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The Thin Film of a Fluorine-Containing Polymer with Cyclodextrin Prepared by the Langmuir–Blodgett Technique and Its Application to Photochromic Thin Films

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A polymer synthesized from polyallylamine by perfluoroacylation was spread on an aqueous solution of a cyclodextrin derivative possessing a carboxyl group, and a thin film of the fluorine-containing polymer to which a cyclodextrin moiety was introduced was prepared by the Langmuir–Blodgett technique. Azobenzenes were incorporated in the polymer thin film as the inclusion complex by using the aqueous solution containing both the cyclodextrin derivative and azobenzenes as a subphase, and novel photochromic thin films of fluorine-containing polymers were obtained. Characterization of these films indicated that they showed excellent low surface energy due to the perfluoroalkyl group in the polymer. The influences of the incorporated cyclodextrin moiety on the molecular arrangement, the surface energy, and the film thickness are discussed.

Photochromic thin films have attracted much attention as functional thin films because of their potentials for useful applications, such as optical recording media and photo-switching devices. Recently, Langmuir–Blodgett (LB) films have been studied because they are uniform ultra-thin films possessing a highly-ordered molecular arrangement and are expected to be functional thin films, and some investigations of LB films using photochromic compounds were reported.[1—3] From a practical point of view, however, LB films have some problems, such as lack of thermal and mechanical stability. These problems must be solved to use the LB films as functional materials.

On the other hand, long chain perfluoroalkyl (Rf) groups have quite unique properties different from the corresponding alkyl groups, such as low surface energy, chemical resistance, gas solubility, etc. Therefore, a polymer containing Rf groups is expected to be a suitable material for functional thin films like surface coating films, separation films and so on because of the excellent properties of the Rf groups and the thermal and mechanical stability of the polymeric compound.

Consequently, a polymer thin film which has both Rf groups and a photochromic moiety can be expected to function as a superior photochromic thin film. As an example, this polymer would be suitable as a surface coating film of optical recording disks, because the film would have not only photochromism but excellent low surface energy derived from the Rf group, which would make the surface of the disk lubricative and protect an optical sensor from damage caused by touching the disk. But concerning the photochromic thin films of fluorine-containing polymers, almost no studies have been reported. Only cast films of mixtures of photochromic organic compounds and fluorine-containing polymers were reported as a patent.[4]

In our study, new types of thin films of polymers modified with Rf groups through covalent bonds have been prepared by means of the LB technique. These films have a highly-ordered molecular arrangement and show excellent low surface energy derived from the Rf groups, and the molecular ordering and the surface energy can be controlled by slight changes of the chemical structure of the polymer.[5] Recently, we have succeeded in incorporation of a cyclodextrin moiety into the thin film of a fluorine-containing polymer using the LB technique to afford a novel type of film equipped with another function as well as Rf groups.[6] Cyclodextrins have the ability to form host–guest complexes with many kinds of molecules,[7] so that an additional function would be provided for this film by including a functional molecule in the cyclodextrin moiety. Accordingly, a photochromic ultra-thin film equipped with the excellent properties of Rf groups can be obtained by introduction of photochromic molecules into the cyclodextrin moiety.

In this report, we describe the detailed results of the introduction of the cyclodextrin moiety into the thin film of a polymer modified with Rf groups and the preparation of photochromic thin films of the fluorine-containing polymer, which was achieved by the incorporation of azobenzenes into the film as host–guest complexes of the cyclodextrin moiety. Characterization of these films is also described.

Experimental

^{1}H NMR spectra were measured with a Fourier transform NMR spectrometer (JEOL JNM-EX270). IR spectra were measured with a Fourier transform IR spectrometer (JASCO FT/IR-7000).

Materials. Polyallylamine hydrochloride (M_w = 8500—11000) was purified by reprecipitation of commercially available material (Nittoubouseki PAA-HCl-3S) from water/methanol (1:20). Ethyl perfluorooctanoate was synthesized from perfluorooctanoic acid (Fluorochem. Ltd.) and ethanol using sulfuric acid as an acid catalyst in the usual manner.[8] The fluorine-containing polymer (PAAF, Fig. 1) was prepared by the reaction between polyallylamine, which was obtained by neutralization of polyallylamine hydrochloride, and ethyl perfluorooctanoate (0.1 equivalents of amino groups in polyallylamine) as previously described.[9] 6^A-*O*-*p*-tolylsulfonyl-β-cyclodextrin (CD-Ts) was synthesized by tosylation of β-cyclodextrin using 0.5 equivalents

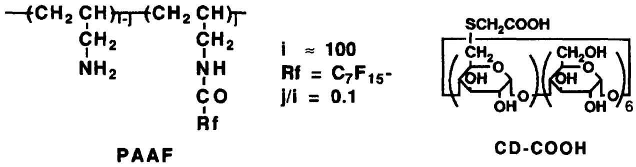

Fig. 1. Structural formulas of PAAF and CD-COOH.

of *p*-toluenesulfonyl chloride in pyridine and recrystallized from water according to the published method.[10] Disodium thioglycolate (mercaptoacetic acid) was prepared by mixing thioglycolic acid and sodium ethoxide in ethanol followed by evaporation of the solvent to dryness. Azobenzene (AB) and *p*-methoxyazobenzene (MAB) were recrystallized from ethanol.

Synthesis of CD-COOH: 6^A-carboxymethylthio-6^A-deoxy-β-cyclodextrin (CD-COOH, Fig. 1) was synthesized from CD-Ts and disodium thioglycolate as described below. CD-Ts(2.43 g, 1.9 mmol) was dissolved in 40 ml of dry *N*,*N*-dimethyformamide, and disodium thioglycolate (0.85 g, 6.2 mmol) was added to the solution. The mixture was stirred at 70 °C for 2 h under a nitrogen atmosphere. To this mixture, 3 ml of water was added, and the solvent was evaporated under reduced pressure at 70 °C. The residue was dissolved in 10 ml of hydrochloric acid (4 mol dm^{-3}), and the solution was poured into 260 ml of ethanol. The white precipitates formed were filtered and recrystallized from a mixed solvent of ethanol and water (4/1) to afford CD-COOH(1.49 g, 65%). Mp 216 °C (uncorrected, decomposition). Found: C, 43.45; H, 6.10; S, 2.20%. Calcd for $C_{44}H_{72}O_{36}S$: C, 43.71; H, 6.00; S, 2.65%. IR(KBr) 3404, 2925, 1717, 1645, 1417, 1157, 1079, and 1032 cm^{-1}. ^{1}H NMR (DMSO-d_6/$CDCl_3$) δ=3.00—4.00 (m, 51H), 4.89 (m, 7H), and 5.60 (br, 14H).

Preparation of the Surface Films. A benzene/methanol (1 : 1) solution (concentration of the Rf group: 5×10^{-4} mol dm^{-3}) of PAAF was spread on pure water, the aqueous solution of CD-COOH (5×10^{-5} mol dm^{-3}), the aqueous solution of AB (3×10^{-5} mol dm^{-3}), and the aqueous solution containing CD-COOH (5×10^{-5} mol dm^{-3}) and azobenzenes (AB: 3×10^{-5} mol dm^{-3}, MAB: 2.5×10^{-5} mol dm^{-3}).

Characterization of the Films. The pH values of the subphases were measured with a pH/ISE meter (Orion 920A). Surface pressure-surface area (F-A) isotherms were measured using a Lauda film balance at 290 K. The surface films were deposited at a surface pressure of 20 mN m^{-1} onto slide glasses, calcium fluoride plates, and quartz glass plates. The introduction of the cyclodextrin moiety to the polymer film was examined by measurement of the IR spectra. The transmission IR spectra of the deposited films on calcium fluoride plates were measured with a Fourier transform IR spectrometer (JASCO FT/IR-7000).

The photochromic bahavior of the deposited films was examined by the UV-visible spectral change of the film on irradiation. The UV-visible spectra of the deposited films on quartz glass plates were measured with a UV-visible spectrometer (Shimadzu UV-3101PC). Irradiation was carried out using a 500 W super-high-pressure xenon lamp (Ushio UXL-500D) through a monochrometer (Shimadzu GRATING 1350).

Critical surface tensions (γ_c values) were obtained from Zisman plots of contact angles of normal alkanes on the deposited films by the method of Hata and Kitazaki.[11] The contact angles were measured with a contact angle meter (Kyowakagaku CA-D).

X-Ray diffraction patterns were measured with an autodiffractometer (Philips PW1800) by using the Cu $K\alpha_1$ line of the wavelength of 1.54050 Å with an acceleration voltage of 40 kV and beam current of 30 mA.

The thickness of the deposited films were measured by the stylus method using a Talystep (Rank Taylor Hobson). Part of the deposited film was peeled off the slide glass and the difference in level between the area with the attached film and the bare slide glass after exfoliation was measured.

Results and Discussion

Preparation of the Films Containing Cyclodextrin. Introduction of the cyclodextrin moiety into the fluorine-containing polymer which has amino groups as hydrophilic groups (PAAF) was carried out by the formation of a polyion complex with a cyclodextrin derivative possessing carboxyl groups (CD-COOH). The polyion complex between PAAF and CD-COOH was insoluble in organic solvents, so that the preparation of the film was attempted by the formation of the polyion complex at the air–water interface. Namely, a benzene/methanol (1 : 1) solution of PAAF was spread on an aqueous solution of CD-COOH. The F-A isotherms of PAAF on the aqueous solution of CD-COOH (PAAF/CD) and on pure water (PAAF/—) are shown in Fig. 2. The surface films were stable up to more than 60 mN m^{-1} and the limiting areas of the Rf unit at zero pressure (A_0) for PAAF/CD and PAAF/— were 44 and 70 Å^2, respectively. This result indicates that the molecular arrangement depended on the subphase. The pH of the subphase of PAAF/CD (pH 4.8)

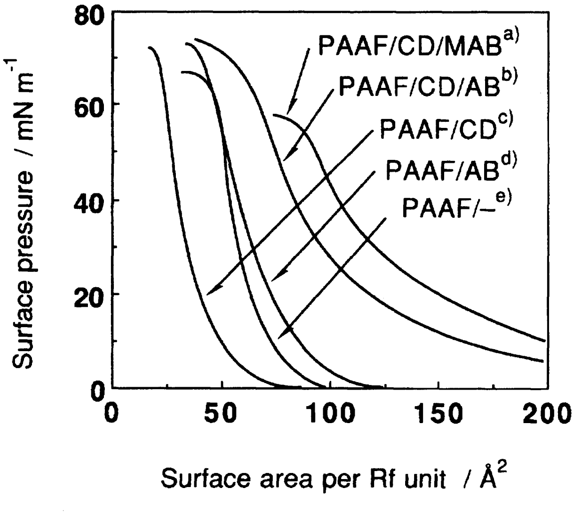

Fig. 2. F-A isotherms. a) Subphase: CD-COOH 5×10^{-5} mol dm^{-3}, MAB 2.5×10^{-5} mol dm^{-3}. b) Subphase: CD-COOH 5×10^{-5} mol dm^{-3}, AB 3×10^{-5} mol dm^{-3}. c) Subphase: CD-COOH 5×10^{-5} mol dm^{-3}. d) Subphase: AB 3×10^{-5} mol dm^{-3}. e) Subphase: pure water.

was lower than that of PAAF/— (pH 5.9), accordingly, the protonation of more amino groups in PAAF on the aqueous solution of CD-COOH would occur than on pure water. And furthermore, it is supposed that polyion complexes between the ammonium ion of PAAF and the carboxylate ion of CD-COOH were formed. The difference in the molecular arrangement is ascribed to the protonation of the amino groups and the formation of the polyion complexes.

The deposition of the surface films of PAAF/— and PAAF/CD on calcium fluoride plates was attempted and Y-type multilayers were obtained. The transmission FT-IR spectra of these deposited films on calcium fluoride plates (19 layers deposited on both sides) were measured. The IR spectra are compared in Fig. 3. Absorptions derived from cyclodextrin (O–H stretching at 3342 cm^{-1} and absorptions from 1150 to 1000 cm^{-1}) were observed in the spectrum of PAAF/CD, which confirms the introduction of CD-COOH into the deposited film.

Introduction of Azobenzenes into the Film and Its Photochromism. Preparation of a film containing a functional molecule as an inclusion complex of the cyclodextrin moiety was attempted using azobenzene (AB) and *p*-methoxyazobenzene (MAB) as photochromic molecules. A benzene/methanol (1 : 1) solution of PAAF was spread on an aqueous solution containing CD-COOH and azobenzenes. F-A isotherms of PAAF on the subphase containing azobenzene (PAAF/CD/AB) and *p*-methoxyazobenzene (PAAF/CD/MAB) are shown in Fig. 2. PAAF/CD/AB and PAAF/CD/MAB showed a larger surface area than PAAF/— and PAAF/CD, and the A_0 values were 115 and 151 Å^2, respectively.

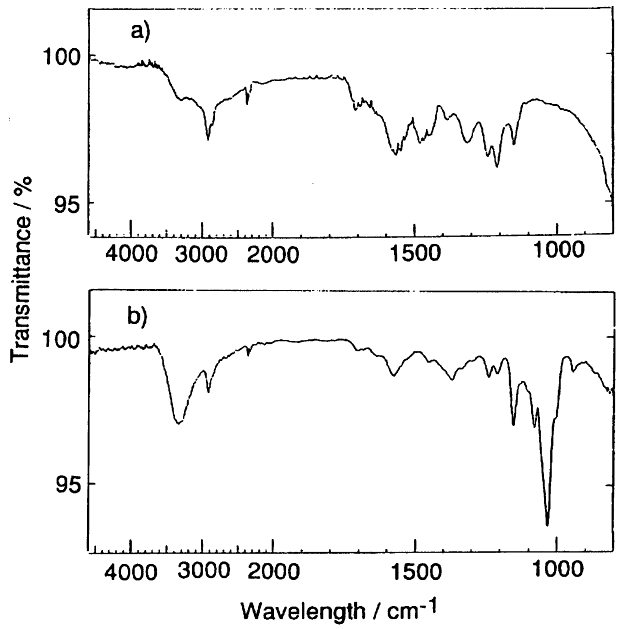

Fig. 3. Transmission IR spectra of deposited films. a) PAAF/—. b) PAAF/CD.

From these results, it was shown that the presence of azobenzenes in the subphase containing CD-COOH had a great influence on the molecular arrangement. The pHs of the subphase for PAAF/CD/AB and PAAF/CD/MAB were 5.0 and 4.8, respectively, almost equal to that of the subphase for PAAF/CD, indicating that the difference caused by the presence of azobenzenes was not derived from the pH of the subphase. The F-A isotherm of PAAF on the aqueous solution of azobenzene was measured, and the F-A isotherm (PAAF/AB, Fig. 2) was close to that on pure water, suggesting that azobenzene itself had only a little effect on the molecular arrangement. The detailed reason remains obscure, however, it is suspected that host-guest compounds formed between CD-COOH and azobenzenes, and that the difference in the molecular arrangement came from the formation of the polyion complexes of PAAF with the host–guest compounds.

The deposition of the PAAF/CD/AB surface film on quartz glass plates was attempted and Y-type multilayers were obtained. Figure 4 shows the UV-visible spectrum of the deposited film (5 layers on both side) and the spectral change on irradiation with 350 nm light. The absorption derived from the π–π* band of azobenzene was observed at 325 nm. On the other hand, the film prepared from PAAF on the aqueous solution containing only azobenzene did not show the absorption of azobenzene. This result suggested that azobenzene was introduced into the film as the host-guest complex of CD-COOH.

The spectral change on irradiation with 350 nm light corresponded to the *trans*-to-*cis* isomerization of azobenzene. After the photostationary state was reached by irradiation with 350 nm light, the film was irradiated with 431 nm light corresponding to the n–π band of the *cis* isomer, the reverse spectral change occurred, and the same spectrum as that before irradiation with

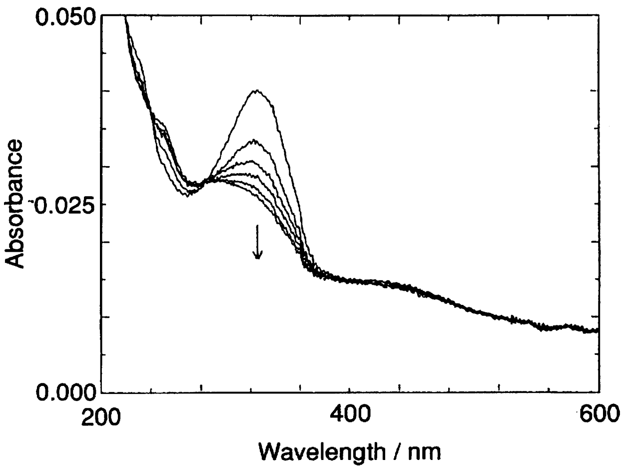

Fig. 4. UV-visible spectral change of PAAF/CD/AB on 350 nm irradiation. Each irradiation time is 10 s.

350 nm light was measured. This spectral change indicated a *cis*-to-*trans* isomerization. In this manner, the PAAF/CD/AB film exhibited photochromism. This photochromic behavior showed excellent reversibility without a decrease in absorbance during ten cycles of irradiation with 350 and 431 nm light, as shown in Fig. 5. And furthermore, after PAAF/CD/AB film was cross-linked by heating at 90 °C,[12] the photochromic behavior of this film was preserved even if the film was dipped in chloroform for 24 h, which indicates the excellent solvent-resistance of this film.

In the case of PAAF/CD/MAB, Z-type multilayers were obtained. As shown in Fig. 6, the deposited PAAF/CD/MAB film (3 layers on both side) also exhibited a spectral change corresponding to the *trans*-to-*cis* isomerization of *p*-methoxyazobenzene by irradiation with 350 nm light. And on irradiation with 433 nm light, the reverse spectral change was observed.

Critical Surface Tension of the Deposited Film. Critical surface tensions (γ_c) of the deposited films on slide glasses (1 and 5 layers; in the case of PAAF/CD/MAB, 1 and 3 layers) are shown in Table 1. All these films had excellent low surface energy characteristic of Rf groups.

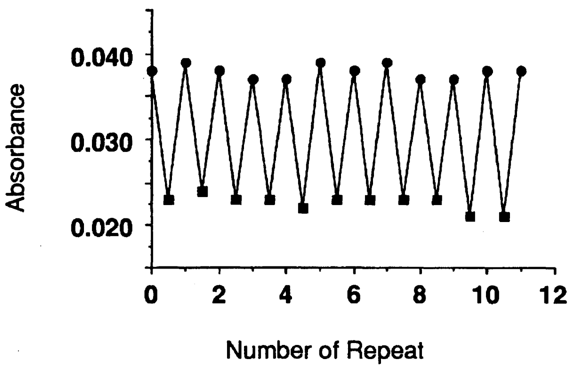

Fig. 5. Absorbance of PAAF/CD/AB at 325 nm in the photostationary state on alternative irradiation with 350(●→■) and 431 nm(■→●) light.

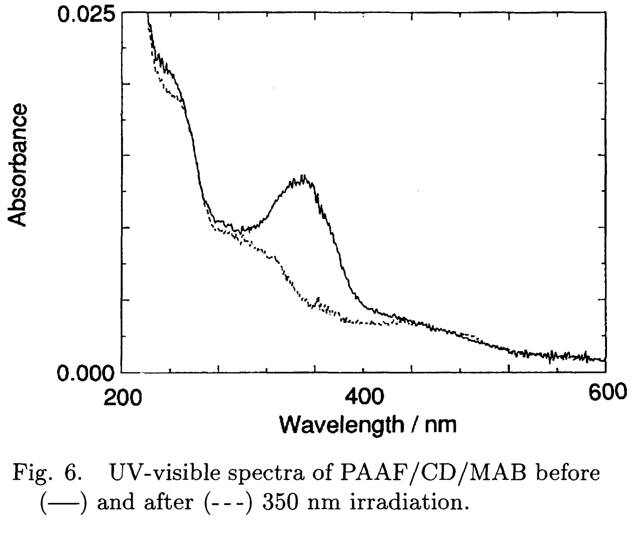

Fig. 6. UV-visible spectra of PAAF/CD/MAB before (—) and after (- - -) 350 nm irradiation.

The γ_c values of 1 layer films were larger than those of multilayer films, which can be ascribed to the influence of the glass surface.[13] The films containing the cyclodextrin moiety showed larger γ_c values than PAAF/—. CD-COOH is a molecule containing may hydrophilic groups, so that the incorporation of CD-COOH would make the critical surface tension increase. And furthermore, the arrangement of Rf groups would be somewhat disordered by the introduction of the bulky cyclodextrin, which would also increase the critical surface tension. The films containing the cyclodextrin moiety, however, still showed very low surface energies (lower than ca. 20 dyn cm^{-1}), especially, the γ_c values of the maltilayer PAAF/CD and PAAF/CD/AB films were lower than that of poly(tetrafluoroethylene) whose surface is covered with $-CF_2-$ chains (18.5 dyn cm^{-1}).[11] These low surface energies suggested the existence of Rf groups on the surface.

Thickness of the Film. The thicknesses of these films were measured by X-ray diffraction and by the stylus method using deposited films on the slide glasses (19 layers for PAAF/— and PAAF/CD, 5 layers for PAAF/CD/AB, 3 layers for PAAF/CD/MAB). A broad peak derived from diffraction between the layers in the film was observed as an X-ray diffraction pattern, and the approximate thickness per one layer was calculated from the diffraction peak by using Bragg's equation ($2d\sin\theta=n\lambda$, n=1, 2, 3...., d is plane spacing, θ is the incident angle of the X-ray, and λ is the X-ray wavelength). In the case of PAAF/—, peaks derived from diffraction between the film surface and the slide glass were observed, and the thickness per one layer calculated from these diffraction peaks agreed with the former calculated value. These results are indicated in Table 2.

The thicknesses measured by the stylus method were somewhat smaller than those measured by X-ray diffrac-

Table 1. Critical Surface Tensions (γ_c) of Deposited Films

Polymer	γ_c/dyn cm^{-1}	
	1 Layer	5 Layers
PAAF/—	18.5	16.4
PAAF/CD	19.4	17.2
PAAF/CD/AB	18.1	17.4
PAAF/CD/MAB	21.9	20.2[a)]

a) 3 layers.

Table 2. The Thicknesses Per One Layer of Film

Polymer	Thickness/Å	
	X-Ray method	Stylus method
PAAF/—	23	21—23
PAAF/CD	44	26—42
PAAF/CD/AB	46	36—40
PAAF/CD/MAB	46	42—43

tion owing to the stylus force;[14] the measurement by the stylus method is expected to give smaller thicknesses than the actual values.

The PAAF/CD film was thicker than PAAF/— by ca. 20 Å. β-cyclodextrin has a cylindrical shape (the diameter is 15—16 Å, the height is 8 Å),[15] so that the difference of the thickness could be mainly ascribed to the bulkiness of the introduced cyclodextrin moiety. The thicknesses of the PAAF/CD/AB and PAAF/CD/MAB films were almost same as that of PAAF/CD. It is assumed that the guest molecule had little effect on the film thickness because it was included in the cavity of the cyclodextrin moiety.

Conclusion

The thin films of polymers containing Rf groups which have the cyclodextrin moiety could be prepared by the formation of the polyion complex between the fluorine-containing polymer and the cyclodextrin derivative using the Langmuir–Blodgett technique. By using the aqueous solution containing the cyclodextrin derivative and azobenzenes as the subphase, novel photochromic thin films of the fluorine-containing polymer having azobenzenes as an inclusion complex of the cyclodextrin moiety could be obtained. These films showed excellent low surface energy due to the Rf group. The thicknesses of these films were larger than that of the film having no cyclodextrin moiety.

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