

NOTES

Polymerization of Triazine Dithiols at the Air and Water Interface

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Reactions conducted in monolayer assemblies have strong potential to enhance the reactivity of molecules since the probability of effective collision of molecules increases markedly. This is because the direction of collision of molecules is two-dimensionally limited. The two dimensional collision of molecules on water would lead to more selective collision of functional groups in molecules than three dimensional collision. It is widely known that reactions in packed and ordered assemblies¹⁻³ and micells^{4,5} generally show high reactivity and give high conversion rates. These merits derived from the two-dimensional optimum packing density of molecules as well as high degree of orientation and regular arrangement.

However, J. Ahmad and K. B. Astin recently reported that expanded films on water show considerably higher reaction rates for dehydration than compressed ones.⁶ This suggests that the reactivity of molecules is more dependant upon facile access of functional groups than the packing density of molecules.

In this paper, it is reported that a very loosely packed monolayer of triazine dithiols on water undergoes oxidative polymerization at remarkably higher rates than close packed or ordered LB films.

EXPERIMENTAL

Monomers (triazine dithiols) used in this work, 6-stearylamino-1,3,5-triazine-2,4-dithiol (ST) and 6-(*cis*-9-octadecenyl)amino-1,3,5-triazine-2,4-dithiol (OL), 6-laurylamino-1,3,5-triazine-2,4-dithiol (L), 6-dilaurylamino-1,3,5-triazine-2,4-dithiol (DL), 6-dioctylamino-1,3,5-triazine-2,4-dithiol (DO) were prepared according to our previously reported method.^{7,8}

The monolayers of triazine dithiols were spread from chloroform solutions (10^{-3} mole/cycle, 0.2 ml) onto distilled, deionized water at 10°C in the dark box to prevent oxidative photopolymerization. The monolayers were placed in an area of 100 cm² for 15 or 90 min at 10°C in a dark box under a pressure of 0.5 mN m⁻¹ (sensitivity, 0.025 mN m⁻¹). The monolayers were then compressed at a rate of 24 cm² min⁻¹. Measurements of surface pressure-area isotherms were carried out with an automatic Langmuir-trough (Kyowa Kaimen Kagaku HBM-AP using a Wilhelmy type film balance). After being compressed to a surface pressure of 20 mN m⁻¹, the condensed ST and OL monolayers were transferred onto quartz slides in alternating downward and upward strokes with a transfer ratio of 1.0 ± 0.1 up to 50 layers (thickness about 100 nm, Z-type LB

uniform). Before use, the quartz slides were cleaned in a boiling $\text{H}_2\text{SO}_4\text{-HNO}_3$ (2:1) solution and hydrophobic surfaces were prepared with dimethyldichlorosilane.⁹

The ST and OL LB films were irradiated with UV light (Wacom R & D Cord Xenon Light KXL-500F, Power 500W).^{10,11}

Electronic absorption spectra and gel permeation chromatography (GPC) patterns were measured with a Nippon Bunkyo-Ubest-30UV spectrometer and Shimadzu type SPD-6A with a Shodex GPC KF-802 column, respectively. Samples for GPC were collected as condensed multilayer films on quartz slides from the water surface and dissolved tetrahydrofuran (THF). THF for GPC measurements was purified using alumina column after distillation.

RESULTS AND DISCUSSION

Little is known about the Langmuir Blodgett films of triazine dithiols having long alkyl chains at the 6-position, despite the interesting

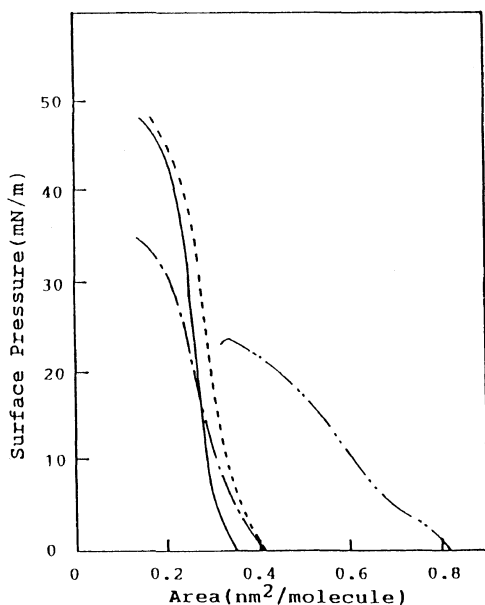


Figure 1. Surface pressure-area isotherms of ST, OL, and DL. —: ST left for 15 min. ----: ST left for 90 min. - · - ·: OL left for 15 min. ·····: DL left for 15 min.

properties displaced by triazine dithiol thin films such as photopolymerization, anticorrosion and lubricity. We investigated surface pressure (π)-area (A) isotherms for various triazine dithiols as shown in Figure 1. First, triazine dithiols with stearyl amino, *cis*-9-octadecenyl amino, dilauryl amino, lauryl amino, or dioctyl amino groups were spread from the chloroform solution onto pure water. The monolayers were compressed at a rate of $24\text{ cm}^2\text{ min}^{-1}$ after standing for 15 min in a dark box. Stable condensed solid monolayers were then prepared on water surfaces for ST and OL only. Namely, in the π - A curves, the surface pressure of ST started to increase at a surface area of $0.355\text{ nm}^2/\text{molecule}$ and increased rapidly at areas less than about $0.33\text{ nm}^2/\text{molecule}$. The collapse of ST solid monolayer in this case occurred at a surface pressure of about 48 mN m^{-1} . On the other hand, the surface pressure of OL first started to increase slowly at an area of $0.42\text{ nm}^2/\text{molecule}$ and increased rapidly at an area of about $0.36\text{ nm}^2/\text{molecule}$, and the condensed OL solid monolayer collapsed at a surface pressure of about 35 mN m^{-1} . This surface pressure is lower than that of ST. The limiting surface area per molecule was determined to be $0.33\text{ nm}^2/\text{molecule}$ for ST and $0.365\text{ nm}^2/\text{molecule}$ for OL, respectively, by extrapolating the steep rise in the π - A curves to zero surface pressure. The value for ST agrees with the molecule, occupied surface areas calculated to be $0.334\text{ cm}^2/\text{molecule}$, using CPK models where triazine rings with thion type are perpendicular to the water surface and is less than that for OL.

Other triazine thiols such as DL, L, and DO did not form condensed solid monolayers on the water surface. Their surface pressure increased slowly from a considerably larger surface area (most near $0.80\text{ nm}^2/\text{molecule}$) than the occupied surface area calculated from CPK models and the prepared liquid monolayers collapsed at a lower surface pressure.

As shown in Figure 1, however, it was found that the π - A curve changed when the mono-

layer was compressed after remaining on the water surface for a long duration in a dark atmosphere under a low surface pressure of 0.5 mN m^{-1} . Specifically, when the ST monolayer on water was compressed after remaining for 90 min, the surface pressure first started to increase slowly an area of $0.43 \text{ nm}^2/\text{molecules}$, similar to the case of OL, and increased rapidly at areas less than about $0.365 \text{ nm}^2/\text{molecule}$. The curve shifted to higher surface areas than that of the ST gas monolayer left for 15 min. The slight change of the curve is not due to the sensitivity of the trough used. We found that the shift of the curve is due to changes in the chemical structure of the ST solid monolayer. This limiting surface area per molecule in the case was about $0.365 \text{ nm}^2/\text{molecule}$, which is near the occupied surface area ($0.370 \text{ nm}^2/\text{molecule}$) calculated using CPK models wherein the triazine ring is of the thiol type. This suggests that the thion type changes to the thiol type by keeping the monolayer at low surface pressure for a long time at the air/water interface. To gather information on the chemical structures of the monolayers, the ST solid monolayers and OL

solid monolayer on water were transferred onto quartz slides at 20 mN m^{-1} , as Z-type LB multilayers, and their UV spectra were measured.¹¹ The UV spectra of the three LB films did not change after standing for 24 h, either as LB films on quartz in a desiccator where ordinary visible light shined or as condensed solid monolayers on water in air in the dark box. As seen in Figure 2, however, clear differences in UV spectra are apparent depending on the time of standing in the gaseous state at a low surface pressure. The spectrum of ST LB film prepared after leaving for 15 min in the gaseous state indicated that the film consisted mainly of the ST monomer. The peaks at 229 and 320 nm are assigned by the presence of $\text{C}=\text{N}$ bonds and $\text{S}=\text{C}-\text{N}<$ groups.¹¹ This means that the ST LB film is mainly composed of a thion type of triazine dithiol, corresponding to the chemical structure before the spreading. By keeping the ST gas monolayer on water for 90 min in dark box, the peak at 320 nm decreased markedly and a new peak appeared at 235 nm. Changes of the peaks show the presence of thiol type in the ST LB film. The stable thiol type in this case suggests the presence of a polymer of triazine dithiols.^{7,8,10,11} To confirm that the ST

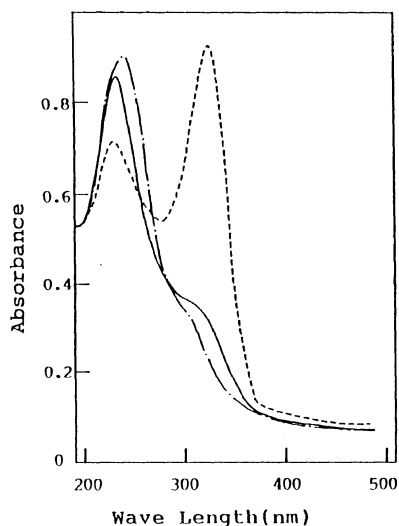


Figure 2. UV spectra of ST and OL LB films on quartz. -----: ST left for 15 min. - · - · - : ST left for 90 min. —: OL left for 15 min.

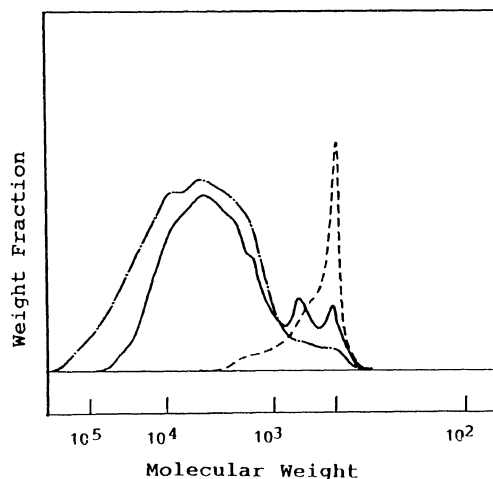


Figure 3. GPC patterns of ST and OL at the interface between air and water. -----: St left for 15 min. — · —: ST left for 90 min. —: OL left for 15 min.

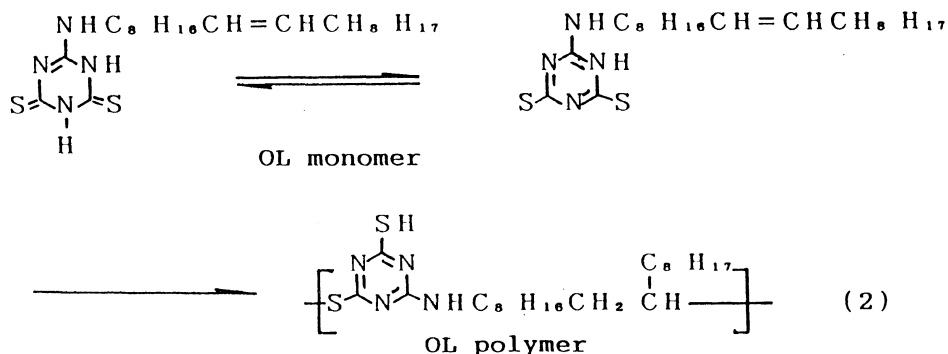
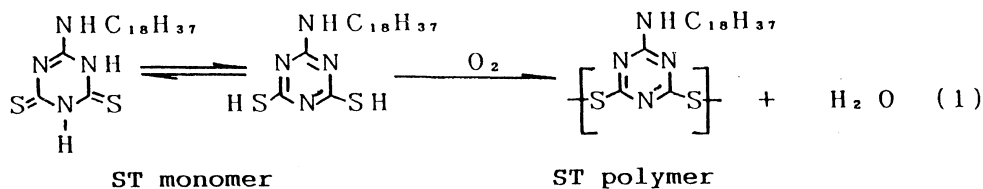
monomer LB film was converted to a ST polymer LB film, UV light was irradiated onto the ST monomer LB film for 60 min.¹¹ The UV spectrum of the UV-irradiated ST LB film agreed completely with that of the ST LB film left for 90 min, indicating that polymerization occurred while the ST monolayer was left on the water surface for a prolonged duration time in the dark box. In contrast, the OL LB film appeared to contain a polymer regardless of the short standing duration in the gaseous state because the deposited film had virtually no peak near 320 nm in UV spectrum but a clearly strong peak at 230 nm.

To confirm the polymerization of triazine dithiols in the gaseous state on water, GPC was measured for the ST and OL LB multilayers collected on quartz. As seen in Figure 3, the ST LB film left for 15 min clearly displayed the molecular weight of a ST monomer, with a slightly small amount of the polymer. However, the ST LB film left for 90 min was composed of a large amount of polymer with high molecular weight, and a small amount of telomer and ST. The OL LB film also consisted of a large amount polymer with high molecular weight, and a very small

amount of telomer and OL, regardless of the very short standing time. This demonstrates that OL has a higher rate of polymerization than ST in the gaseous stage. The above results indicate that the ST and OL monolayers on water are easily polymerized when left for a long duration time in the gaseous stage at the air/water interface.

To make polymer structure clear, NaSH treatment of ST and OL polymers was conducted, according to a previously reported procedure.¹¹ By their treatment, SS bonds in polymers are converted into SH groups. That is, the treatment makes clear whether polymers contain SS bonds. To find out the molecular weight of the obtained products, GPC was measured and the ST polymer was completely converted to the ST monomer. That is, the ST polymer was produced by the formation of SS bonds. However, the GPC pattern of OL polymer after treatment was the same as that in Figure 3. This shows that OL polymer does not contain SS bonds at all.

From the above results, the polymerization of ST and OL monomer at air/water interface may be explained as follows. Triazine dithiols are tautomers consisting of thion and thiol



types. The polymerization of ST is carried out between the thiol groups, forming a disulfide bond as shown in eq 1. On the other hand, the OL monomer has two functional groups of thiols and double bonds. Therefore, the OL polymer is formed by the addition of thiol groups to double bonds as shown in eq 2. The addition polymerization may occur stereospecifically and be considerably faster than oxidative polymerization. UV irradiation and heated air accelerate the addition and oxidative polymerization of triazine dithiols.^{7,8,10,11} However, visible light and air at ordinary temperatures barely induce polymerization. That is, under ordinary and mild reaction conditions, such as low temperature and a dark atmosphere, triazine dithiols were not polymerized at all. Furthermore, the polymerization of the condensed monolayer on water and highly ordered multilayer on quartz is also inhibited markedly in a dark atmosphere. Therefore, this is a special polymerization taking place in the expanded monolayer on the air/water interface. We propose that such polymerization is dependent upon the following two factors.

The difference in the reaction rate of condensed and expanded monolayers is due to differences in the concentrations of thiol-type triazine dithiols under both conditions. That is, the expanded monolayer has a higher concentration of the thiol type than a condensed monolayer because triazine dithiol molecules contact polar water and form hydrogen bonds with water, and the thion type has the small occupied surface area and is thus more stable in the compressed state. In addition, the expanded monolayer has more

molecules in the intermediate state between thiol and thion types than the condensed monolayer. The intermediate state was confirmed to be present in the cast films of triazine but absent in the ST LB film.¹¹ The intermediate state is more active than the thion type, but less active than the thiol type. On the other hand, two dimensional reactions such as packed and ordered assemblies and micells provide higher probability of collision of functional groups than three dimensional reactions as in solutions and gases. Namely, thiol groups in the intermolecular triazine dithiols can collide with great efficiency at the air/water interface. The expanded state of triazine dithiols on the water surface provides excellent access for thiol groups.

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