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Photochemical Stabilization of Ultrathin Polymer Films Prepared by the Langmuir−Blodgett Technique

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ABSTRACT: Photoreactive Langmuir−Blodgett films were made of poly(vinyl octanal acetal-*co*-vinyl cinnamate) (P(VO-VC)), and the effect of photo-cross-linking on the stability of a layered structure against thermal and chemical treatments has been demonstrated by energy transfer and surface plasmon spectroscopy. Photochemical cross-linking in P(VO-VC) layers easily occurred by UV irradiation for a few minutes, and consequently, the polymer became insoluble in a good solvent, dichloromethane. The durability against the solvent was measured by both UV absorption and surface plasmon resonance. A clear contrast between the irradiated part and nonirradiated part was seen in the picture taken by a surface plasmon microscope. The curing effect on the thermal relaxation of the layered structure was studied by the energy transfer method, which is very sensitive to changes in the layer distances. These findings indicate that photochemical cross-linking of the LB film greatly improves the thermal stability without any serious disordering of the layered structure.

Introduction

The ultrathin polymer film prepared by the Langmuir−Blodgett (LB) technique is a fascinating material in the field of microelectronics.[1,2] Besides the thinness of each layer, the designed structure in a molecular dimension enables one to give various functions to the polymer film. For application of the LB films, the mechanical and thermal stability of the layered structure is crucial.[3−13] Polymer LB films are expected to be more stable than the films made of conventional long-chain fatty acids.[14,15] Furthermore, they have many advantages as LB materials, e.g., variety of chemical structure,[14,16] easy introduction of functional groups,[17] fewer pinholes, and so on.[18] Introduction of reactive groups to a polymer LB film gives rise to a further possibility of realizing high thermal and mechanical stability, keeping such advantages arising from the intrinsic character of amorphous materials.

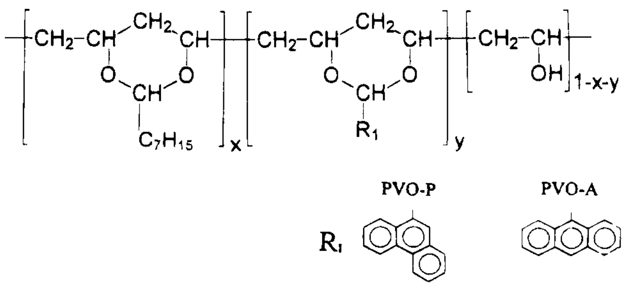
Poly(vinyl octanal acetal) (PVO) is known to form a stable monolayer on water[19] and is easily transferred onto solid substrates with a good transfer ratio around unity under a wide range of transfer conditions. Therefore, this polymer is useful for application as an insulating thin layer and as a base polymer modified with various functional groups.[20] However, the layered structure deposited on a substrate was found to be disordered under elevated temperatures.[21,22] To overcome this drawback, one effective method is the cross-linking of polymer chains. We have already reported that the formalization reaction markedly improves the thermal stability.[23] However, there is a possibility of decomposition of the fluorescent probes during the chemical treatment. Another way to improve the thermal stability is to utilize the photochemical reaction after the LB deposition. Cinnamate ester is one of the well-known photoreactive moieties for this purpose.[24−27]

Recently, we have applied the energy transfer method as a probing technique for the structural relaxation and the thermal stability of polymer LB films.[21,28] The energy transfer efficiency is determined by the inverse sixth power of distance between energy-donating and energy-accepting chromophores. Therefore the energy transfer method is capable of probing a small change in the layer distance, and a sensitive detection is possible even for the weak fluorescence from a monolayer containing only a few percent of fluorescent probes.[29]

Herein, we will demonstrate the photocontrol of the thermal and chemical durability of ultrathin polymer films made by the LB method. This technique will be of great importance in the field of coatings, adhesives, and interfacial materials.

Experimental Sections

Materials. Poly(vinyl octanal acetal) (PVO) was synthesized from commercial poly(vinyl alcohol) (PVA; dp = 2000, Wako Pure Chemical Industries, Ltd.) according to the report by Ogata et al.[19] For the energy transfer measurement, PVO with a phenanthrene group (PVO-P) and PVO with an anthracene group (PVO-A) were also prepared with the same procedure. Cinnamoyl groups were introduced in PVO as a photoreactive side chain by esterification of cinnamoyl chloride. The structure of poly(vinyl octanal acetal-*co*-vinyl cinnamate) (P(VO-VC)) obtained is shown in Scheme 1.



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Scheme 1

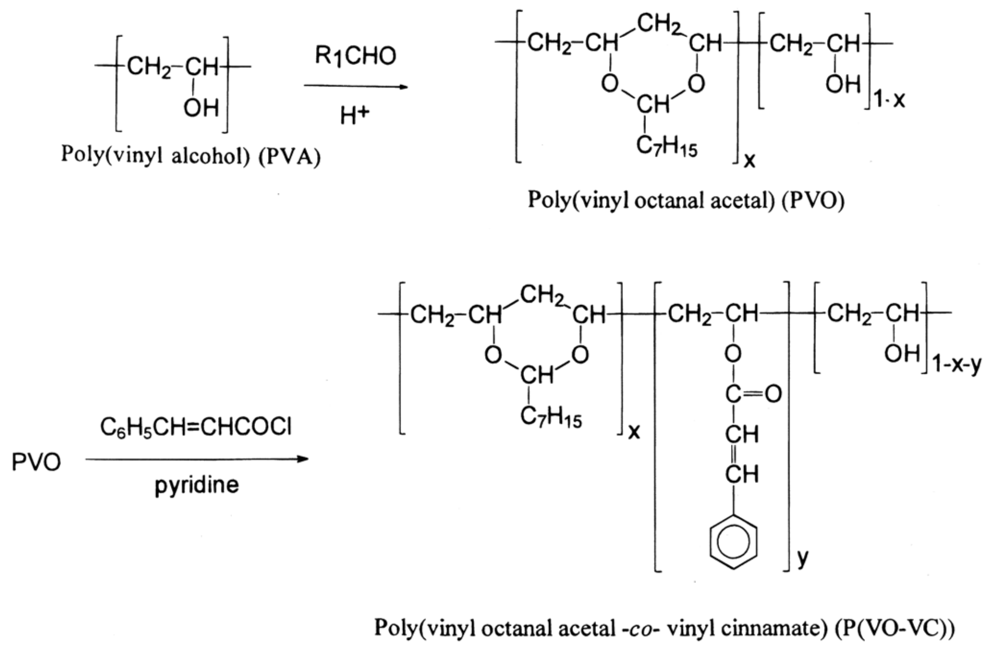

Table 1. Compositions of Synthesized Polymers and Glass Transition Temperatures

samples	octanal unit (%)	chromophore unit (%)	cinnamate unit (%)	hydroxyl unit (%)	T_g (°C)
P(VO-VC)	60.4		34.9	4.7	32
PVO-P	57.0	12.0		31.0	50
PVO-A	55.0	7.0		38.0	48

The extinction coefficient of cinnamoyl units was determined to be 17 230 L mol^{-1} cm^{-1} at 278 nm in dichloromethane using ethyl cinnamate, which is regarded as a model compound of the cinnamoyl unit. The fractions of octanal units and cinnamoyl units in the obtained polymers were calculated from the UV absorbance of cinnamoyl groups and the carbon fraction in elementary analysis. The glass transition temperature (T_g) of this polymer was determined by differential scanning calorimetry (DSC). Table 1 shows these data together with the data for PVO-P and PVO-A.

Sample Preparations. The LB films were prepared as follows. Pure water for the subphase was ion-exchanged, distilled, and finally passed through a water purification system (Barnstead Nanopure II). A benzene solution of each polymer (0.01 wt %) was spread on pure water at 19 °C in a Teflon-coated trough (Kenkosha Model SI-1). The surface film was allowed to stand for 15 min to evaporate the solvent and compressed at a rate of 15 mm/min. The surface pressure of the film was measured by a Wilhelmy-type film balance (Shimadzu Model ST-1).

A clean nonfluorescent quartz plate (10 mm × 40 mm) was made hydrophobic by trimethylchlorosilane and was used as a substrate for the UV irradiation and the fluorescence measurements. A silicon wafer was used for ellipsometry. The surface film on water was successfully transferred onto a substrate by the vertical dipping method at 17.5 mN/m for PVO-P, 21.0 mN/m for PVO-A, 22.0 mN/m for PVO, and 12.5 mN/m for P(VO-VC). These films were all deposited as Y-type films with good transfer ratios around unity.

Measurements. Surface Plasmon Spectroscopy. The use of evanescent waves has proved to be greatly helpful for the characterization of thin organic films.[30,31] Surface plasmon (SP) is one of the effective measurements which uses the evanescent waves. Figure 1 shows a schematic view of optics. The nearly free electron gas in the thin silver film evaporated onto the base of a prism acts as an oscillator that can be driven by the electromagnetic wave impinging on that interface. The sharp resonant excitation of a coupled state between the plasma oscillations and photons occurs at a particular angle in the range of total internal reflection. A thin dielectric coating on the bottom of the prism causes a shift of the resonance to a higher angle. From this shift and Fresnel's equations, one can evaluate the optical thickness of the coating.

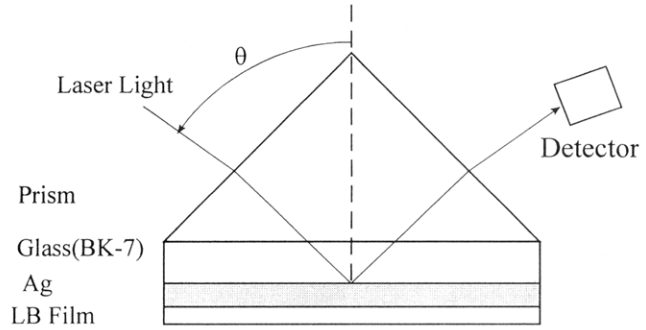

Figure 1. Attenuated total reflection (ATR) setup for the excitation of surface plasmon in Kretchmann geometry. A thin silver film is evapolated onto the base of the prism and acts as a resonator driven by the photon field.

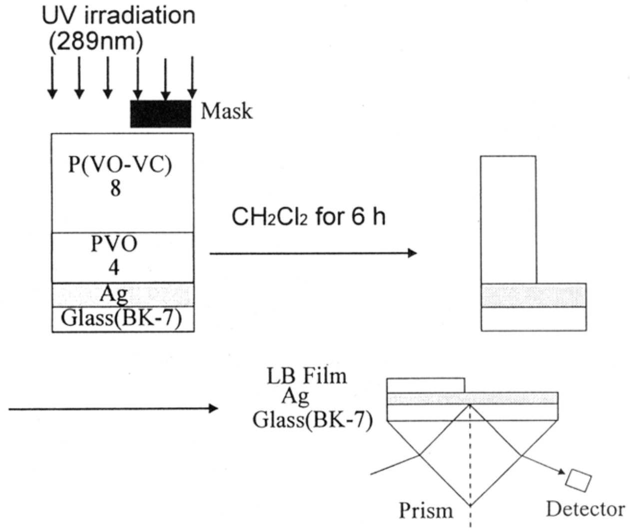

Figure 2. Schematic illustration of the multilayer structure of the LB film for surface plasmon measurements.

Figure 2 shows the layer structure of the sample for the surface plasmon experiment. The sample was fabricated on the silver-coated glass plate, and UV light at 289 nm was

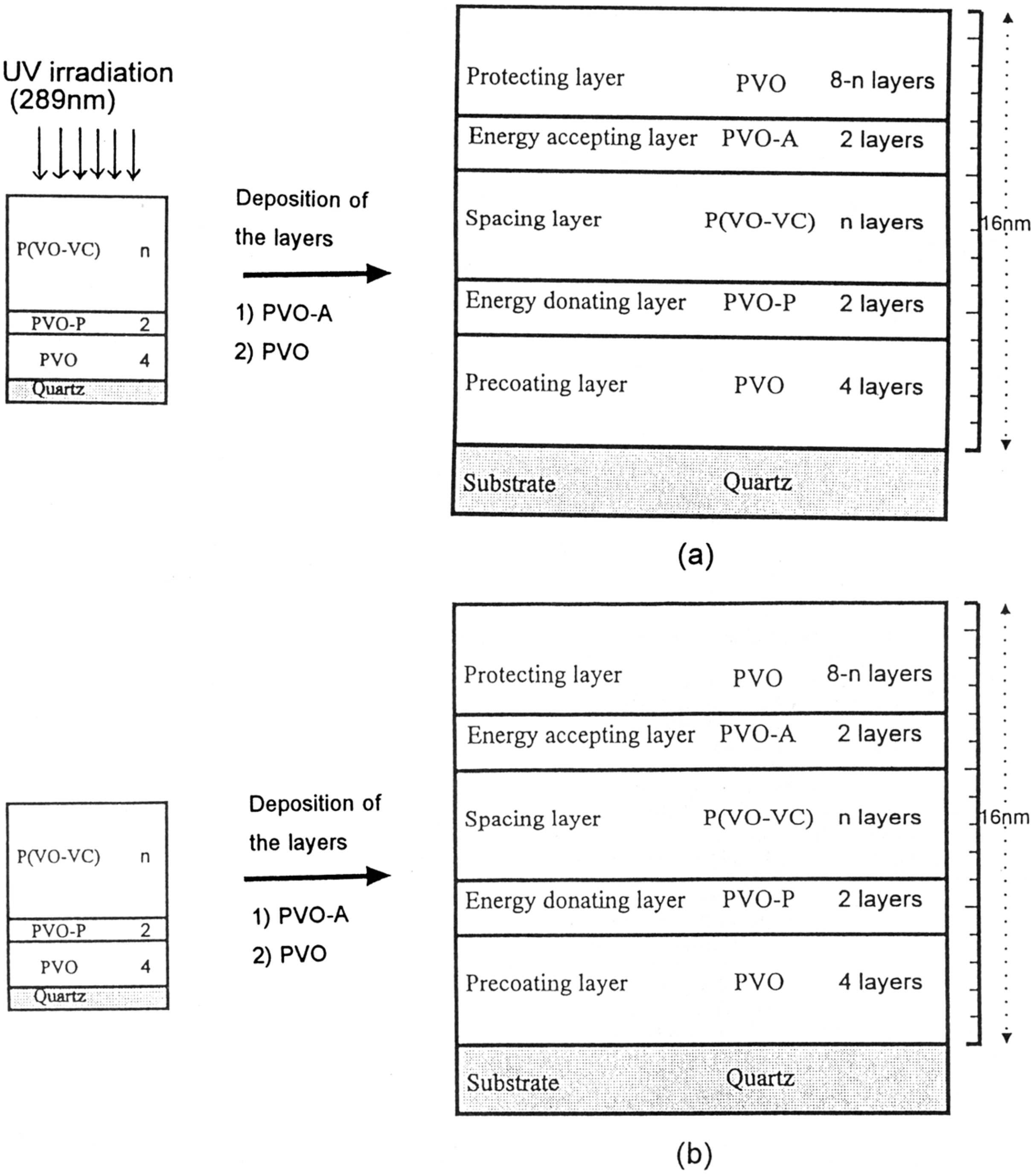

Figure 3. Schematic illustration of the multilayer structure of the LB film for the energy transfer measurement: (a) sample with UV irradiation (PVO-PnC′A); (b) sample without irradiation (PVO-PnCA).

irradiated with or without masking. Then, both portions were immersed into dichloromethane to develop the image by the difference of solubility. For the SP measurement, the glass plate was placed on the bottom of the prism, both the glass plate and the prism being optically coupled with an index-matching oil. The sample was mounted on a $\theta-2\theta$ goniometer, and a linearly polarized beam from a He−Ne laser, 5 mW at 632.8 nm, was focused on the prism with a beam diameter less than 0.1 mm. The p-component of the reflected light was detected by a photodiode.

Energy Transfer Method. Figure 3 illustrates the fabrication of LB films for the energy transfer measurements. The sample films were prepared on a quartz plate in the following sequence; At first, (1) 4 layers of PVO for the precoating layers, (2) 2 layers of PVO-P for the energy donating layers, and (3) n layers (n = 0, 2, 4, 6) of P(VO-VC) which act as a photoreactive spacer between the donating layers and the accepting layers were deposited. Then half of the sample was irradiated at 289 nm light for 5 min and the other half was kept under a mask. After this treatment, (4) 2 layers of PVO-A for the energy accepting layers and (5) ($8 - n$) layers of PVO for the protecting layers were deposited. In order to fix the composition of the film, the total number of layers was kept to 16 by adjusting the number of protecting layers; i.e., the total thickness was ca. 16 nm. Thus, the sample film having irradiated or nonirradiated spacing layers was obtained. Irradiated samples (Figure 3a) are abbreviated as P*n*C′A and nonirradiated samples (Figure 3b) are abbreviated as P*n*CA, where n is the number of spacing layers.

To probe the structural relaxation of the LB films, the energy transfer efficiencies between phenanthrene- (P) and anthracene-labeled (A) layers were measured. The critical radius of energy transfer (Förster radius) between P and A is 2.12 nm, and the donor chromophore P is selectively excited by 298 nm light. The excitation energy on a P unit transfers to the A unit over the spacing layers. Here, energy transfer

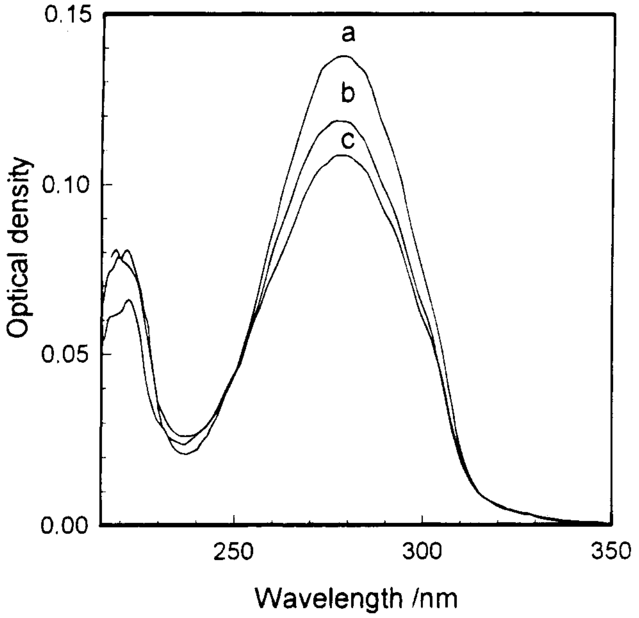

Figure 4. Spectral change of a P(VO-VC) 20-layer film by UV irradiation: (a) before irradiation; (b) after 0.5 min irradiation; (c) after 1 min irradiation.

efficiency is determined by the distance between P and A chromophores. We previously showed that the chromophores are randomly distributed in the polymer layers. The transfer efficiency was evaluated using the fluorescence intensity ratio I_A/I_P on the spectrum, where I_A is the intensity of the A emission at 438 nm and I_P is that of the P emission at 350 nm. This method is convenient for eliminating the errors of intensity measurements among samples and for detecting a small change of the distance between P and A chromophores.

Other Measurements. The thickness of the LB films was measured by ellipsometry (Mizojiri Kogaku) to be 1.02 nm for a monolayer of PVO, PVO-P, and PVO-A and 0.95 nm for P(VO-VC). The glass transition temperature (T_g) for the bulk polymers was obtained by a Rigaku Thermoflex DSC-8320. The samples having a cinnamoyl group were irradiated with 289 nm light from a high-pressure mercury lamp (Ushio USH-102D: 100 W) for the photo-cross-linking reaction. UV absorption spectra were measured by a Hitachi U-3210 spectrophotometer. The fluorescence spectra for the energy transfer measurement were recorded by a Hitachi 850 fluorescence spectrophotometer equipped with a thermoregulated sample chamber. Heating and cooling rates were fixed to be 0.5 deg/min in the range 20−100 °C.

Results and Discussion

Photoreaction of P(VO-VC) LB Films. Figure 4 shows UV absorption spectra of P(VO-VC) LB films before and after irradiation with 289 nm light. The sample consists of 4 layers of precoating PVO, 20 layers of photoreactive P(VO-VC), and 2 layers of protecting PVO on a clean quartz plate in this order. The absorption band of the cinnamoyl group at 280 nm decreases with a few minutes of irradiation. IR studies have shown that the photodimerization mainly occurs by the UV irradiation.[24−27] The decrease at the 280 nm absorption band suggests that the irradiation effectively causes photodimerization between double bonds of cinnamoyl groups which happen to be located at a position adjacent to each other in the LB film.

Figure 5 shows the fraction of cinnamoyl groups remaining in P(VO-VC) layers as a function of irradiation time. Within 5 min, about 35% of the cinnamoyl groups reacted with each other and the photoreaction was saturated. Although we changed the number of cinnamoyl layers from 8 to 24, the feature of the reaction curve was the same for all samples. This shows that the LB films are thin enough to be excited homogeneously across the film thickness. In order to compare the reactivity with the 3D-random system, we prepared a cast film of P(VO-VC) from the benzene solution and then irradiated it under the same conditions. The saturated values of the photoreaction curve were similar in both cases of the LB and the cast films. This indicates that there is no specific aggregation of the cinnamoyl groups, being randomly dispersed in the layer plane.

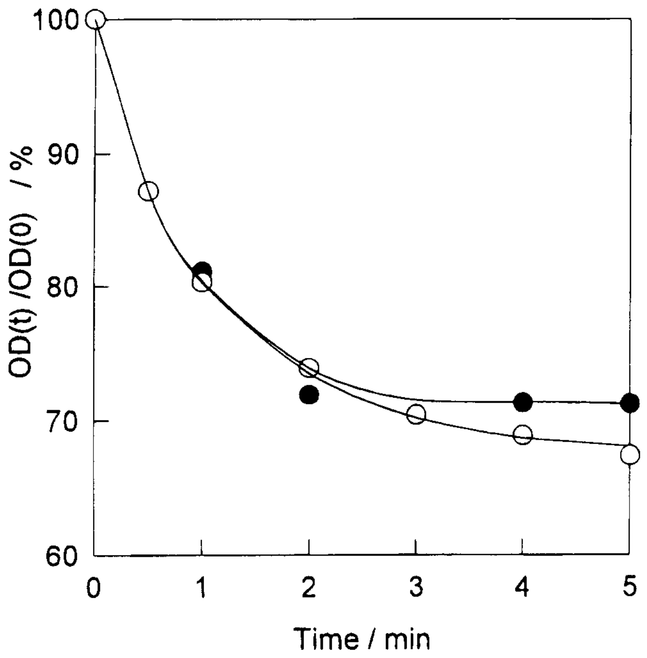

Figure 5. Residual cinnamoyl groups of P(VO-VC) with 289 nm irradiation as a function of time: (○) P(VO-VC) 20-layer film (ca. 26 nm in thickness); (●) P(VO-VC) cast film (ca. 40 nm in thickness).

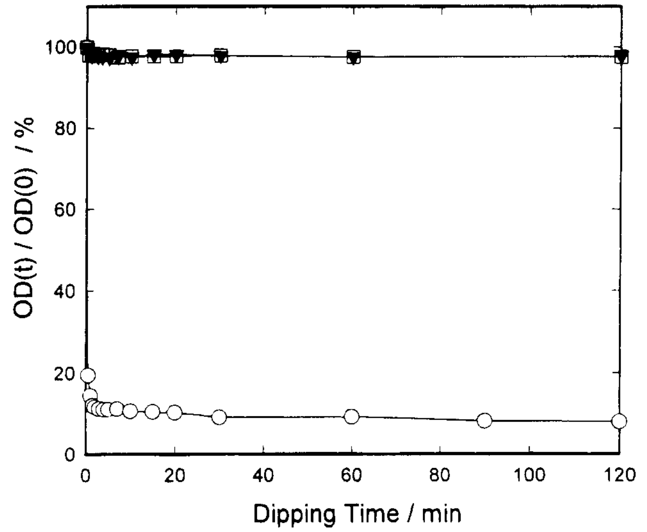

Figure 6. Solubility of the UV-irradiated P(VO-VC) 20-layer film vs dipping time in dichloromethane: irradiation for (○) 0 min, (▼) 0.5 min, and (□) 1 min.

After the exposure to UV light with various irradiation periods, the LB film was dipped into dichloromethane in order to measure the solubility in the good solvent of PVO. Figure 6 shows the residual fractions of cinnamoyl units in the P(VO-VC) 20-layer films as a function of dipping time. The nonirradiated film dis-

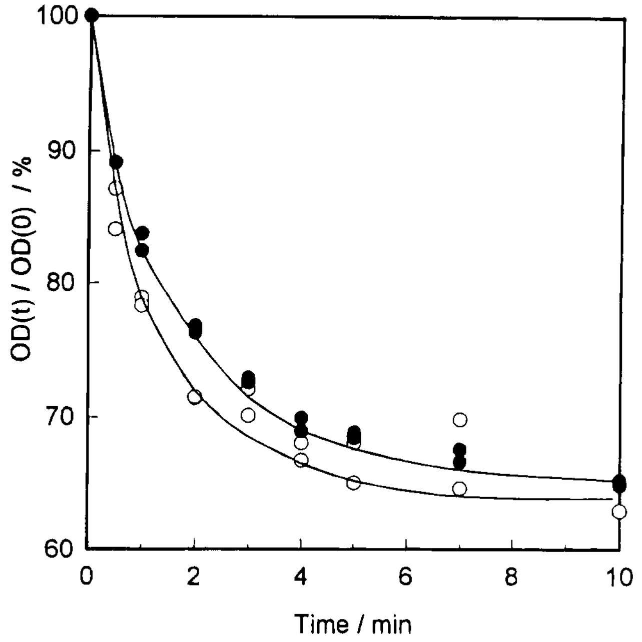

Figure 7. Comparison of the reactivity of a P(VO-VC) LB film having different layered structures: (○) alternative LB layers of PVO and P(VO-VC); (●) P(VO-VC) LB film protected with a PVO layer.

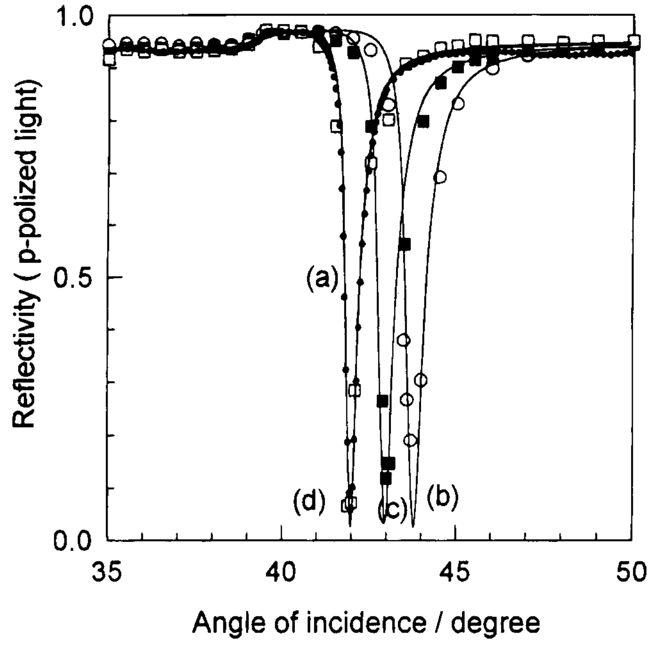

Figure 8. Reflected intensity vs angle of incidence for the LB film. Resonance curve of (a) bare silver, (b) no treatment film covered with 4 layers of PVO and 8 layers of P(VO-VC), (c) the film irradiated for 1 h and immersed in CH_2Cl_2 for 6 h, and (d) the nonirradiated film immersed in CH_2Cl_2 for 6 h. Solid lines are the Fresnel calculation.

Table 2. Fitting Parameters of Surface Plasmon Measurement

sample	ϵ_r[a]	ϵ_i[b]	d[c]	θ_{min}[d]
bare silver	−16.2	0.68	56.0	42.0
PVO (4) + P(VO-VC) (8)[e]	2.19	0	4.1	43.8
	2.26	0	7.6	
irradiated part	2.22	0	7.6	43.0
nonirradiated part	–	–	0	42.0

[a] Real part of dielectric constant. [b] Imaginary part of dielectric constant. [c] Film thickness (nm). [d] Angle of incidence at the minimum (deg). [e] The LB film consists of 4 layers of PVO and 8 layers of P(VO-VC).

solved in dichloromethane within a few minutes of dipping, but the film became completely insoluble when it was irradiated by 289 nm light for more than 30 s. Only 1% of the film dissolved in the solvent after 1 min of irradiation. Judging from this solubility data, one can say that the film structure was completely fixed by the photoirradiation.

We examined whether the reaction in the photo-cross-linking of the P(VO-VC) LB film proceeds in the inter- or intralayer process. An alternating structure of PVO and P(VO-VC) layers (PVO-*alt*-P(VO-VC)) was prepared and compared with 4 layers of P(VO-VC) LB film covered with PVO layers. These two samples have different layer structures but the same number of layers and the same compositions of PVO and P(VO-VC). Both samples were irradiated with 289 nm light, and the absorbance due to the remaining cinnamoyl groups was plotted as a function of irradiation time (Figure 7). No obvious differences in the reaction curve could be seen between these two samples. This result suggests that the intralayer photo-cross-linking is predominant in the reaction of LB films.

Solvent Durability of Cross-linked LB Films Measured by the Surface Plasmon Method. The stabilization of layered structure has been studied by surface plasmon microscopy (SPM). Figure 8 shows the reflectivity of the laser light from the sample film (see Figure 2) as a function of the angle of incidence. The solid lines were calculated by Fresnel's formula with parameters listed in Table 2.

From this experiment, the thickness of the bare silver was obtained as 56 nm. Deposition of the LB film on the silver layer made the resonance curve shift to the larger angles. With the Abbe refractometer, the refractive indices of PVO and P(VO-VC) were measured to be 1.480 and 1.491, respectively. Using these values, the thicknesses of 4 layers of PVO and 8 layers of P(VO-VC) were determined as 4.1 and 7.6 nm, respectively. Then, the sample was irradiated with 289 nm light for 1 h to complete the photoreaction; photo-cross-linking was not sufficient with 5 min of irradiation owing to the effect of the silver coating. The contrast of the irradiated portion and nonirradiated portion in the film became clear by the treatment with dichloromethane for 6 h. After this treatment, the thickness of the nonirradiated part of the film was obtained as 0 nm; i.e., the bare silver, and that of the irradiated part, became 7.6 nm by the shift of resonance curve. This indicates that the masked portion dissolved completely in dichloromethane, while the irradiated portion dissolved partially. The decrease of layer thickness for the irradiated part is probably due to the dissolution of the precoating PVO layers; the underlying layers were selectively lost by the treatment. Further investigation is required for this problem.

The example presented in Figure 9 concerns the application of the surface plasmon. This method can be used for the microscopic characterization of the lateral thickness homogeneities of a polymeric planar waveguide structure prepared by the LB technique. This figure shows the surface plasmon microscope (SPM) picture taken with p-polarized light of 632.8 nm reflected from the LB sample. Irradiation of 289 nm light with masking (the upper side of the picture) or without masking (the lower side) was done for 1 h prior to the observation. While the angle of incidence was varied from 41.2 to 44.0°, one can see a clear contrast between

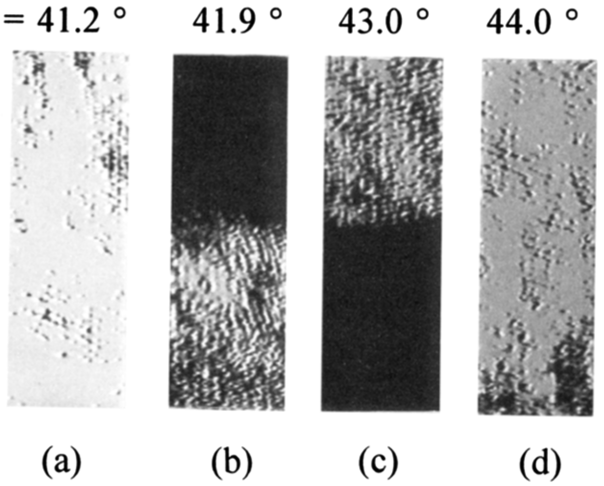

Figure 9. Surface plasmon microscopic image of 4 layers of PVO and 8 layers of P(VO-VC) LB film: (a) $\theta = 41.2°$; (b) $\theta = 41.9°$; (c) $\theta = 43.0°$; (d) $\theta = 44.0°$.

the two parts. The dark portion of Figure 9b (41.9°) corresponds to the sharp dip in Figure 8d, and the dark portion of Figure 9c (43.0°) corresponds to the sharp dip in Figure 8c. Optical waveguide microscopic pictures clearly demonstrated the flatness of the LB film. Furthermore the SPM has a possibility of an optical storage with an ultrathin film in the future.

Thermal Stability of the Layered Structure. In the previous reports,[21,23,28] we have successfully applied the energy transfer method to study the thermal stability of polymeric LB films consisting of poly(vinyl alkanal acetal)s. In these cases, there were no photosensitive moieties in the sample except for energy donor and acceptor chromophores. In the present case, however, spacing layers also have a photosensitive moiety and one should examine the interaction between chromophores and the photo-cross-linkable cinnamoyl unit before applying the energy transfer method. The following three points were checked.

(1) The durability of the phenanthrene probe against the 289 nm irradiation for the cross-linking of the cinnamoyl unit: the PVO-P LB film was irradiated for 5 min by 289 nm light of a high-pressure Hg lamp, but no decrease of fluorescence intensity of the phenanthrene probe was observed with this treatment. Consequently, 289 nm irradiation for the cross-linking of the cinnamoyl unit does not destroy the phenanthrene probe under this experimental condition.

(2) The effect of the phenanthrene probe on the photoreaction of the cinnamoyl group: The decrease of cinnamoyl groups by the UV irradiation was compared between the samples containing PVO-P layers (see Figure 3) and the samples without PVO-P layers. No obvious difference was seen in the reaction curve; i.e., the photoreaction is not affected by the presence of phenanthrene units.

(3) Quenching of donor fluorescence by the cinnamoyl group: Various numbers ($n = 0-20$) of P(VO-VC) layers were deposited over the 2 layers of PVO-P, and the fluorescence intensity of the phenanthrene probes (I_P) was measured. A slight decrease of I_P intensity with the increase of P(VO-VC) layers was observed. There was a linearity between log I_P and n according to the Lambert–Beer law. This result indicates that the decrease of I_P results from the absorption of the excitation light by the cinnamoyl group which has a large extinction coefficient in the wavelength range of P excitation. Thus, it can be concluded that the excitation energy on P does not transfer to cinnamoyl units.

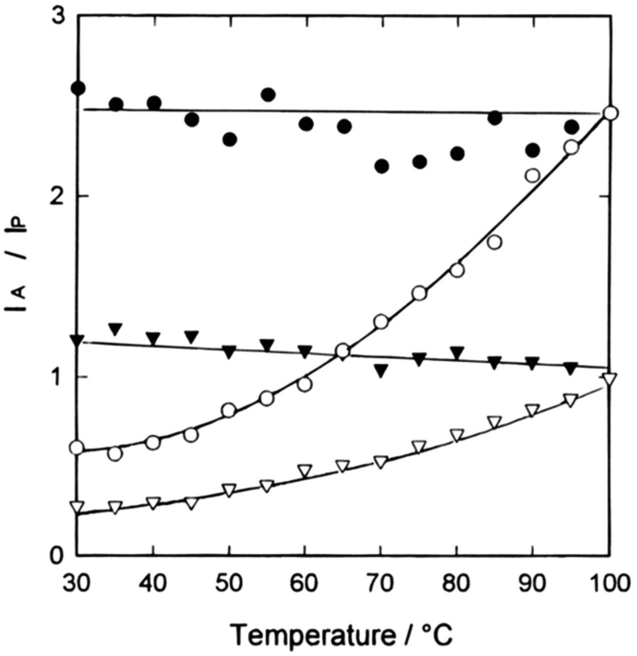

Figure 10. Energy transfer efficiency vs temperature. Heating and cooling rates were 0.5 °C/min. The energy transfer efficiency was measured at every 5 deg in both the heating mode (open symbol) and the cooling mode (closed symbol). Triangles represent P6C′A (5 min irradiation), and circles represent P6CA (without irradiation).

These three experiments strongly indicate that the thermal relaxation process can be measured by the energy transfer method without interfering with cinnamoyl units.

Figure 10 shows the thermal stability of the P6CA film and P6C′A film by plotting the ratio I_A/I_P as a function of temperature. The heating rate was 0.5 °C/min. The energy transfer efficiency was measured at every 5 deg in both the heating and cooling processes. The energy transfer efficiency became higher with the approach of P and A chromophores by thermal relaxation. As seen in the P6CA film which was nonirradiated, a steep rise of the ratio I_A/I_P was observed on the heating process. The film was completely disordered when the temperature rose to 100 °C. After heating the film to 100 °C, the energy transfer efficiency reached a plateau region and maintained its value even when the temperature decreased, indicating that this thermal relaxation process is an irreversible process. Moreover, the energy transfer efficiencies of all samples after the complete relaxation gave a similar value around 2.5, regardless of the number of spacing layers at the initial stage. The theoretical value of I_A/I_P calculated on the basis of a random distribution of P and A chromophores showed good agreement with the observed value: 2.5. On the other hand, I_A/I_P of the P6C′A film gave a rather low value on the heating process compared with that of the P6CA film. This means that the spacing layer was fixed by the photo-cross-linking, and the thermal relaxation of the film was suppressed. However, a slight increase of I_A/I_P was still observed. This is explained by the relaxation mechanism that the donor and acceptor polymers penetrate into the network of fixed spacing layers. To suppress the relaxation of the LB film completely, all the layers must be fixed, including the chromphoric layers.

Conclusion

LB films containing fluorescence probes and photoreactive groups were prepared from PVO. Photochemical cross-linking after the deposition makes the LB film highly durable to a good solvent of PVO. Using energy transfer measurements, we demonstrated that the thermal stability of the layered structure is greatly improved without any serious disordering of the layers. It should be noted that photochemical cross-linking is an effective method to fix the layered structure of thin films.

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