pulses. Such a homogeneous scission into smaller units would result in the etched image being a closer representation of the light intensity distribution striking the polymer film, in a manner analogous to the use of finer grain sizes in a photographic film for higher resolution photography. Thus, periodic patterns such as in Figure 3A are observed for films with high pyrene concentrations. This kind of periodic image is not observed with films having the low dopant concentration, because ablated fragments are bulkier in this case (a larger "grain size"), leaving relatively large residues, particularly with smaller laser fluences.

The presence of the periodic images in films heavily doped with pyrene is an indication that the temperature of the film during the ablation was not high enough for the polymer to undergo extensive thermal flow. PMMA is a UV-softened polymer,[9] which flows below its T_g after UV irradiation, different from UV-hardened materials like novolac resins and poly(hydroxystyrene).[10] In contrast, with a low concentration of pyrene dopant, the etched area shows evidence of having been heated to its melting point (Figure 3B). It is interesting to compare these differing surface conditions to those observed in the laser ablation of PMMA at 193 nm and at 248 nm.[5,6,8] In that work, the presence of periodic patterns in the etched image after irradiation at 193 nm is associated with an ablation mechanism believed to be largely photochemical, while the presence of signs of melting in an area etched with 248-nm light is considered evidence that photothermal ablation is dominant. A similar switching between photochemical and photothermal mechanisms depending on optical absorption may be operative in the present work.

The lowest T_1 excited states of benzophenone and pyrene are 69 and 48 kcal/mol, respectively; the excited S_1 state of benzophenone is 74 kcal/mol.[7] Since the C–C bond energy in PMMA is about 85 kcal/mol, single electronic energy transfer from these excited dopants may not be sufficient for main-chain scission of PMMA. The laser ablation induced by the dopant's presence must involve multiphoton excitation of the dopant or annihilation of two dopant excited states. Higher electronic energy transfers made possible in such mechanisms may trigger the primary bond scission. The energy transfer from these higher excited states of PMMA and/or thermal energy attained by fast dissipation of electronic excitation energy from the latter state resulted in bond scissions of PMMA. With benzophenone as a dopant, a Norrish type II process may have contributed to a certain degree. Enhanced ablation through addition of a dopant to PMMA films has been reported for 248-nm excimer laser exposure;[4,6] however, competitive absorptions by the polymer film and dopant at this wavelength complicate the analysis and mechanistic discussion. We will study the mechanism in detail from a photophysical viewpoint in the near future.

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Registry No. PMMA, 9011-14-7; $C_6H_5COC_6H_5$, 119-61-9; pyrene, 129-00-0.

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(11) IBM Summer Faculty Fellow (June–August 1986); permanent address: Department of Polymer Science and Engineering, Kyoto Institute of Technology, Kyoto 606, Japan.

(12) IBM Visiting Scientist (April 1985 to September 1986); permanent address: Research Laboratory for Resource Utilization, Tokyo Institute of Technology, Yokohama 227, Japan.

Hiroshi Masuhara,[11] Hiroyuki Hiraoka,* and Kazunami Domen[12]

Almaden Research Center, IBM Research
San Jose, California 95120-6099

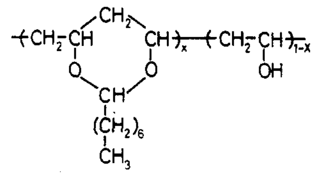
Received October 17, 1986

Stepwise Deposition of Oriented Monolayer-Polymer Films by the Langmuir-Blodgett Technique

The Langmuir–Blodgett (LB) technique is an excellent method for obtaining ultrathin films with a well-defined molecular assembly, and there has been much interest in LB films because of this molecular assembly.[1] Studies of LB films have been conducted primarily on amphiphilic molecules, such as long-chain fatty acids and dyestuffs with long alkyl chains. However, there has been little study of LB films consisting of monolayers of synthetic polymers.[2–9] Orientation of synthetic amphiphilic polymers at the air/water interface and transfer of the monolayer films onto substrates are of interest as a route to oriented, ultrathin, synthetic polymer films.

We have demonstrated[10] that poly(vinyl acetals) spread on the air/water interface can be transferred onto various substrates by Y-type deposition and that the one-layer thickness increases with increasing length of the alkyl side chain. We report here that the one-layer thickness of LB films of poly(vinyl octal) is constant at 1.1 nm from one monolayer to 100 layers and that the films have an oriented structure.

Poly(vinyl octal) (OA-PVA) was prepared from commercially available poly(vinyl alcohol) (Wako Pure Chemicals, >98% hydrolyzed, average molecular weight 8.8 × 10^4) and octaldehyde in the presence of hydrochloric acid in chloroform.[10] The mole fraction of acetalized units (x) was 0.7. The OA-PVA was amorphous, with a glass transition temperature of 25 °C.



OA-PVA

A benzene solution of OA-PVA (0.126 g/L) was dropped on the surface of distilled water (10–11 °C) in a Langmuir trough. The solution spread on the surface immediately. After evaporation of the solvent, a surface pressure–area curve was recorded by using a Lauda film balance with a

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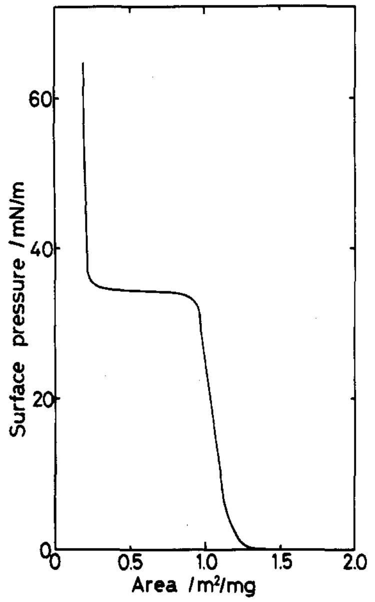

Figure 1. Surface pressure–area curve for poly(vinyl octal) measured at 11 °C (subphase temperature) and a compression rate of 0.8 cm/min.

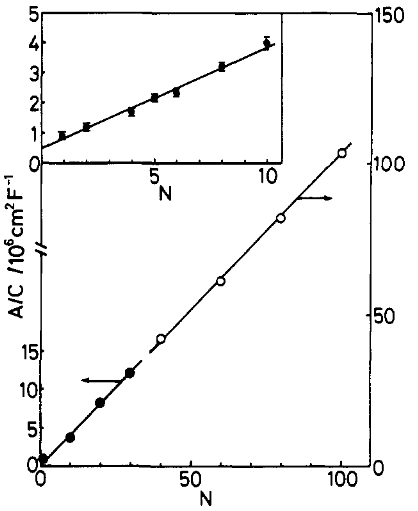

Figure 2. Film thickness measured by ellipsometry (right axis) and A/C (A, electrode area; C, capacitance at 1 kHz and −125 °C) (left axis) as functions of the number of deposited layers (N).

compression speed of 0.8 cm/min (Figure 1). The isotherm showed a plateau region in which a drastic conformation change occurred, followed by collapse of the surface film. The steep rise in surface pressure in the region less condensed than the plateau corresponded to packing the polymer into a two-dimensional monolayer film. The limiting area, estimated by extrapolating the steepest region to zero surface pressure, was 1.15 m^2/mg, corresponding to 0.29 nm^2/average repeat unit. At a surface pressure of 30 mN/m, the surface film could be transferred by Y-type deposition onto various substrates, including glass, Si, Cr, and Al, with a transfer ratio of 1.00 ± 0.05.

In order to investigate the homogeneity of the transferred films and their structure on substrates, we determined their thickness as a function of the number of depositions (N) by ellipsometry and capacitance measurements (Figure 2). For ellipsometry, the surface films were transferred onto Si wafers to form multilayered films (N = 40–100). Figure 2 shows that the film thickness was proportional to N and that the one-layer thickness was 1.1 nm. For capacitance measurements, thinner films were formed on Al substrates, and the capacitance of Al/film/Al cells was measured at 1 kHz. The capacitance was nearly constant in the temperature range −125 to +20 °C, irrespective of N. The reciprocal of the capacitance at −125 °C, shown in Figure 2, was proportional to N (1–30) and had a definite intercept, attributable to a layer of Al_2O_3 on the Al substrate. Assuming that the relative dielectric constant of Al_2O_3 is 8,[11] the thickness of the Al_2O_3 layer was calculated from the intercept to be 3.7 nm. The relative dielectric constant of the transferred films, estimated from the slope of the linear relation, was 3.7. Both of these measurements confirmed that the transferred films were homogeneous and that the one-layer thickness was constant (1.1 nm) from one monolayer to 100 layers.

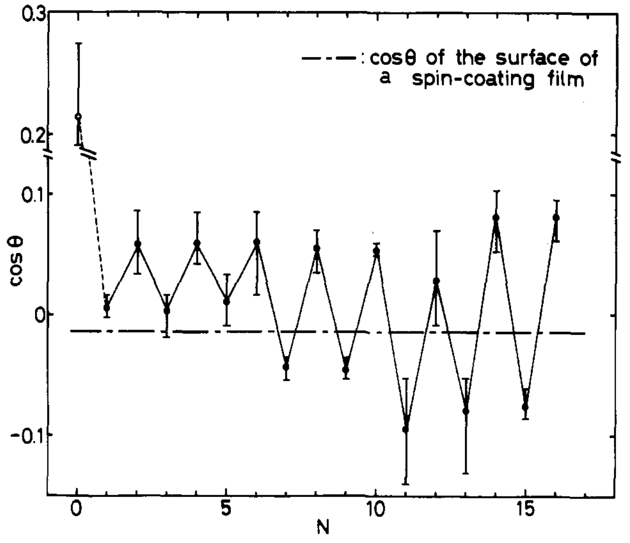

Figure 3. Wettability of the surfaces of poly(vinyl octal) films transferred onto Al substrates as a function of the number of deposited layers (N).

This constant one-layer thickness seems to reflect an oriented structure of OA-PVA on the substrates, the orientation probably forming at the air/water interface because of the amphiphilic nature of the polymer. Figure 3 shows the wettability of the surfaces of films transferred onto Al substrates as a function of N. The wettability was estimated by measuring the contact angle of water 1 min after dropping distilled water onto the surfaces. The wettability was higher when N was even than when N was odd. This difference appeared on freshly prepared films, including monolayer films, and did not change after transferred films had stood for a few days. The wettability of the surface of a spin-coating film lay between the values for the transferred films of even and odd N when N was larger than 6 or 7. These results suggest that the transferred films have an oriented structure where the main chain and the side chain function as hydrophilic and hydrophobic groups, respectively.

In conclusion, films of amphiphilic OA-PVA transferred from spread films at an air/water interface onto substrates have a constant one-layer thickness of 1.1 nm from one monolayer to 100 layers and have an oriented structure. The structure of the transferred films seems to depend on the stereoregularity of the starting poly(vinyl alcohol), the stereostructure of the trisubstituted 1,3-dioxane rings, and the conformation at the air/water interface. We are now investigating these factors.

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Masayoshi Watanabe,* Yozo Kosaka, Kohei Sanui, and Naoya Ogata

Department of Chemistry, Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan

Kiyoshi Oguchi* and Tomoko Yoden

Research Development Corporation of Japan
c/o Department of Chemistry, Sophia University
7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan

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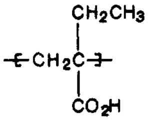
On the Mechanism of Polyelectrolyte-Induced Structural Reorganization in Thin Molecular Films[†]

We reported in 1985 that polyelectrolyte adsorption can be used to control the structural and functional properties of bilayer membranes prepared from double-chain surfactants in water.[1] In particular, the pH-dependent adsorption of hydrophobic poly(carboxylic acids) on phosphatidylcholine films[2] can be used to design surfactant vesicles that release their contents rapidly and quantitatively in response to changes in environmental parameters such as pH,[1] temperature,[1] or the concentrations of an organic solute, e.g., glucose.[3] Composite thin films prepared in this way offer intriguing technological opportunities in information storage and transfer, in sensing and control (including biosensing), and in medical diagnosis and therapeutics.

Much of our work has concerned the pH-dependent interactions of poly(2-ethylacrylic acid) (PEAA, 1) with bilayer vesicles of natural or synthetic phosphatidylcholines (2). Hydration of dipalmitoylphosphatidylcholine (DPPC, **2a**) at a concentration of 1 mg/mL in a phosphate-buffered solution of PEAA at pH 7.5 affords a turbid suspension of multilamellar vesicles.[4] Depression of the pH to 6.5 or below causes a marked loss of turbidity (Figure 1); similar treatment of egg yolk phosphatidylcholine (**2b**) vesicles also causes rapid, quantitative loss of vesicle-entrapped carboxyfluorescein, a fluorescent marker.[1,5,6] We have suggested that it is the pH-induced conformational transition of PEAA[7-9] that causes this structural reorganization and the concomitant loss of membrane integrity. We describe in this paper a series of photophysical and calorimetric experiments that support this hypothesis.



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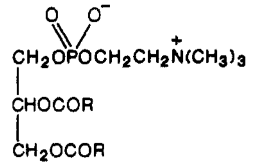

2a, R = $C_{15}H_{31}$
b, R = mixed hydrocarbon chains
c, R = $C_{18}H_{35}$

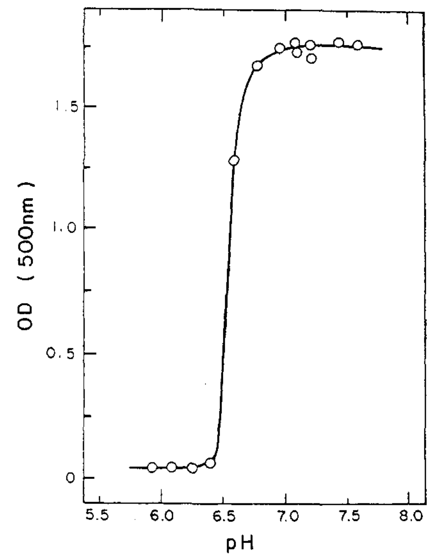

Figure 1. Optical density (500 nm) of a 1 mg/mL suspension of DPPC in phosphate-buffered aqueous PEAA (1 mg/mL).

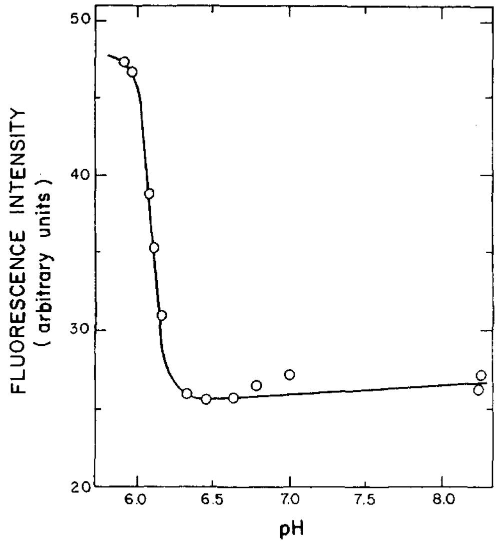

Figure 2. Fluorescence intensity (375 nm) emitted by 5 × 10^{-6} M pyrene in phosphate-buffered solutions of PEAA as a function of pH. Excitation at 337 nm, excitation and emission slit width 3.0 nm.

Thomas and co-workers have shown pyrene to be a useful photophysical probe of polyelectrolyte conformation in aqueous solution.[10-12] Figure 2 shows a plot of the intensity of fluorescence emitted by 5 × 10^{-6} M pyrene in a series of PEAA solutions of varying pH.[13] The large increase in fluorescence intensity at low pH is consistent with Thomas' observations regarding poly(methacrylic acid) (PMAA)[10] and signals the collapse of the PEAA chain from an expanded conformation at high pH to a relatively hydrophobic, globular coil in acidic solutions. The changes in the vibrational fine structure of the fluorescence emission are also consistent with a decrease in the polarity of the pyrene microenvironment at low pH.[14] The midpoint of the conformational transition of PEAA occurs at

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[†] Part 13 in the series "Interactions of Synthetic Polymers with Cell Membranes and Model Membrane Systems". Part 12: Turek, A. B.; Tirrell, D. A. *J. Bioactive Compatible Polym.* **1986**, *1*, 309.

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