change of two components is also correlated because both processes, exciplex formation and dissociation, occur for anthracene/DMOT pair in the excited state. The detailed work on exciplex formation and dissociation processes for anthracene/DMOT which depend on solvent viscosity as well as temperature is in progress.

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A Two-Dimensional Network of a Melamine-Formaldehyde Monolayer

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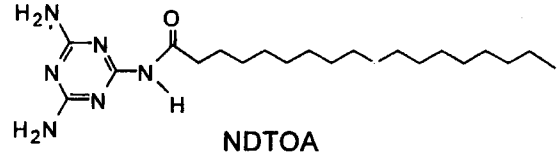
The network structure is important for molecularly-thin films such as the Langmuir-Blodgett (LB) film in order to improve the intrinsic fragility and to make their technological applications possible. In particular, for selective permeations of gases or biomolecules through the LB films which covered the pores of substrate membranes, the mechanical stability of the LB films should be importantly taken into account.[1] Crosslinking of the LB films is an alternative breakthrough for the stability improvement. For examples, crosslinked monolayers have been obtained by polycondensation of octadecylureas[2] and amino acid esters.[3] Bauer *et al.*[4] carried out crosslinking of hydroxy moieties with epichlorohydrin in a lipid monolayer. Jones *et al.*[5] have prepared monolayers from crosslinkable polymers with a vinyl side group and made network structure from the LB film by UV irradiation. Kunitake *et al.* have reported stabilization of monolayers and LB films by electrostatic interaction of ionic polymers with oppositely-charged amphiphiles[6] and by covalent crosslinking of ionically interacting polymers.[7] We have also used the technique of polyion complexation at the air-water interface in order to prepare stable LB films on porous substrates.[8] However, two-dimensionally crosslinked monolayer films of thermosetting resins have not been reported as yet.

We report a monolayer network of a melamine resin produced by the LB method. As the spreading molecule, N-(4, 6-diamino-1,3,5-triazin-2-yl) octadecanamide (NDTOA) was synthesized from the condensation reaction of melamine and



NDTOA

stearic acid. The chemical structure of NDTOA was confirmed by IR, ^{1}H NMR, and elemental analysis. The chloroform solution (1 mM) of NDTOA was spread to monolayer on water subphase. The surface pressure-area (π-A) isotherms (Figure 1) show the formation of stable monolayers, *i. e.*, the collape pressure of monolayer rised up to 60 mN/m. The monolayer shows condensed phase, which is attributed to the strong H-bonds of amino and amide groups of NDTOA. When the pH of water subphase was controlled to acidic (pH=2.2) or basic (pH=11.1) by adding 0.1 M aq. HCl or NaOH, the molecular area increased (Figure 1a). The charge repulsion between the molecules and the increase of hydration extent at the low or high pH are thought to be related to the area expansion. When NDTOA was spread on 1% aq. formaldehyde subphase, the π-A isotherm (Figure 1b) showed very expanded phase. This means that the N-hydroxymethylation of melamine amino groups occurs at the air-water interface, *i.e.*, two-dimensional reaction between formaldehyde and amino group of melamine moiety proceeds on the water surface. A spontaneous increase of surface pressure was also found from the NDTOA monolayer on the aq.

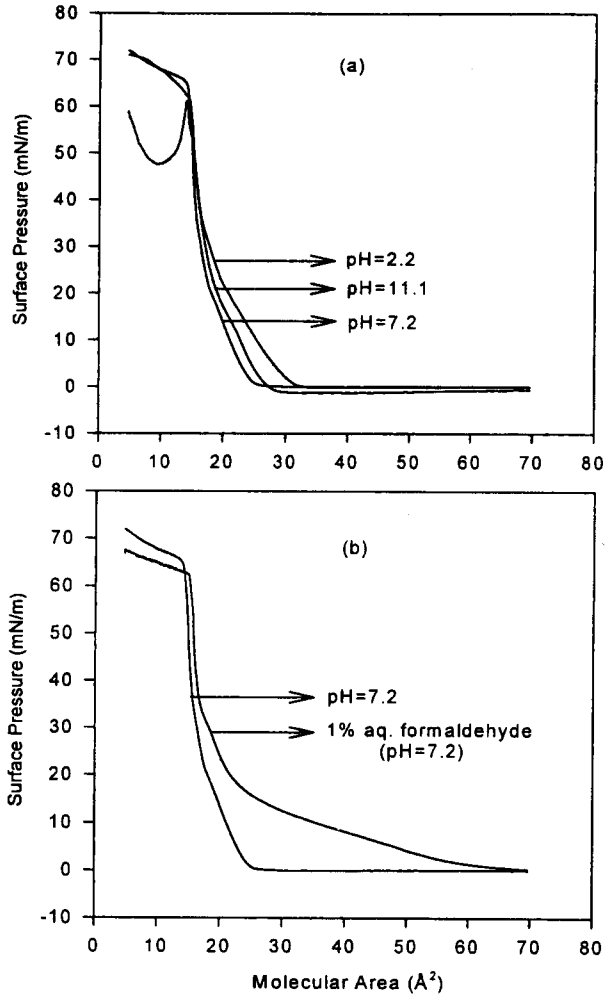


Figure 1. Surface pressure-area isotherms of NDTOA monolayers measured at a barrier speed of 50 mm/min: (a) on water subphases with different pHs and (b) on 1% aq. formaldehyde subphase. The 1 mM chloroform solution of NDTOA was spread on subphases.

formaldehyde subphase (Figure 2). The increase of surface pressure continued to 2 hr after the monolayer spreading and reached the plateau at surface pressure of *ca.* 8 mN/m. This phenomenum also supports the reaction at the air-water interface.

The monolayers at the air-water interface were transferred on solid substrates such as calcium fluoride plate (GL Sciences) and porous fluorocarbon membrane filter (FP-010). The Y type deposition was produced from the monolayer on aq. formaldehyde, while Z type was found from the one on pure water at a surface pressure of 30 mN/m and a lifter speed of 60 mm/min. The transfer ratio was over 0.7 at pH 7.2.

The structures of the LB films on calcium fluoride plates were estimated by means of FT-IR spectra. The FT-IR spectra of NDTOA LB films deposited from pure water and the aq. formaldehyde subphases showed almost the same peaks pattern besides increased O-H (3348 cm^{-1}) and C-O (1020 cm^{-1}) stretching peaks intensity in the LB films from the aq. formaldehyde subphase. The NDTOA LB film deposited from the aq. formaldehyde subphase was subjected to aq. acidic solution (pH=3) for 3 hr and followed by heat

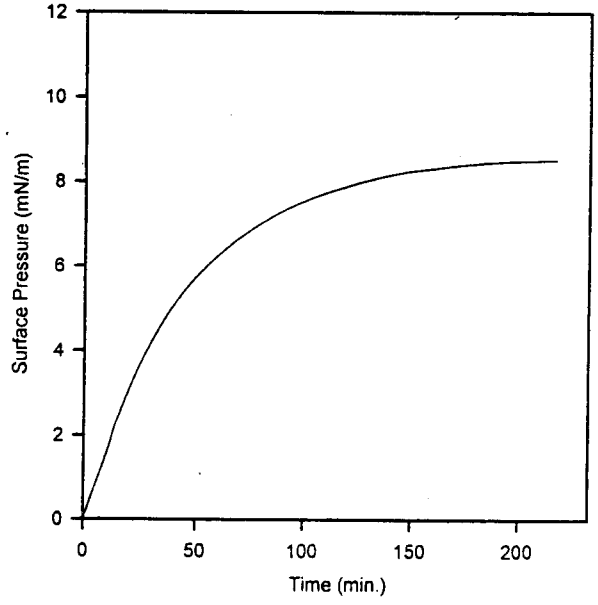


Figure 2. Spontaneous change of surface pressure of NDTOA monolayer on 1% aq. formaldehyde subphase during incubation at 25 °C.

treatment (200 °C) for 2 hr in a vacuum. The FT-IR spectrum of the resulting LB film showed the decrease of relative peaks intensity of aliphatic C-H (2918, 2850 cm^{-1})

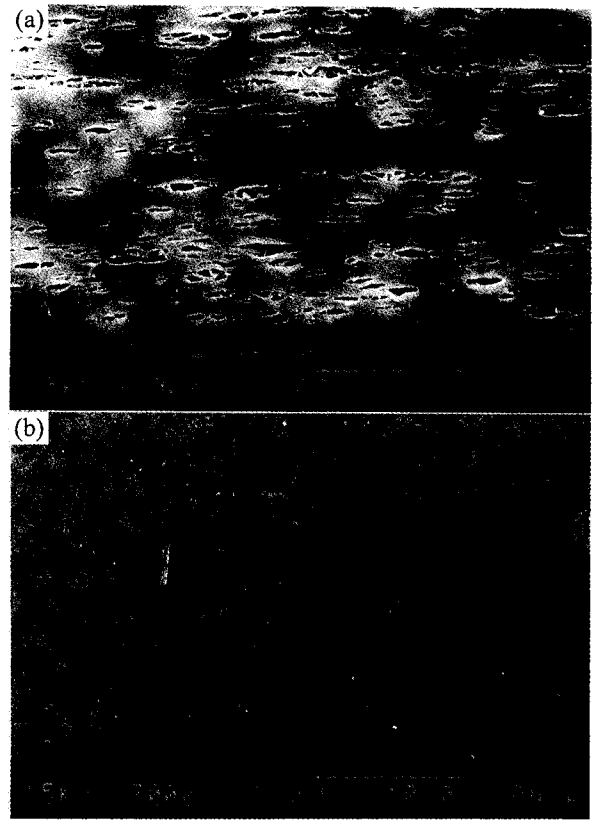


Figure 3. Scanning electron micrographs of NDTOA LB films deposited on fluorocarbon membrane filters: (a) the membrane filter only; (b) as-deposited film of 8 monolayers from 1% aq. formaldehyde subphase. The samples were sputtered with Au and observed at 15 kV.

and amide C=O (1701 cm^{-1}) stretching modes. From the results, some alkyl chains were thought to be removed during the acid or/and heat treatment. Meanwhile, the peaks intensity due to the stretching or bending modes of O-H (3348 cm^{-1}), C-O, and C-N (1000-1150 cm^{-1}, peaks overlapped) groups are increased. Therefore, it is supposed that the amino groups of the melamine ring were hydroxymethylated and their dehydrations resulted in crosslinking in part. However, the quantitative extent of the hydrxymethylation and the crosslinking was not clear at this point.

SEM micrographs of Figure 3 show the surface morphology of the porous fluorocarbon membranes. We can readily observe the original pores, which are seen as longish and somewhat dark appearance (Figure 3a), of the substrate membrane. When the monolayer of NDTOA was deposited on the substrate membrane from pure water subphase, the large defects with sizes of *ca.* 2 μm were seen as dark spots even in 12 layers. However, good covering of the pores was found in the 8 monolayers film which was transferred from acidic (pH=3) aq. formaldehyde subphase (Figure 3b). The covering capability is thought to be enhanced through the partially crosslinking between the melamine moieties at the air-water interface. The surface morphology observed through the SEM micrograph was not changed when the LB film was heat-treated as described above.

In conclusion, we demonstrated a molecularly-thin network film of a melamine-formaldehyde resin which is a well-known thermosetting resin. A modification of a porous solid surface by ultrathin thermoset film could be done by using the LB technique.

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Hydrosilation of Ketones Catalyzed by Dimethylzirconocene

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While catalytic hydrosilation reactions of a carbonyl group by late transition metal complexes have been reported,[1] few hydrosilation reactions catalyzed by early transition metal complexes are known.[2] Since catalytic activities of group 4 metallocene derivatives for the dehydrogenative coupling of organosilanes[3] have been known, the catalytic activation of organosilanes by the metallocene derivatives has been utilized for the olefin hydrosilation.[4] We have successfully applied the activation of phenylsilane by dimethylzirconocene to O-silation of various alcohols and aldehydes.[5] It has also been reported that diphenyltitanocene is effective as a catalyst for the hydrosilation of various ketones to give alkoxysilanes.[2a]

In this paper we wish to report the hydrosilation of ketones with phenylsilane catalyzed by dimethylzirconocene under mild conditions. A catalytic amount of dimethylzirconocene (**1**) prepared by the literature procedure[6] was added to a stoichiometric mixture of a ketone and phenylsilane (**2**) in benzene. The initially colorless solution turned yellow with evolution of H_2 gas. In a typical procedure, a mixture (0.5 mL) of **1** (0.06 M), **2** (3.7 M), and a ketone (3.7 M) in benzene was stirred under argon for 72 hours at room temperature. The resulting mixture was subjected to the GC/MS analysis.[7] All manipulations were carried out under argon atmosphere using either standard inert-atmosphere techniques or argon filled glove box. The solvent, phenylsilane, and ketones were saturated with argon before use.

The results of the O-silation reaction catalyzed by **1** are summarized in Table 1. For relatively simple ketones such as 2-butanone and 2-pentanone, bis(alkoxy)phenylsilanes are major products (64-74%) and tris(alkoxy)silanes are minor products (6-15%). In the case of 4-hexene-3-one which is sterically rather bulkier than 2-butanone or 2-pentanone, only bis(alkoxy)phenylsilane is observed in a good yield (84%). The results are comparable with those of the diphenyltitanocene system.[2a] A similar reaction of phenylsilane and 2-heptanone by a catalytic amount of diphenyltitanocene under