

## The Thin Film of Fluorine-containing Polymer Having Cyclodextrin Prepared by Langmuir-Blodgett Technique

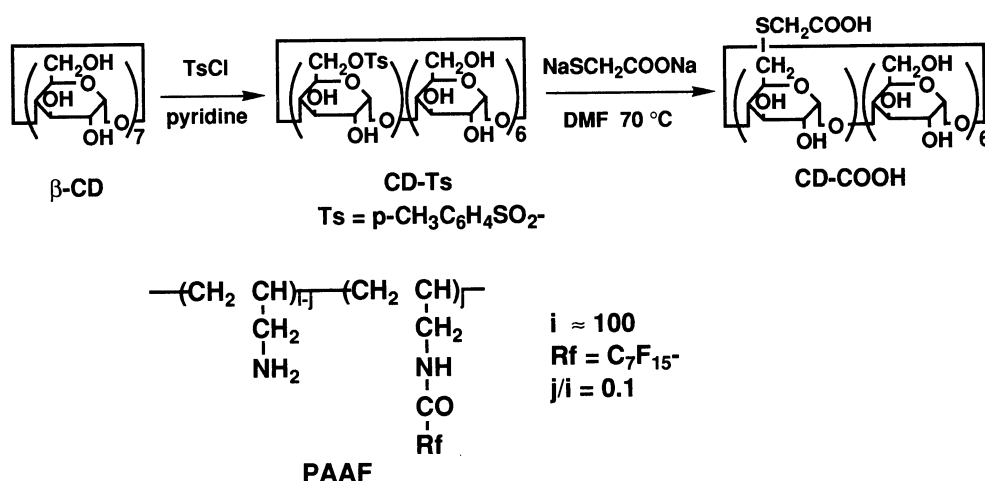
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Polyallylamine modified with perfluoroalkyl groups was spread by Langmuir-Blodgett technique and reacted on the aqueous solution of a cyclodextrin derivative. The cyclodextrin moiety was first introduced to the thin film of fluorine-containing polymer. The film of the polymer having the cyclodextrin moiety was characterized.

Long chain perfluoroalkyl (Rf) groups show excellent properties, such as water- and oil-repellency, chemical resistance, gas solubility, hence, the thin films possessing Rf groups are to be very useful for surface coating films, separation films and so on. Recently, we have prepared the new type thin films of polymers modified with Rf groups through covalent bonds by means of Langmuir-Blodgett (LB) technique, which have highly ordered molecular arrangement and show excellent surface property.<sup>1)</sup> On the other hand, cyclodextrins attract much attention owing to the ability to form host-guest complexes with many kind of molecules,<sup>2)</sup> and the LB film of cyclodextrin derivatives have been investigated as the functional thin film which can include various functional molecules by the formation of host-guest complex.<sup>3)</sup> A new functional thin film is expected to be obtained by incorporating cyclodextrin moiety into the thin film of the polymer modified with Rf group using LB technique. It would be possible that this film includes some molecule as host-guest complex of the cyclodextrin moiety. Furthermore, if this film includes functional molecule, additional function would be provide for this film. Here, we report the introduction of the cyclodextrin moiety into the thin film of polymer modified with Rf group prepared by LB technique. The preparation of the film containing guest molecule in the cyclodextrin moiety as the inclusion complex is also reported.

$\beta$ -Cyclodextrin ( $\beta$ -CD) was tosylated with 0.5 equivalent of p-toluensulfonyl chloride in pyridine, and mono-6-p-toluensulfonyl- $\beta$ -cyclodextrin (CD-Ts) was purified by recrystallization from water.<sup>4)</sup> The cyclodextrin derivative having a carboxyl group (CD-COOH) was synthesized by the reaction of CD-Ts with disodium thioglycolate in dimethylformamide (Scheme 1). The polymer modified with Rf groups (PAAF, the



Scheme 1. Synthesis of CD-COOH and structural formula of PAAF.

content of Rf groups to the amino groups  $j/i = 0.1$ ,<sup>5)</sup> Scheme 1) was synthesized by the reaction of polyallylamine ( $M_w = 5200 - 6700$ ) with ethyl perfluorooctanoate.<sup>6)</sup> The introduction of CD-COOH to PAAF was attempted by the formation of ion complex between PAAF and CD-COOH. The benzene / methanol (1 : 1) solution of PAAF (the concentration of Rf group :  $5 \times 10^{-4} \text{ mol dm}^{-3}$ ) was spread on the aqueous solution of CD-COOH ( $5 \times 10^{-3} \text{ mol dm}^{-3}$ , pH 4.8) at 290 K, and the surface pressure - surface area (F-A) isotherm was measured. The F-A isotherm of PAAF on pure water (pH 5.9) was also measured in the same manner and these F-A isotherms are shown in Fig. 1. PAAF on the aqueous CD-COOH (PAAF/CD) showed different F-A isotherm from that on pure water (PAAF/—), and the limiting areas of perfluoroalkyl unit at zero pressure ( $A_0$ ) were 44 and  $70 \text{ \AA}^2$ , respectively. It is supposed that more amino groups in PAAF were protonated on the aqueous solution of CD-COOH than on pure water because of low pH, and that the ion complexes were formed between ammonium cation of PAAF and carboxylate anion of CD-COOH, so that the molecular arrangement would change resulting in the difference of F-A isotherm.

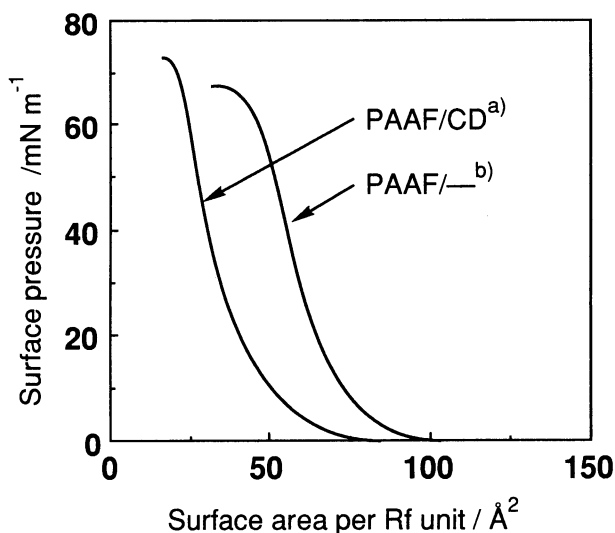


Fig. 1. F-A isotherms.

- a) Spread on aqueous CD-COOH ( $5 \times 10^{-5} \text{ mol dm}^{-3}$ ).  
 b) Spread on pure water.

The deposition of the surface films on slide glasses and calcium fluoride plates was attempted under surface pressure of  $20 \text{ mN m}^{-1}$ , and Y type multilayers were obtained in both case of PAAF/— and PAAF/CD. The transmission FT-IR spectra (instrument, Jasco FT/IR-7000) of these deposited films on a calcium fluoride plates (19 layer deposited on both sides) were measured, and the obtained spectra are compared in Fig. 2. As apparent from Fig. 2, absorptions derived from cyclodextrin (O-H stretching at  $3342 \text{ cm}^{-1}$  and absorptions from  $1150$  to  $1000 \text{ cm}^{-1}$ ) were observed in the spectrum of PAAF/CD. This result confirms the introduction of CD-COOH to the deposited film.

The  $\gamma_c$  values of Zisman plot were measured with n-alkanes on the deposited films (1 and 5 layer) in usual manner.<sup>6)</sup> The  $\gamma_c$  values of PAAF/— and PAAF/CD were  $18.5$  and  $19.4 \text{ dyn cm}^{-1}$  for 1 layer films, and  $16.4$  and  $17.2 \text{ dyn cm}^{-1}$  for 5 layer films, respectively. The larger  $\gamma_c$  values of 1 layer films than 5 layer films would be ascribed to the influence of the glass surface.<sup>7)</sup> The  $\gamma_c$  values of 5 layer films are lower than that of polytetrafluoroethylene ( $18.5 \text{ dyn cm}^{-1}$ ), indicating that  $\text{CF}_3$  groups exist on the surface of the films.<sup>6)</sup> The  $\gamma_c$  values of PAAF/CD are larger than those of PAAF/—. It is assumed that CD-COOH incorporated in the film has an

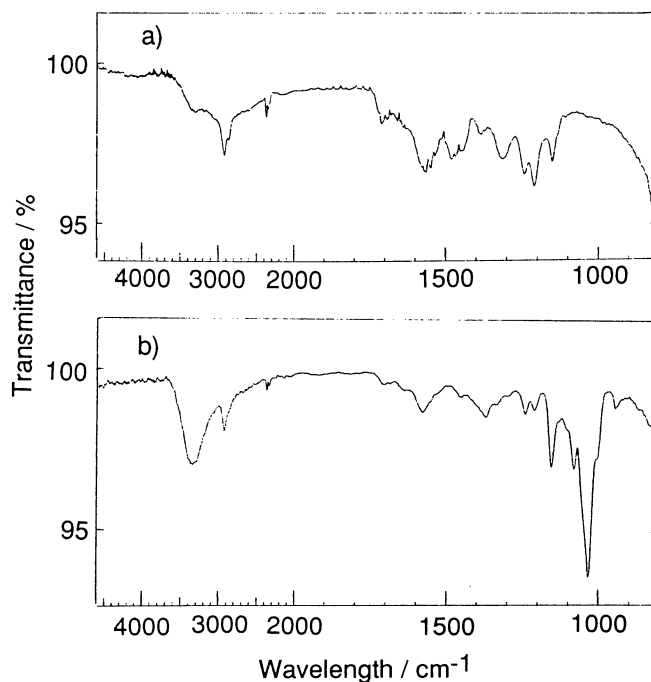


Fig. 2. Transmission FT-IR spectra of deposited films.  
a) PAAF/—; b) PAAF/CD.

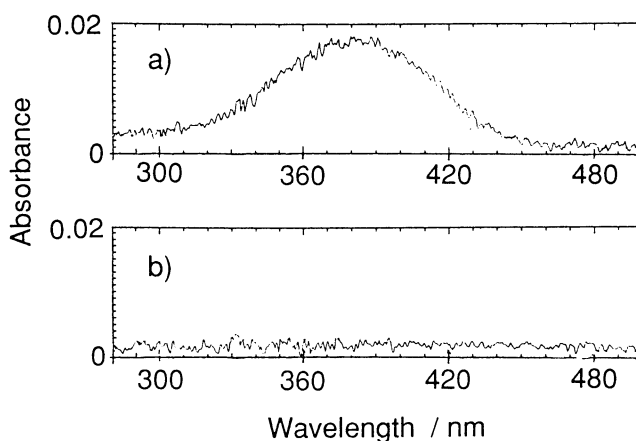


Fig. 3. UV spectra of deposited films.  
a) The film prepared on the aqueous solution containing CD-COOH and p-nitroaniline.  
b) The film prepared on the aqueous solution containing only p-nitroaniline.

effect on the surface of the film and increases the  $\gamma_c$  value.

The thicknesses of these films were measured by X-ray diffraction, and the thicknesses per one layer of PAAF/— and PAAF/CD were 23 and 44 Å<sup>2</sup>, respectively. This result indicates that the thickness of the film increases by introduction of cyclodextrin moiety.

The preparation of the film containing guest molecules in the cyclodextrin moiety as inclusion complex was attempted using p-nitroaniline as a model of guest molecule. The benzene / methanol (1 : 1) solution of PAAF was spread on the aqueous solution containing CD-COOH ( $5 \times 10^{-3}$  mol dm<sup>-3</sup>) and p-nitroaniline ( $3 \times 10^{-3}$  mol dm<sup>-3</sup>) at 290 K, and the obtained surface film was deposited onto a quartz glass (1 layer on both side) under surface pressure of 20 mN m<sup>-1</sup>. The surface film on the aqueous solution containing only p-nitroaniline ( $3 \times 10^{-3}$  mol dm<sup>-3</sup>) was also prepared and deposited onto a quartz glass (1 layer on both side). The UV spectra (instrument, Shimadzu UV-3100) of these deposited films were measured and shown in Fig. 3. The absorption derived from p-nitroaniline at 382 nm was observed only when the subphase contained CD-COOH. This result suggests that p-nitroaniline was introduced into the film as the host-guest complex of CD-COOH.

In conclusion, we have demonstrated the introduction of the cyclodextrin moiety into the thin film of polymer modified with Rf groups prepared by the LB technique, and the film including guest molecule as the host-guest complex of the cyclodextrin moiety have been prepared. Attempts to prepare new type functional film by incorporating functional molecule into this film are in progress.

## References

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