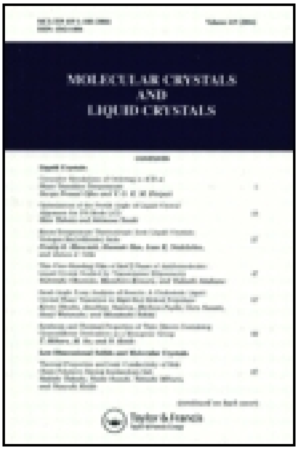

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Comparison of Monolayer Behaviors between ω - Tricosenyl Alcohol and ω - Tricosenoic Acid

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Comparison of Monolayer Behaviors between *ω* - Tricosenyl Alcohol and *ω* - Tricosenoic Acid

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The effect of subphase pH on the surface pressure-area isotherms and the variation of transfer ratio according to the stroke number were investigated for the monolayers of ω -tricosenyl alcohol and ω - tricosenoic acid. The monolayer of ω -tricosenyl alcohol showed more stable spreading behaviors and more efficient deposition than that of ω - tricosenoic acid.

Keywords: π -A isotherm; deposition efficiency; ω -tricosenyl alcohol

INTRODUCTION

As the fabrication method of ordered ultrathin organic films, the

Langmuir-Blodgett(LB) technique has been utilized due to the various advantages such as highly ordered packing and controllable and homogeneous thinness of a few nanometers[1]. These advantages may lead to the application of LB films in such areas as microelectronics sensor technology and photoresist[2].

In this study, ω -tricosenyl alcohol(ω -OH) was selected due to the potential photoresist application of polymerized LB film and ω - tricosenoic acid(ω -COOH) was also studied for the comparison with ω -OH. But because of the ionization of carboxylic acid, ω -COOH which has been extensively studied on the photopolymerization of LB film needs to add an acid or a counterion in subphase for stabilizing the monolayer at air-water interface[3]. If the counterion is utilized, the application for photoresist will be difficult due to the decrease of the solubility difference between the monomer and the polymer.

EXPERIMENTAL

ω -OH was synthesized by the reduction of ω -COOH(E.P. grade, Tokyo Chemical Industry) with lithium aluminium hydride in dry ether at 50℃ for three hours and then the addition of 10% sulfuric acid solution into the reaction flask.

The measurement of surface pressure(π)-area(A) isotherm and the deposition of LB films were carried out using a home-built Langmuir trough in an environmentally controlled dust-free room with a temperature of 23℃. The deionized ultrapure water(resistivity, 18.2 MΩ /cm; pH5.4, Milli-Q system, Millipore Ltd.) was used as a subphase. The pH of subphase was adjusted by addition of either 0.1N HCl, 0.1N

$KHCO_3$, and NaOH solution. As the subtrate materials, KRS-5(TiBr/TiI) and silicon wafer were used. For hydrophobic substrates in all experiments, KRS-5 plate was rinsed in an ultrasonic bath in toluene and then dried in an oven. Silicon wafer was immersed in 3% solution of dichlorodimethylsilane in chloroform for about 20 minutes and rinsed with chloroform and then dried in oven. ω -OH and ω -COOH solution(0.5 mM) dissolved in benzene were spread on the subphase using a 100 μl microsyringe, respectively. After the solvent evaporation period of ca. 10 minutes, the monolayer was compressed at a rate of 1.3 $Å^2$/molecule·min for the measurement of π -A curves. 20 minutes after reaching the desired surface pressure(33mN/m) were allowed for the equilibration. Hydrophobic substrate was dipped through the surface of monolayer-covered subphase 40 times with the deposition speed of 1 mm/sec(KRS-5) or 5 mm/min(silicon wafer). A delay time of 5 minutes was allowed after every upstroke in order to avoid film peeling off during the subsequent downstroke.

RESULTS AND DISCUSSION

In order to compare the influence of hydrophilic groups on the behaviors of monolayers, π -A isotherms for ω -COOH and ω -OH monolayers were measured as a function of subphase pH at 23℃ and the results are shown in Figure 1. A comparison of the results of Figure 1-(a) with those of Figure 1-(b) reveals that the monolayer of ω -COOH is more sensitive to the subphase pH than that of ω -OH. A plausible explanation on these results is that the repulsive force in ω -COOH is large in a basic subphase due to the ionization of carboxylic acid group.

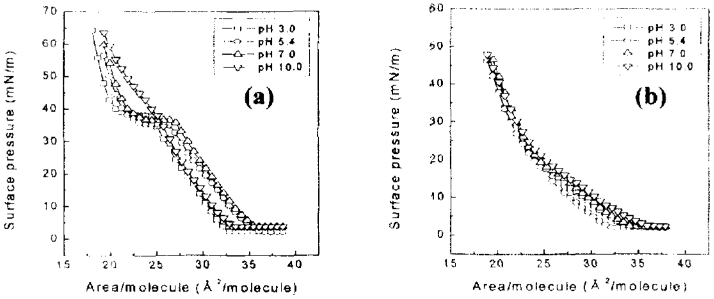

FIGURE 1. π -A isotherms of (a) ω -tricosenoic acid and (b) ω -tricosenyl alcohol monolayer at 23℃.

However, the monolayer of ω -OH exhibits very similar isotherms at a wide range of pH values. The limiting surface area of ω -COOH monolayers changed greately from 23 Å^{2}/molecule(pH 3.0) to 29.5 Å^{2}/molecule(pH 10.0). However, that of ω -OH monolayers changed slightly from 25.5 Å^{2}/molecule(pH 3.0) to 27 Å^{2}/molecule(pH 10.0). The deposition efficiency expressed as the transfer ratio for ω -OH and ω -COOH monolayers was examined. The transfer ratio is defined as the ratio of monolayer area lost to the area swept by KRS-5 substrate. The minus(-) symbol in the transfer ratio represents downstroke. As shown in Figure 2, the transfer of ω -OH monolayer to KRS-5 substrate was more consistent than that of ω -COOH. In the case of ω -COOH, the average transfer ratio was 0.81 on up-stroke and 0.62 on down-stroke. In the case of ω -OH, however, the average transfer ratio was 0.95 on up-stroke

0.83 on down-stroke. These results indicate that the deposition efficiency of ω -OH is higher than that of ω -COOH and the ω -COOH monolayer transferred on up-strokes is returned more to the subphase on subsequent down-strokes than the ω -OH monolayer, resulting in little net deposition. These results may be associated with the monolayer viscosity and the interaction difference between the monolayer on the subphase and the solid layer on the substrate.

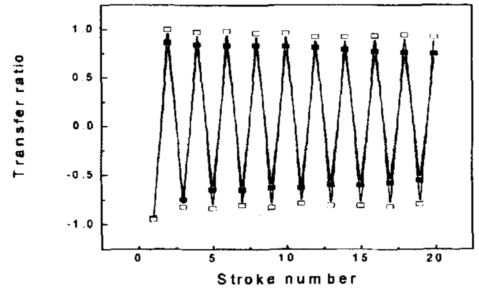

FIGURE 2. Transfer ratio variation of ω -tricosenyl alcohol (-□ -) and ω -tricosenoic acid monolayers (-■ -).

Acknowledgements

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