셀룰로오스 에스터의 LB막 제조 및 분석

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Preparation and Characterization of Cellulose Esters Langmuir-Blodgett(LB) Films

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요 약. 세룰로오스 에스터의 LB막을 제조하여 분석하였다. 탄화수소 사슬 길이에 대한 압력-면적 곡선의 변화를 알아보았으며, 압력-면적 곡선의 온도에 대한 의존성으로부터 상전이 과정을 설명하였다. 수평증착법으로 X-type의 다층막을 만들 수 있었으며 접축각, 두께 및 XPS를 측정하였다.

ABSTRACT. The reparation and characterization of cellulose esters LB films with various alkyl chain lengths were studied. Monolayers of cellulose triesters with medium chain length such as trioctanoate(C-8), tridecanoate(C-10), and tridodecanoate(C-12), exhibited a characteristic phase transition from expanded to condensed states. The mechanism of phase transition was discussed on the basis of the temperature dependence of the surface pressure-area(π-A) isotherms. By the horizontal dipping method, X-type multilayers of cellulose esters were prepared and characterized using the contact angle and XPS spectra.

INTRODUCTION

Recently much attenton has been paid to the preformed polymer monolayer and multilayer Langmuir-Blodgett(LB) films for practical application[1~5].

Monolayer and multilayers properties of cellulose alkylesters and comb-like polymer, amine-modified poly(octadecene maleic anhydride) were reported[6].

The pressure-area isotherms of cellulose derivatives have been studied by many investigators[7~11]. However the cellulose ester monolayers with medium alkyl side chains were rarely studied, and very little report has been found on the multilayers of cellulose esters[12].

In this paper, we report the phase transition behavior of cellulose ester monolayers and also the prepatation and characterization of multilayers.

EXPERIMENTALS

The commercial cellulose triacetate with acetyl content of 44.8% (Eastman Kodak Co.) was used. And other cellulose alkyl esters were synthesized by Schotten-Baumann condensation of cellulose[12]. These cellulose esters were purified by repeated precipitations from chloroform solutions into a large excess of ethanol, followed by Soxhlet extraction of impurities with ethanol for 60 h. The degree of substitution was determined by the saponification-titration method described by Malm *et al.*[12]

The monolayers were prepared by spreading the dilute chloroform solutions (0.15 mmol/glucose residue) on the surface of water. Pressure-area (π-A) isotherms were measured by a modified film balance of the Wilhelmy type together with Lauda film balance.

Multilayers of cellulose esters were prepared by horizontal dipping method. The transfer ratios of the monolayers in the horizontal dipping method were determined by the decrease in the area of spread monolayers when a substrate (solid plate) just fitted to the inner side of Teflon barrier was lifted from the surface with the deposited monolayers. The X-ray photoelectron spectrum was measured by an electron spectroscopy for chemical analysis spectrometer(JESCA, JEOL) with magnesium X-ray at 8 kV and 50 mA. The contact angles of water droplets resting on the surface of the multilayers were measured by a Contactangleme-ter (Kyowa Kaimenkagaku Co., model CA-1). The thickness of the built-up film was calculated using the refractive index of cellulose esters layer ($N_f=$ 1.46) and that of substrate ($N_s=3.512$) as measaured from a blank sample by ellipsometry. Ellipsometric measurements were made with Rudorf EL ellipsometer.

RESULTS AND DISCUSSION

Fig. 1 shows the surface pressure-area isotherms of cellulose triesters with various alkyl chains, cellulose triacetate (C-1), a; cellulose tributylate (C-4), b; cellulose trioctanoate (C-8), c; cellulose
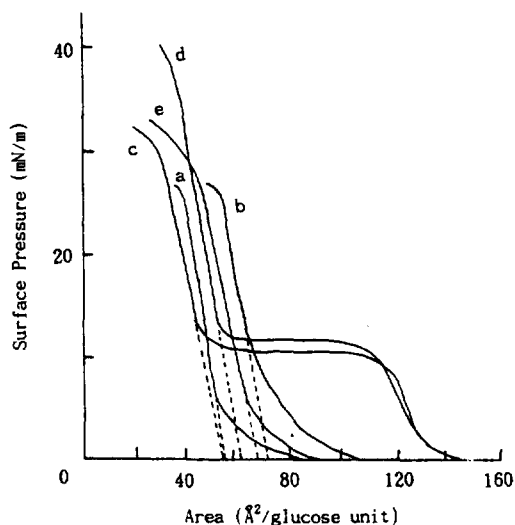

Fig. 1. Surface Pressure-area isotherms of cellulose ester monolayers: curve (a) C-1; curve (b) tributylate; curve (c) C-8, C-10; curve (d) C-12; curve (e) C-16.

tridecanoate (C-10), c; cellulose tridodecanoate (C-12), d and cellulose trihexadecanoate (C-16), e. The medium chain length such as trioctanoate, tridecanoate and tridodecanoate exhibit a characteristic phase transition from expanded to condensed films. Cellulose triesters with shorter chains such as triacetaete and tributylate and longer chains such as trihexadecanoate form solid condensed monolayers without such a transition. The limiting area of C-10 (55 Å^2 per glucosc unit) were similar with the results of Takeyuki *et al.*[13] and larger than the values (40~48 Å^2) reported by earlier investigators[7-11]. This discrepancy may be attributed to the incomplete spreading of the monolayers on the water surface in their experiments, as Adam had mentioned in his paper[8]. Takeyuki *et al.*[13] studied in the case of cellulose triesters with medium chain length, the films in the expanded region (100~140 Å^2 per glucose unit) were really fluid, while viscoelastic behaviours. We have observed similar results, the behaviours in the plateau region (60~110 Å^2). and the film then became rigid in the condensed region (below 60 Å^2) with low compressibility.

In the liquid expanded region, the long alkyl side chains are in a random liquid-like conformation and have a plasticizing effect on the cohesion of cellulose main chains. In the plateau region, it is probable that the expanded and condensed monolayers are in a thermodynamic equilibrium where gradual organization of the methylene chains to fully extended form perpendicular to the water surface may occur. The rigidity of the monolayer in the condensed state can be ascribed to the close packing of the hydrocarbon side chains together with the cellulose main chains.

The pressure-area isotherms of di-substituted cellulose dodecanoate exhibits a higher compressibility and smaller areas in both the exanded and the condensed states and also a higher transition pressure than that of tridodecanoate. These can be attributed to the lack of close packing of the side chains, because the size of a glucose ring plane is larger than the cross-sectional area of two hydrocarbon chains.

In the case of cellulose trihexadecanoate and

cellulose triacetate as well as tributyrate, the expanded region disappears, probable because of the stronger cohesive interaction of longer side chains in the former and of main chains without long substituents in the latter.

The limiting molecular areas $(A_{\pi \to 0})$ for the condensed region of these monolayers (except for C-4) fall into the range $54 \sim 66 \, \text{Å}^2$ per glucose unit, which corresponds to three times the cross-sectional area of a vertical hydrocarbon chain and also to the area of a tri-substituted glucose ring plane.

In order to investigate the mechanism of the phase transition observed for the monolayers of cellulose esters with medium side chains, we have measured the temperature dependence of the pressure-area isotherms for cellulose tridodecanoate, as shown in Fig. 2.

It appears to be unusual that the transition pressure decreases with increasing temperature. The change of enthalpy (ΔH) between the expanded and condensed states can be calculated by applying the Clausius-Clapeyron equation to the two-dimensional monolayer equilibria[14~16]:
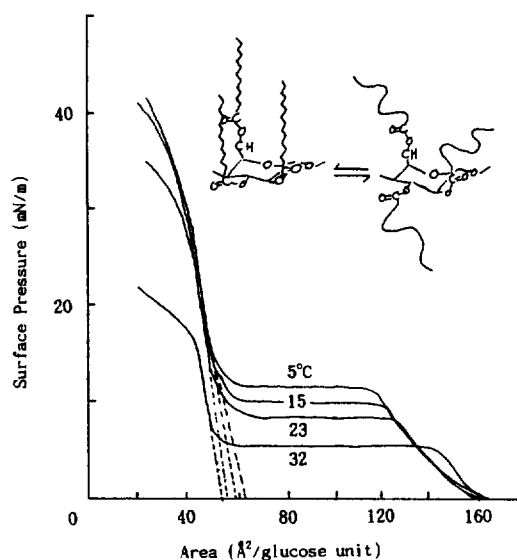
$$d\pi_t/dT = \Delta H/T\Delta A \qquad (1)$$

where π_t is the surface ressure at the plateau region and ΔA is the difference between the areas of these two states. The value of $d\pi_t/dT$ can be determined by the slope of the transition pressure-temperature correlations as shown in Fig. 3, where the values of ΔA are also shown. The enthalpy change of the transition from the expanded to the condensed states was thus calculated to be $+19.0 \, \text{kJ}/(\text{mol glucose unit})$ according to the method described by Alexander and Glazer[17], the change of internal energy (ΔE) was determined to be $+25.3 \, \text{kJ}/(\text{mol glucose unit})$ by extrapolating ΔH to $\pi_t = 0$ in the equation

$$\Delta E = \Delta H - \pi_t \Delta A \qquad (2)$$

as shown in the inset in Fig. 3. A plausible explanation for the unusual positive values of ΔH and ΔE is that the energy for breaking the hydrogen bonds between water molecules and cellulose ester groups overcomes the cohesional energy between alkyl side chains of medium length through the conformational change on compression in the transition region. Fig. 4 shows the temperature dependence of π-A isotherms of cellobiose hexado-
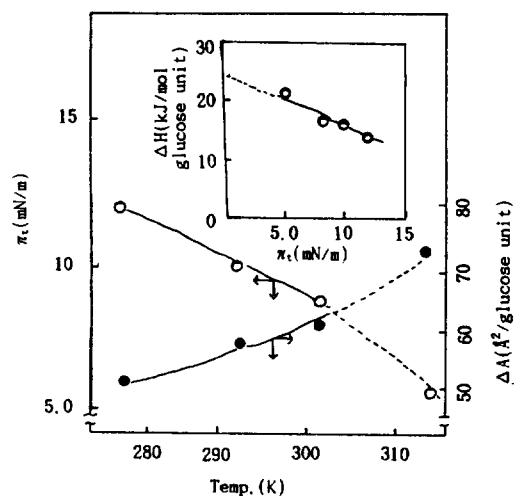

Fig. 2. Temperature dependence of the pressure-area isotherms of the cellulose tridodecanoate monolayer.

Fig. 3. Temperature dependence of π_t and ΔA of the cellulose tridodecanoate monolayer. The inset shows the dependence of ΔH on the transition pressure (π_t, transition pressure; ΔA, the area of the transition state from expanded to condensed regions of the cellulose tridodecanoate monolayer).
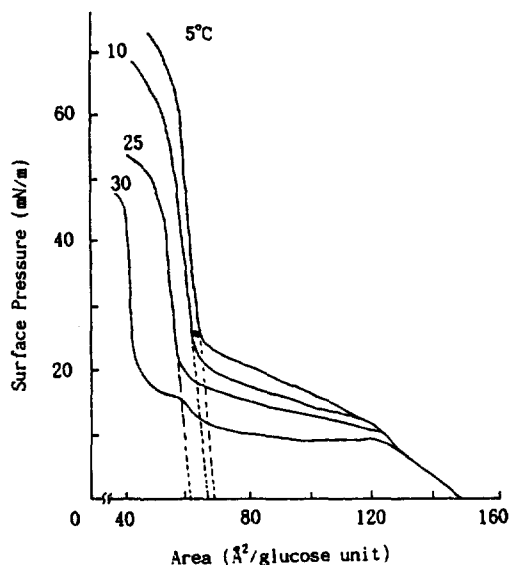
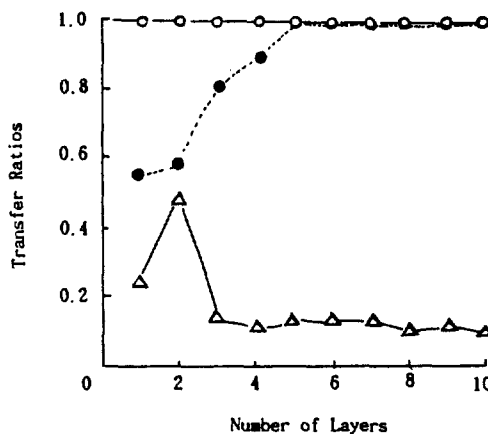Fig. 4. Temperature dependence of the pressure-area isotherms of cellobiose hexadodecanoate mono-layer.

Fig. 5. Transfer ratios of cellulose tridodecanoate monolayers (○, ●, horizontal dipping method at 21 mN/m and 7 mN/m respectively; △, vertical dipping method at 21 mN/m).
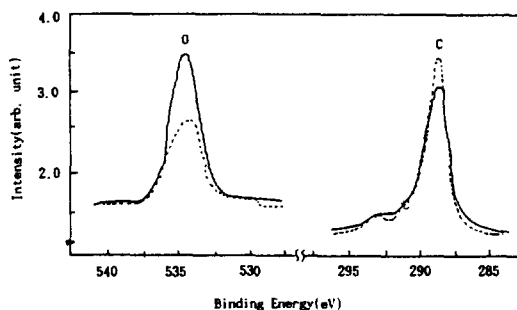

Fig. 6. X-ray photoelectron spectra of the multilayers and the cast film of cellulose tridodecanoate (——, multilayers deposited at 20 mN/m; ----, cast film).

decanoate as a model compound: these are similar on the whole to those of cellulose tridodecanoate, although each isotherm was slightly different. These results suggest that the phase-transition behaviour of cellulose ester monolayers is control-led mainly by the side chain interaction rather than by the polymer main chain interactions.

Both the LB method (vertical dipping method and horizontal dipping method) were examined for use with the C-12 monolayer. Fig. 5 shows the transfer ratios on a glass plate precoated with a stearate monolayer. Withe the vertical LB method, one monolayer could be imperfectly transfered onto a plate through the first uptrip (deposition ratio, 0.47), but successive deposition were diffi-cult. In contrast, with the horizontal dipping me-thod, 10~60 layers can be deposited successively on the plate even at a low surface pressure of 5.0 mN/m (expanded region) as well as at 20 mN/m (condensed region). The deposition ratios of the condensed monolayer were nearly 1.0, indi-cating almost perfect depositions, while those of the expanded monolayer ranged from 0.5 for the initial few layers to 1.0 for the succeeding layers.

The surface of the deposited multilayers were

wettable just after each horizontal deposition, sug-gesting the formation of X-type multilayers. The optically measured thickness of the multilayer was found to be about 23~24 Å per single layer of the condensed film. This gives additional support to the suggested molecular orientation and packing as described above. With cellulose trihexadeca-noate, however, building-up of the multilayer was difficult because the monolayer was too brittle to be transfered onto a solid substrate.

In order to evaluate the surface constitution of the C-12 multilayer prepared by the horizontal dipping method, contact angles θ with water and X-ray photoelectron spectra(XPS) were measured. The surface of the multilayer from the condensed
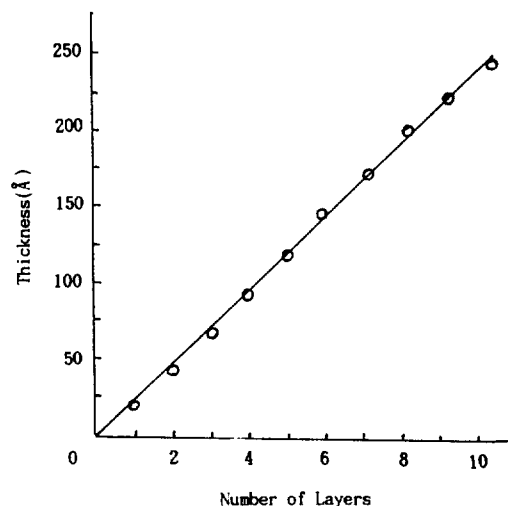
Fig. 7. Thickness versus number of layers of cellulose tridodecanoate multilayers.

monolayer ($\theta = 67 \sim 73°$) was more hydrophilic than that from the expanded monolayer ($\theta = 83 \sim 92°$). the latter value being similar to that of the cast film. This fact supports the proposed nearly perfect X-type deposition of the monolayer in the condensed region. Fig. 6 shows the results of the X-ray photoelectron spectroscopy analysis for the two types of built-up films from the condensed monolayers, together with the cast film. The atomic ratios of oxygen to carbon were found to be 0.35 and 0.23 for each films respectively. Since the O : C ratio calculated for the cellulose tridodeconate molecule as a whole is 0.19, the observed values imply that the multilayer deposited at 20 mN/m (condensed region) has a higher concentration of the hydrophilic glucose rings with ester groups at the outermost surface. These results are consistent with those of the contact angle measurements. Fig. 7 shows the thickness versus number of layers of cellulose tridfodecanoate. We observed linear relation and about $23 \sim 24$ Å per one layer.

CONCLUSION

Langmuir-Blodgett(LB) monolayers and multi-

layers of cellulose triesters were prepared and characterized. Monolayers of cellulose triesters with medium chain length exhibithed a characteristic phase transition from expanded to condensed states. The mechanism of the phase transition is discussed of the basis of the temperature dependence of the surface pressure-area isotherms.

Well-oriented multilayers were obtained from monolayers of cellulose triesters with moderately long side chains by applying the horizontal dipping method and characterized. Transfer ratios, contact angles, θ with water and X-ray photoelectron spectra were measured.

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