Uniform Chromophore Distribution in Langmuir–Blodgett Films of Poly(vinyl octanal acetal)

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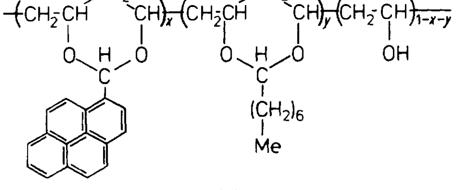
Uniform chromophore distribution in Langmuir–Blodgett (LB) monolayers has been attained using a preformed polymer, poly(vinyl octanal acetal), containing the pyrene chromophore as a fluorescence probe.

Recently, photophysical and photochemical processes in ordered molecular structures of Langmuir–Blodgett (LB) films have been studied extensively.[1] The distribution of the chromophore is a significant factor in determining the photophysical processes,[2] but amphiphilic chromophores dispersed in a LB film of long-chain fatty acids are known to form various aggregates.[3] Here we report the preparation of a LB layered film with uniform distribution of the chromophore by a preformed polymer, poly(vinyl octanal acetal), the film showing energy migration between adjacent layers.

Poly(vinyl octanal acetal) was prepared by acetalization of poly(vinyl alcohol) with octanal in the presence of hydrochloric acid.[4] The pyrenyl group was introduced by a similar reaction using pyrenecarbaldehyde together with octanal. The molecular structure (**1**) of copolymers prepared with varying pyrenyl compositions is shown. The mole fraction of acetalized units ($x + y$) was in the range 0.65—0.80, and the percentage of pyrenyl groups in the acetal units $x/(x + y)$ varied from 0 to 12.5%: P1 (0.2), P2 (2.0), P3 (4.6), P4 (9.0), and P5 (12.5%).



(**1**)

The surface pressure–area isotherm of each copolymer shows a slight decrease in the collapse pressure as the percentage of pyrenyl groups increases. However, it was possible to transfer all the polymers to a substrate quartz plate as *Y*-type film; deposition takes place at each downward and upward dip. The transfer ratio (the ratio of deposited area to the decrease of spread area on water) was unity. Introduction of 10% of pyrenyl units [$x/(x + y) = 0.1$] did not much affect the deposition. Films of up to 20 layers were easily prepared. To remove the interface effect, the layered film was sandwiched by a few layers of poly(vinyl octanal acetal).

Figure 1 shows the fluorescence spectra of the 6-layered films of P2 and P5; below a few percent of pyrenyl groups, the shapes of the emission spectra are the same and there is no excimer emission. The structureless broad band around

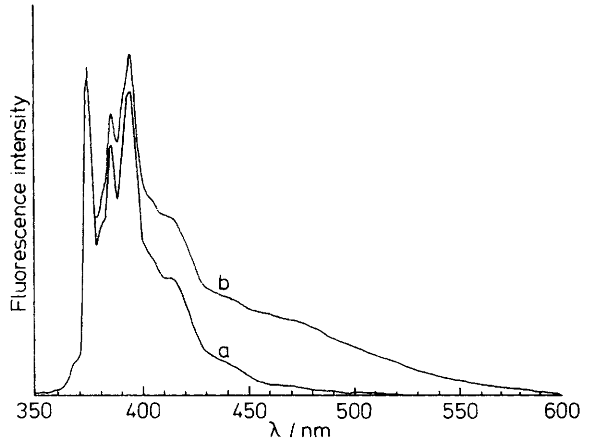


Figure 1. Fluorescence spectra of 6-layered films for (a) P2 and (b) P5.

480 nm for P5 is due to excimer emission (E_2) of the pyrenyl group. In multi-layered films, the excimer emission is enhanced by energy migration between adjacent layers as described below. However, the excimer emission for P5 is very weak compared with that in long-chain fatty acid LB films.[3] At higher pyrene concentration, there is some increase in fluorescence intensity at 400—440 nm; this emission is assigned to another kind of excimer (E_1), as reported for the pyrene chromophore in a LB film of stearic acid.[3] Although the pyrene chromophore is one of those which most easily forms an excimer, there is much less excimer emission by pyrene in the polymer LB film than when dispersed in the LB films of low molecular weight fatty acids, at the same layer concentration of pyrenyl groups.[3] For the LB film of stearic acid, a shift in the excitation spectrum was reported when the fluorescence was observed at excimer emission. This shows that the excimer is formed from the ground state dimer. In the polymer film, the excitation spectra correspond to the absorption spectrum, whether the spectra were monitored at the monomer emission or excimer emission bands. This means that the pyrenyl groups do not form any aggregates such as the ground state dimer and they uniformly distribute in the plane of monolayer.

For polymers with a high concentration of pyrenyl groups (*ca.* 10% of pyrenyl groups in acetal units), the fluorescence behaviour of the LB films depends on the number of layers: the excimer emission and the decay rate of monomer fluorescence increase with an increase in the number of layers. The ratio of excimer emission (E_2) to monomer emission for a 20-layered film was 1.5 times stronger than that for a 6-layered film. The results can be explained by energy migration between pyrenyl groups in adjacent layers. It is necessary to take into account the interaction between neighbouring layers. The energy flow to the excimer-forming site was shown by the uniform chromophore distribution in the layered structure.

In summary, polymer LB films were obtained, in which the distribution of chromophores is uniform and the excimer formation is restricted. Such a polymer LB film provides a new material for constructing photo-functional thin films.

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