Polymerization of *N*-octadecylacrylamide in Langmuir–Blodgett multilayers

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N-Octadecylacrylamide (ODA) monomer spread from benzene solution on a water surface forms a stable solid condensed monolayer, which could be deposited on solid supports successively by the Langmuir–Blodgett (LB) technique with transfer ratios of about 1.0. The ODA multilayers were polymerized completely by ultra-violet (u.v.) irradiation. The polymerized multilayers were uniform thin films with a high stability against solvents. It was found that there is a large difference in solubilities between the unpolymerized (monomer) and the polymerized LB film, and this ODA multilayer has the possibility of application as a deep u.v.-sensitive negative resist.

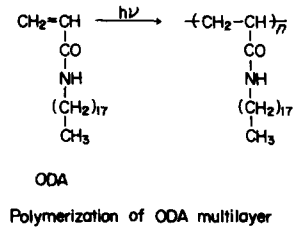
(Keywords: Langmuir–Blodgett technique; monolayer; multilayer; Fourier transform infra-red spectrum; polyacrylamide)

INTRODUCTION

Recently various molecular assembly systems have been extensively investigated[1,2]. Langmuir–Blodgett (LB) multilayers, which can be built up from condensed monolayers on air–water interfaces by multiple depositions onto solid supports[3,4], have received considerable attention from the viewpoint of functional ultrathin films. LB multilayers have the possibility of forming ultrathin films with highly oriented molecule arrays and with controlled thickness. These multilayers, however, have lacked mechanical, thermal and solvent stability. Some attempts to construct polymer multilayers have been made in order to increase these stabilities. Several multilayers of vinyl monomers having long alkyl chains were found to be polymerized by γ-ray or electron beam irradiation[5–9].

Some attempts have been carried out on the polymerization of *N*-octadecylacrylamide (ODA) monolayer and LB multilayer. Ringsdorf *et al.*[10] examined the polymerization of a mixed monolayer of ODA monomer, *p*-octadecylacetophenone (photosensitizer) and azobisisobutyronitrile (AIBN) (radical initiator) on water. Although the π–A isotherm of the mixed monolayer was changed by u.v. irradiation, the occurrence of polymerization was not clear. On the other hand, Lando *et al.*[11,12] reported the radiation-induced polymerization of an octadecylacrylamide LB multilayer. In their papers, however, no information on the structure of the monomer is given; that is, it is not clear whether the monomer is *N*-octadecylacrylamide or α-octadecylacrylamide†. The characteristic amide I and II absorption bands in their assignments of Fourier-transform infra-red (*FT*i.r.) spectra seem to be at too high wavenumbers to be those of the former monomer.

In the present work, we have investigated the characterization of a multilayer of *N*-octadecylacrylamide monomer built up by the Langmuir–Blodgett method, and the polymerization of the multilayer by u.v. irradiation. We have found that the polymerization proceeds completely and uniform thin polymerized LB multilayers with a high stability against solvents can be formed.



ODA

Polymerization of ODA multilayer

EXPERIMENTAL

N-Octadecylacrylamide monomer, which was synthesized by the reaction of acrylamide with octadecyl bromide in anhydrous dimethylformamide (DMF) in the

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†Two register numbers ([75413-68-2] and [1506-54-31]) for their ODA monomer are labelled in their papers in *Chemical Abstracts*; the former means α-octadecylacrylamide and appeared in ref. 12 (*Chem. Abst.* **93**, 221167g) and the latter *N*-octadecylacrylamide in ref. 11 (*ibid.* **93**, 95770h)

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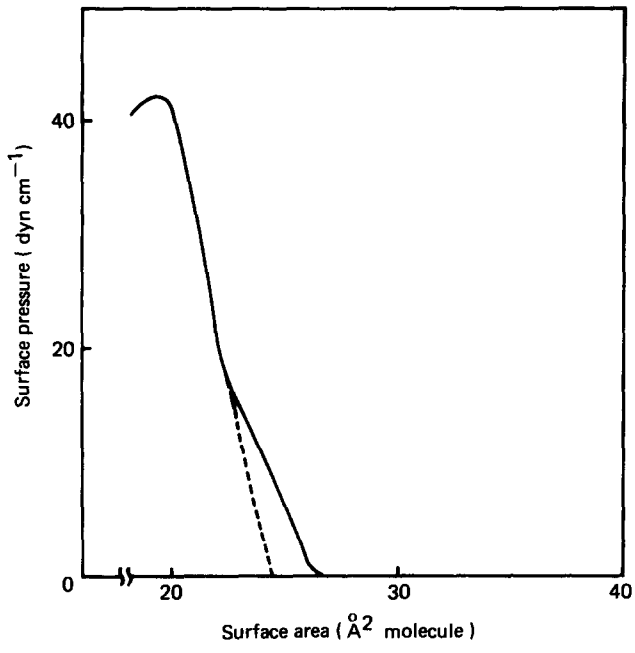

Figure 1 Surface pressure–surface area isotherm of ODA monolayer at 17°C

presence of KOH, was kindly presented by Dr Ito (Mitsui Toatsu Chemicals Inc.)[13].

The product was washed with hexane to remove residual octadecyl bromide and further washed with water to remove residual acrylamide, and then purified by preparative thin-layer chromatography (eluant: benzene/methanol 95/5) and by recrystallization from ethanol (m.p. 72–73°C). Distilled and deionized water was used. Benzene and chloroform used for spreading were of spectroscopic grade. The plates (quartz slide or silicon wafer) onto which the multilayers were deposited were cleaned in boiling H_2SO_4/HNO_3 solution and made hydrophobic with dimethyldichlorosilane. CaF_2 plates used for infra-red spectroscopy was treated with ferric stearate. The surface pressure–surface area isotherms were measured with an automatic Langmuir trough (Kyowa Kaimen Kagaku HBM-AP using a Wilhelmy-type film balance). Fourier-transform infra-red (*FT*i.r.) spectra and X-ray diffractions were measured with a Jeol JIR-100 *FT*i.r. spectrophotometer and a Shimadzu VD-1 X-ray powder diffractometer, respectively. U.v. irradiation for polymerization was carried out with a 500 W ultra-high-pressure Hg lamp.

RESULTS AND DISCUSSION

Multilayer formation

The ODA monomer monolayer was spread from benzene solution (2×10^{-3} M) on a water surface. The surface pressure (π)–surface area (A) isotherm of the ODA monolayer at 17°C is shown in *Figure 1*. The isotherm indicates the formation of a stable solid condensed monolayer with a collapse pressure of 40 dyn cm^{-1}. The limiting area extrapolated to $\pi = 0$ was 24.5 Å^2 per molecule. The monolayers on the water were transferred onto the solid supports at a surface pressure of 20 dyn cm^{-1}. At this pressure, the surface area per molecule is 22 Å^2, which approximates that of close-packed hydrocarbons (20 Å^2). Depositions in both down and up trips could be achieved and the transfer ratios for both trips were between 0.96 and 1.1 at a dipping velocity of 5–10 mm min^{-1}. Even at high dipping velocity of 100 mm min^{-1}, a transfer ratio of 0.9 could be obtained, supporting stable monolayer formation. The deposition in both trips suggests the formation of typical Y-type multilayers (solid–tail–head–head–tail–...). The X-ray diffraction pattern, though weak and broad due to no heavy atom being present, gave about 48 Å as the film spacing, which corresponds to twice the monolayer thickness, suggesting again that this LB film is Y-type.

Transmission infra-red spectra give information on molecular orientation and structure, and have often been used in the characterization of multilayers. The *FT*i.r. spectrum of the ODA multilayer is shown in *Figure 2*. Banerjie and Lando have also reported the *FT*i.r. spectrum of an ODA multilayer[11], which is, however, different from the present spectrum. There was no information on the structure of the monomer in their papers[11,12]. Their monomer seems to be α-octadecylacrylamide from their series of works[12] (see earlier footnote). The assignments of the main absorption bands and their absorption intensities are given in *Table 1*, together with the results in KBr pellet form where ODA monomers are considered to be oriented randomly. The positions of the absorption bands were not appreciably changed by the environments, whereas the intensities of the absorptions were changed. In LB films, the absorption intensities due to the stretching of C–H (2918, 2850 cm^{-1}) and C=O (amide I at 1655 cm^{-1}) increased; in contrast, that of the stretching of N–H decreased (*Table 1*). As the infra-red beam is directed perpendicular to the plane of the multilayer, the bands associated with bonds oriented more or less parallel to the plane are increased. The results in *Table 1* suggest that the octadecyl group is oriented perpendicular to the multilayer (C–H bonds are parallel to the layer), and the carbonyl group lies on the plane, whereas the NH group is perpendicular. Further *FT*i.r. studies using polarized radiation are necessary for more detailed description of the molecular orientation.

Polymerization

The ODA monomer multilayers transferred by the LB method onto solid supports were polymerized by u.v.

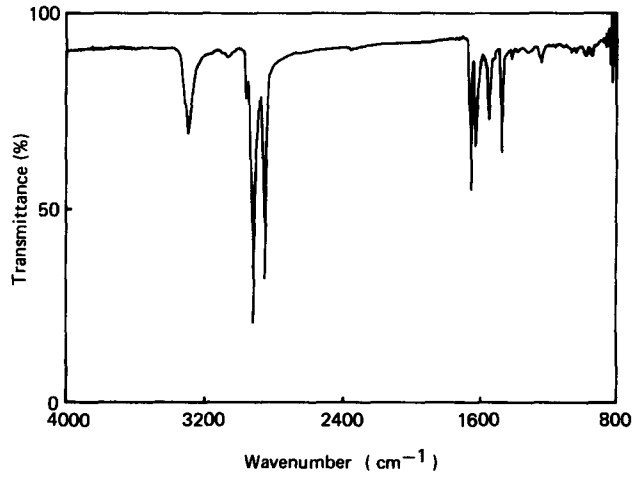

Figure 2 *FT*i.r. spectrum of ODA multilayer built up on CaF_2

Table 1 Intensities and wavenumbers of main absorption bands of ODA in LB multilayer and bulk KBr pellet

Assignment	LB multilayer		KBr pellet	
	Wavenumber (cm^{-1})	Absorbance (relative ratio)	Wavenumber (cm^{-1})	Absorbance (relative ratio)
ν_{NH}	3303	0.13 (1.0)	3303	0.34 (1.0)
ν_{CH_2}	2918	0.65 (5.1)	2918	0.98 (2.9)
ν_{CH_2}	2850	0.47 (3.7)	2850	0.69 (2.1)
Amide I	1655	0.25 (2.0)	1655	0.50 (1.5)
$\nu_{C=C}$	1624	0.15 (1.2)	1626	0.33 (1.0)
Amide II	1545	0.10 (0.8)	1541	0.34 (1.0)
δ_{CH_2}	1471	0.16 (1.3)	1470	0.27 (0.8)
$\delta_{=CH}$	985	0.01 (0.08)	990	0.07 (0.2)

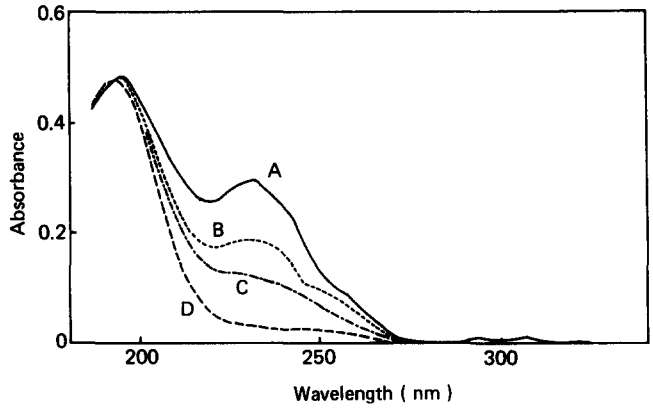

Figure 3 Change of u.v. absorption spectra of ODA multilayer built up on quartz slide with time during u.v. irradiation: A, before irradiation; B, 5 min irradiation; C, 12 min; D, 60 min

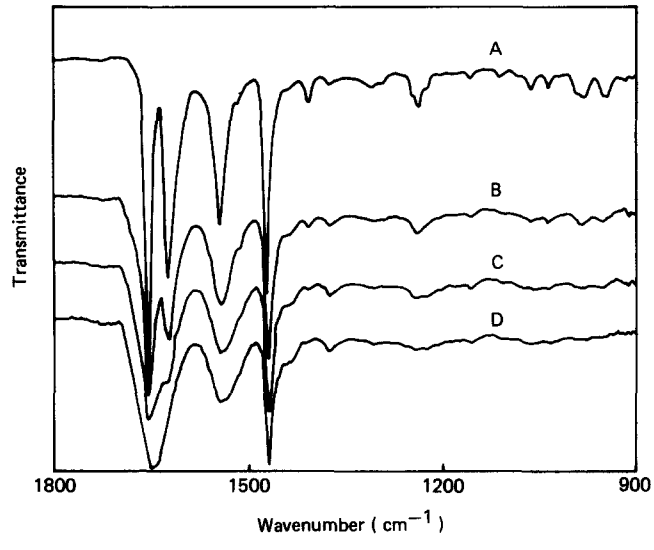

Figure 4 Change of *FT*i.r. spectra (1800–900 cm^{-1}) of ODA multilayer with time during u.v. irradiation: A, before irradiation; B, 10 min irradiation; C, 30 min; D, 60 min

Table 2 Comparison of stability against various solvents between unpolymerized and polymerized ODA LB film

	Hexane	Ethanol	Benzene	*o*-DCB[a]	DMF[b]	THF[c]	Chloroform
Polymerized LB film	–	–	–	–	–	–	s
Unpolymerized (monomer) LB film	–	s	s	s	s	s	s

[a] *o*-Dichlorobenzene [b] Dimethylformamide [c] Tetrahydrofuran
s soluble, – Insoluble

irradiation under N_2 atmosphere. The polymerization can be followed by observation of the change in both u.v. absorption and *FT*i.r. absorption spectra. In the former, the absorbance around 230 nm due to a π–π^* transition decreases with time during u.v. irradiation (*Figure 3*). The polymerization proceeded completely (100% conversion). The *FT*i.r. spectrum after polymerization shows the disappearance of the vinyl stretching band at 1624 cm^{-1} and the deformation band of vinyl hydrogen at 990 cm^{-1} and broadening of the remaining bands (*Figure 4*). Microscope observation of the irradiated multilayer using the differential interference method showed that a uniform thin film with no crack was obtained. The irradiated multilayers have been immersed in benzene solution for at least 30 min to remove unpolymerized monomer. However, the *FT*i.r. spectrum did not change after the rinse in either intensities or wavenumbers of the absorptions. This fact also supports 100% conversion of polymerization. The dissolution of the polymerized LB film was examined by observing the change of *FT*i.r. spectrum after dipping in various solvents (*Table 2*). As can be seen from *Table 2*, the polymerized ODA LB film has a high stability against solvents, and there is a large difference in solubility between the unpolymerized (monomer) and the polymerized LB film of ODA. The large difference in solubility generated by u.v. irradiation is very interesting and suggests that the ODA multilayer can be applied to a deep u.v.-sensitive negative resist. An investigation on applications of the resist has been started.

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