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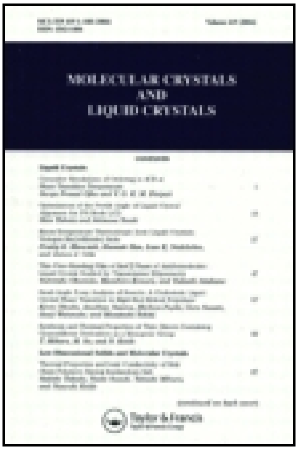

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THE MONO- AND MULTI-LAYER BEHAVIORS OF 2,4-HDDA DOPED WITH STEARIC ACID INCLUDING IN SITU POLYMERIZATION

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Abstract The properties of the mono- and multi-layer of 2,4-HDDA doped with stearic acid including *in-situ* UV-polymerization were investigated by studying surface pressures(*i.e.*, film miscibility in mixed monolayers) and its transferability onto the substrate(*i.e.*, interactions and film depositions in mixed monolayers). The collapse pressure of monolayers increased in proportion to the amount of SA. For the polymerized monolayer, the isotherms showed only a single inflection point of the surface pressure. For the undoped case it was hard to prepare multilayer, but the transferability was much enhanced by doping SA.

INTRODUCTION

As the properties of any polymeric materials may depend on the structure and internal organization of repeating units, the method to produce highly ordered and oriented polymers of any required structures have been interested in. For many polymers, if they form an insoluble monolayer, it is possible to prepare oriented polymer films on a solid surface by LB technique under pertinent experimental conditions. However, for many insoluble monolayers, it has been shown to be poorly transferred on the solid surface and even in the transferred polymer it is readily peeled off during the successive dipping processes.[1]

Therefore for overcoming such problems, namely to enhance the transferability of the resulting polymer film as well as unpolymerized molecules onto the solid surface, we investigated the monolayer behaviors and transferability of the LB films of 2,4-HDDA doped with stearic acid(SA) including *in-situ* UV-polymerization at the air/water interface. The former major component is a polymerizable amphiphile with a conjugated diene unit to the carboxyl group and a second material is added to help transferring the film onto the solid surface.

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EXPERIMENTAL

Materials

2,4-HDDA was synthesized and purified by the procedure described in a previous paper and identified by the various chemical methods.[2] SA(99%), supplied by the Aldrich Chemical Company, Inc., was used as purchased. Chloroform used as the spreading solvent was of a chromatography grade supplied by J.T.Baker Inc., USA. The solution consists of 2,4-HDDA doped with a fixed molar ratio of SA (*i.e.*, the molar ratio of 2,4-HDDA/SA in the solution was 1/0, 7/3,5/5 and 3/7) was spread on to the distilled and deionized water. Multilayer films were prepared on the surface of various substrate.

Mono- and multi-layers Preparation

The preparation and measurement of the monolayers on the water subphase were carried out on a constant perimeter barrier type LB trough in a dark clean room at room temperature. The water subphase(resistivity: 18.2 Mohms/cm) was purified with a Milli-Q purification system(Millipore Corp.) and a HCl solution was added to adjust the subphase pH. The chloroform solution of monomer with a fixed composition was spread onto the subphase, and after evaporating the solvent, the compression started. After compressed to the desired surface pressure for polymerization(*i.e.*, 10mN/m), the monolayer was polymerized *in-situ* by UV-irradiation(λ_{max}=252.1 nm), maintaining the surface pressure constant by a feedback control system. After irradiating UV light for a few minutes, the film was reexpanded to a zero pressure and the monolayer behaviors of the resulting polymer film was investigated again. After it, the resulting polymer film was transferred onto the clean substrate at the constant surface pressure.

RESULT AND DISCUSSION

Mixed Monolayer of 2,4-HDDA and SA

The monolayer properties of 2,4-HDDA and SA have been reported previously.[2] In that report, the monolayer isotherms of 2,4-HDDA were reproducible below the collapse pressure of *ca.*20mN/m near the molecular area of 30 Å^2/molecule without any phase transitions between the expanded and condensed states[$C_S{}^{-1}{}_{(max)}$: *ca.* 60mN/m] which indicate the loose packing of molecules.[3] This may be attributed

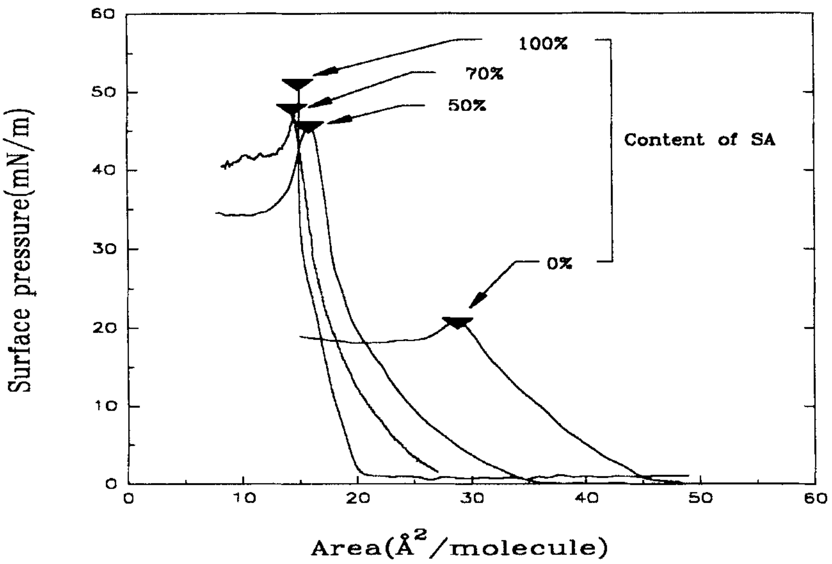

FIGURE 1. The Π-A isotherms of 2,4-HDDA, stearic acid(SA) and the mixed film before polymerization. Though 2,4-HDDA has a low collapse pressure and a high surface molar area at the expanded phase, the mixed film showed an intermediate collapse pressure between that of 2,4-HDDA and that of SA. The collapse pressure of the mixed film increased with the content of SA.

to the weaker cohesion between the hydrocarbon chains than between the corresponding saturated acid. As the content of SA increases, the collapse pressures increased in comparison with that of 2,4-HDDA[Figure 1].

Another serious question in this experiment is whether an intimately homogeneous monolayer is formed or not when doped molecules were spread. The collapse pressure often offers a useful information in determining miscibility.[4] If two components are immiscible and have different collapse pressures, it is possible to extract the information on the miscibility of the doped monolayer from the collapse pressures. The collapse pressures of 2,4-HDDA and SA are quite different from each other as shown in the Figure 1. All the doped monolayers showed only a single collapse pressures, which are different from those of either component. This indicates that the two materials are miscible.

In Figure 2, the molecular areas at certain surface pressure(*i.e.*, 15, 10 and 5 mN/m) were given as a function of doping molar ratios of SA. As shown in this figure, the average molecular areas at constant pressures were deviated from the linear combination of the two components. This nonadditivity of the average molecular areas

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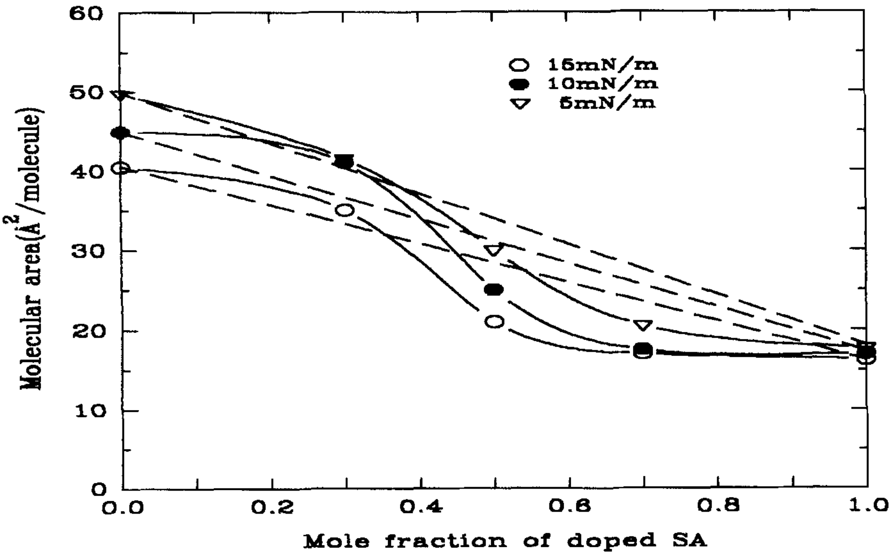

FIGURE 2. Plots of the molecular area of doped 2,4-HDDA film as a function of SA mole fraction at different applied surface pressures. Dot lines were drawn from the additive linear line : $A_{HS} = X_H A_H + X_S A_S$, where A denotes the average molecular area at the same pressure, X for the mole fraction of the component and subscript H and S indicates 2,4-HDDA and SA, respectively.

indicates that this systems are not ideally miscible. For the pure film, it forms only an expanded state owing to the conjugated double bond connected to hydrophilic acid group.[2] So the small dope of SA may not be enough to orient the hydrocarbon chains, which partly lie flat in contact with water, vertically. However, as the amount of SA increases, the positive deviations turned to the negative deviations. This may be resulted from the development of cohesive forces between the hydrocarbon chains owing to those of SA. Therefore, it is believed that the doping of SA consequently facilitates the monolayer deposition on the substrate by polarizing the hydrophobic/hydrophilic balance between molecules.

In-situ polymerization

The photoreaction of butadiene groups may depend on the arrangement of molecules, but not strictly restricted by the topochemical control as the diacetylene groups polymerized exclusively under topochemical control. Therefore, the degree of polymerization may be affected by the content of SA as well as the surface pressure of polymerization.

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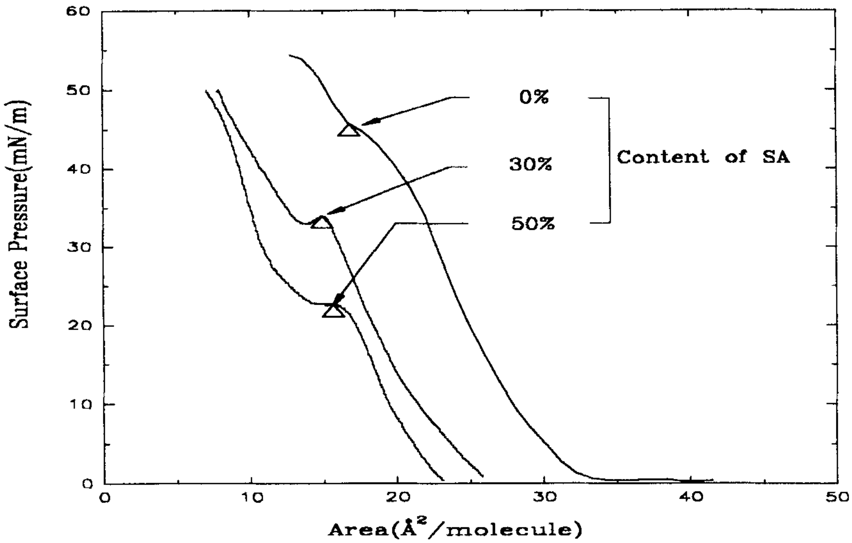

FIGURE 3 The Π-A isotherms of 2,4-HDDA, stearic acid(SA) and the mixed film after polymerization at a surface pressure of 10mN/m. The collapse pressures of the resulting polymer films were not shown, but only the first inflection points of surface pressures in all case.

In a previous study,[2] the highest degree of polymerization of 2,4-HDDA was observed at a surface pressure of 10mN/m. So at the surface pressure we polymerized the doped monolayers with various mole fractions of SA[Figure 3]. The collapse pressures of resulting polymer films were not shown, but only the first inflection points of surface pressure were given in all case. As the molar ratio of SA increases, the first inflection pressure was significant and its degree of decrease was gradually grown. This fact indicates that SA acts as inhibitor for the polymerization reaction and reduces the polymer stability. Therefore, we can anticipate that the dope of SA into the 2,4-HDDA may enhance the transferability of the resulting polymer film onto the substrate by reducing the film rigidity as well as by polarizing the hydrophobic/hydrophilic balance.

Multilayer Transfer

Polymerized monolayer films were transferred on the surface of various substrate by normal deposition technique maintaining the surface pressure constant by a servo-feedback control system. In general the type of the multilayers can be easily identified from the monolayer transferred during the descending and raising of the solid substrate.

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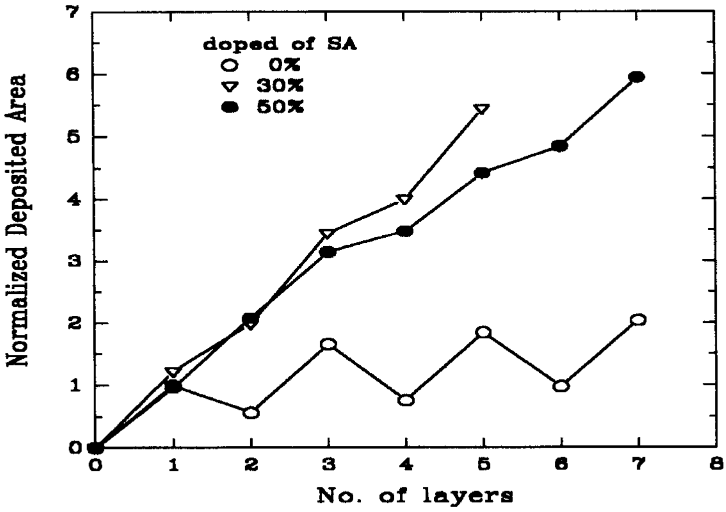

FIGURE 4 Plots of normalized deposited area during the deposition process as a function of number of layers. Used substrates were a Cr-coated Si-wafers.

The deposition of a monolayer onto the substrate forces the surface pressure to be lowered and the surface pressure can be kept constant by adjusting the surface area. At this case the variations of area can be measured and consequently the normalized deposition area(N_a) can be easily calculated for both downward and upward passage.

$$\text{Normalized deposition} = \frac{\text{area change in the monolayer}}{\text{total area of substrate to be coated}} \qquad (2)$$

In the case of unpolymerized monolayers, it is hard to deposit the film from an undoped monolayer. This is because 2,4-HDDA molecules with conjugated double bond which forms only expanded state, may lie flat on the subphase. Therefore, even in the case of deposited, the multilayer is readily peeled off during the another sequential dipping procedure[Figure 4].

Here we could deposit monolayer doped with 0.5 mole fraction of SA successfully. But the quality of film was not good enough, further studies on the deposition is in progress. As shown in Figure 4, the transferability of film was much enhanced by doping SA. Apparently the first multilayers forms Y-type film, but the type of the film shifted to X-type as the dipping proceeded. These phenomena coincide with the report that the character of the film gradually turns to a X-type for fatty acid monolayers.[6] In the case of polymerized films, the undoped polymer films are hard to be deposited on the substrate, but it is not the case for the doped films. The film quality of doped multilayer was better than that of undoped multilayer. It is believed that the polymerized films suffer from film rigidity more than the unpolymerized films do. Often an excessive film rigidity limits the transport and other active processes to some degrees.[7] In summary the deposit of film onto the substrate could be modulated somewhat by doping a second material of similar structure.

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