$, depends on the manner of distribution. If the molecules take a 2-dimensional orientation in the substrate plane, the absorbance should be proportional to $\cos^2\theta$. Considering the effect of the path length, the absorbance is given as

$$A_{\theta H}/A_{0H} = \cos\theta \tag{2}$$

If the molecular orientation has a 3-dimensional distribution, the absorbance becomes independent of the tilting angles. Thus, the dependence of $A_{\theta H}/A_{0H}$ is again given by eq 1. Figure 6 shows the result. The solid lines represent the curves for eqs 1 and 2. To fit the experimental data, the angle θ in eqs 1 and 2 should be rewritten by the effective angle θ' given by

$$\sin\theta' = \sin\theta/n \tag{3}$$

where n is the refractive index of the sample. The exact refractive index of the LB films at the interface cannot be determined yet. Therefore, we used the result for vertical light as the reference of eq 1, since the tilting angle dependence has no relation with the manner of distribution and is determined only by the effective path length, $(\cos\theta')^{-1}$. The upper broken line in Figure 6 shows the corrected line of eq 1 by using an appropriate value of n so as to fit the experimental data. The lower broken line is the reciprocal of it according to eq 2. For the horizontal light, the experimental data clearly fit the downward line, indicating a 2-dimensional molecular distribution.

The orientation analysis should then be performed for a 2-dimensional system. The absorbance for the light parallel to the dipping direction (Z axis: vertical), A_Z, and the absorbance for the perpendicular direction (X axis: horizontal), A_X, are related to the orientation angle, ω, of the transition dipole by

$$A_Z = A_0\langle\cos^2\omega\rangle \tag{4}$$

$$A_X = A_0\langle\sin^2\omega\rangle \tag{5}$$

where A_0 is a constant. Then, the second moment of orientation, $\langle\cos^2\omega\rangle$ is given by

$$\langle\cos^2\omega\rangle = A_Z/(A_Z + A_X) \tag{6}$$

This value for the 2-dimensional system is 1.0 for perfect uniaxial orientation and 0.5 for random distribution. For example, the absorbances, A_Z and A_X, of a 42-layer LB film at 290 nm were 0.323 and 0.212, respectively. Then, the dichroic ratio A_Z/A_X is 1.52, and the second moment of orientation for this sample is calculated as 0.604. This means that the orientation of polymer chain is slightly inclined to the dipping direction.

(b) Fluorescence Method. The high sensitivity of the fluorescence method renders it applicable to a single layer of polyimide LB film containing the perylene pigment (1). The perylene chromophore is known to have a transition dipole parallel to the longer molecular axis.[23,24] Therefore, the fluorescence polarization of the perylene pigment represents the orientation of the polyimide chain. The optical system was shown in Figure 1b. Vertically polarized light was always used for excitation. When the dipping direction was set at the position parallel to the Z axis, the fluorescence intensity observed through the vertical polarizer, I_{ZV}, and the intensity through the horizontal polarizer, I_{ZH}, are given by

$$I_{ZV} = I_0\langle\cos^4\omega\rangle \tag{7}$$

$$I_{ZH} = I_0\langle\cos^2\omega\sin^2\omega\rangle \tag{8}$$

where I_0 is a constant. When the dipping direction was set at the position parallel to the X axis, the intensities I_{XV} and I_{XH} become

$$I_{XV} = I_0\langle\sin^4\omega\rangle \tag{9}$$

$$I_{XH} = I_0\langle\sin^2\omega\cos^2\omega\rangle \tag{10}$$

Then, the intensities I_{ZH} and I_{XH} give the same value. With these relations, the second moment of orientation can be expressed by

$$\langle\cos^2\omega\rangle = (I_{ZV} + I_{ZH})/(I_{ZV} + I_{ZH} + I_{XV} + I_{XH}) \tag{11}$$

Figure 7 shows components of the fluorescence spectra observed for a thick LB film (21 layers) with a conventional spectrometer. The intensity I_{ZV} is larger than I_{XV}, since this sytem has a slight preference for orienting in the dipping direction. Orientation of the LB films was measured for the specimens having various numbers of layers by the photon-counting system. Figure 8 shows the fluorescence intensity (total number of photons

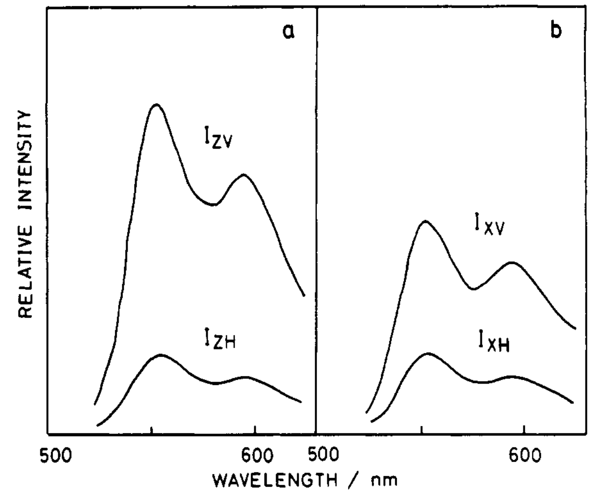

Figure 7. Component fluorescence spectra of 21-layer polyimide film. The dipping direction was in a (a) vertical direction (Z axis) and (b) horizontal direction (X axis). Spectra were recorded with the excitation wavelength of 490 nm and the band-width of 10 nm.

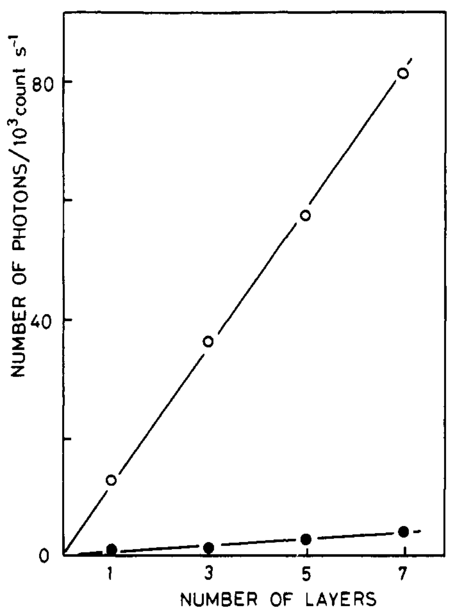

Figure 8. Total fluorescence intensities (number of photons) as a function of number of layers. The symbols ● are the intensities of control samples.

counted) as a function of the number of layers. Here, the intensity was proportional to the number of layers in this thickness range. The solid circles represent the intensities measured for the control samples, which were prepared by using unlabeled polyimide LB films under the same conditions. The values can be regarded as the background (noise level) in this experiment; the source is partly due to the weak fluorescence of polyimide[25,26] and partly due to the scattering of incident light. It is clear that sufficient signal-to-noise ratios are obtained even for the monolayer film.

The observed second moment is plotted against the number of layers in Figure 9. The open circles show the result for the labeled polyimide for a varying number of layers. The LB films show a slight preference for orientation ($\langle \cos^2 \omega \rangle = 0.54$–$0.58$) in the dipping direction. The degrees for the one- and three-layer films are slightly smaller than the others. The values for these thin films are scattered; the maximum and minimum values are represented by the error bars. The orientation of films thicker than five layers gives a constant value, ca. 0.58.

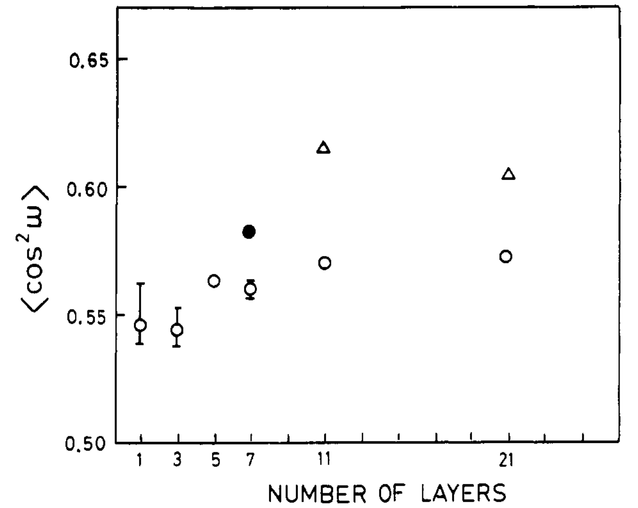

Figure 9. Plot of degree of orientation against number of layers for polyimide LB films: (○) labeled polyimide, (●) 2-layered fluorescent polyimide on 5-layered unlabeled polyimide. The symbols △ show the values measured by absorption dichroism.

The solid circle shows the surface orientation of a seven-layer film that was made by depositing five layers of unlabeled polyimide and then by coating two layers of labeled polyimide. The second moment of orientation for this film is slightly higher than that for one- or three-layer films of only labeled polyimide. This means that the one- and three-layer films have some defect or disorder affected by the substrate. However, the deposition seems to be uniform for the specimens having more than five layers. In Figure 9, triangles represent the orientation for the thick samples measured by UV absorption dichroism. The value is larger than that obtained by the fluorescence method. The absorption method represents the orientation of the transition dipole of biphenyl groups, while the fluorescence method represents that of perylene pigment. The lower values obtained by the fluorescence method show that the orientation of the perylene label is slightly disturbed compared with that of the biphenyl group. It is probably the reason that the perylene pigment has no alkyl chain and is disordered at the spreading on water, but the biphenyl part is stabilized with two amphiphilic alkylamine salts at both ends.

Liquid-Crystal Orientation. The orientation of liquid crystals can be controlled by the surface orientation of the polyimide film.[27] The rubbing procedure is often used for this purpose, but the mechanism is not clear. The present polyimide LB films are also able to align liquid crystals. To elucidate the relation between surface structure of the polyimide film and the orientation of liquid crystals, the orientation behavior was observed under a polarizing microscope. The liquid crystal, EBBA ($T_{\text{C-N}}$ = 37 °C, $T_{\text{N-I}}$ = 80 °C), was placed into the space between two sheets of quartz plates and kept at 45 °C. The liquid crystal between bare surfaces of quartz plates forms small microdomains oriented randomly. However, when the quartz plates are coated with the monolayer of polyimide film, the domains grow, and each of them aligns to the dipping direction. Even one layer of polyimide (thickness: 0.5 nm) controls a very large number of EBBA molecules. To evaluate the orientation quantitatively, the liquid-crystalline cell was placed on a rotatable hot plate, and the transmitted light intensity under the crossed polarizers was measured as a function of rotational angle ϕ, as shown in Figure 10a. Angle 0° was defined as the position where the dipping direction coincides with the polarization axis of the polarizer. Under this condition, the trans-

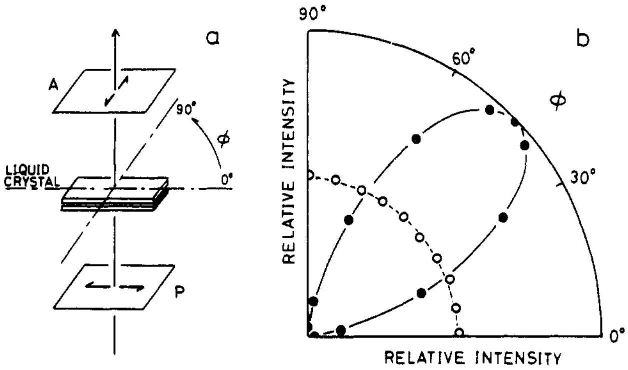

Figure 10. (a) Optical system for measuring the orientation of liquid crystals. (b) Transmitted intensities for liquid-crystal samples between bare quartz plates (○) and between polyimide films after rubbing treatment (●).

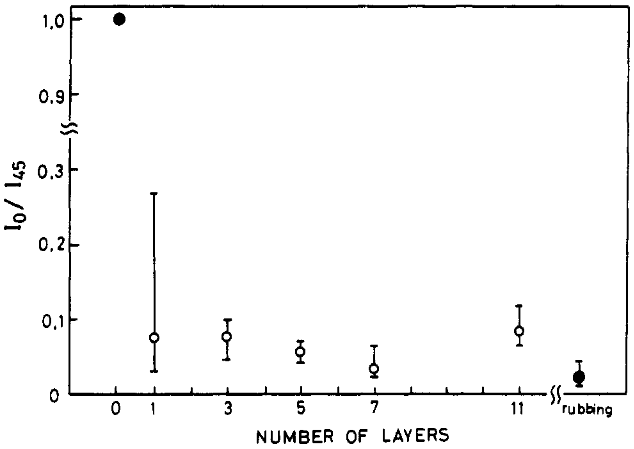

Figure 11. Plot of transmittance ratio against number of layers for polyimide LB films. The symbol ● at 0 is for the liquid crystal between bare quartz plates. The point at the right-hand side (●) is for polyimide films treated by the rubbing procedure.

mittance ratio of the angle 0° to 45° was adopted as a measure of the degree of orientation. The value I_0/I_{45} is unity when the liquid crystal consists of randomly oriented domains and becomes 0 when it orients uniaxially to the dipping direction. Figure 10b shows two typical cases; the open circles are the results obtained in the random distribution under bare quartz surfaces, and the solid circles are of the uniaxially oriented liquid crystals obtained with the rubbed surface of polyimide. For perfect uniaxial orientation of liquid-crystal domains, the transmitted intensity is proportional to $\sin^2 2\phi$.

In Figure 11, the ratios I_0/I_{45} were plotted against the number of layers. The observed values of each sample are slightly scattered because of the heterogeneity of the orientation. However, a relatively good orientation was confirmed for the samples above five layers. Thus, the liquid-crystal molecules highly amplify the effect of surface orientation of the polyimide LB film.

Concluding Remarks

Fluorescence polarization was applied to the measurement of molecular orientation of polyimide LB films. The monolayer on the substrate showed a slight preference of orientation in the dipping direction. The orientation tends to be improved with further deposition, but the degree of orientation was not very different from that of the monolayer. This tendency was also observed in the uniaxial arrangement of liquid crystals. The orientation is probably produced by deformation caused by deposition on the substrate. To elucidate the relation between the orientation behavior and the viscosity of monolayer on water, we prepared many samples under various surface pressures and deposition temperatures. There was no appreciable difference in the degree of orientation. This point needs to be investigated further.

As mentioned above, the fluorescence quantum yield of this probe was not high, and the content in the polymer was kept below 0.5% so as not to disturb the polymer behavior. If we can use a soluble dye having a high quantum efficiency, the signal-to-noise ratios, in principle, will be increased above 100 times. The single-layer orientation is detectable in situ by the fluorescence polarization method, which will be a powerful technique for mechanistic studies of the orientation process.

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