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Langmuir-Blodgett Films of Long Chain Derivatives of Carbazoledioxazines

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Long chain derivatives of carbazoledioxazines with a linear and an angular type structures were synthesized. Monolayers were spread on water surface from toluene solution and deposited onto solid supports. From pressure-area isotherms and thickness together with polarized visible and IR spectra of multilayers, the molecular orientations in the films were investigated.

Carbazoledioxazine is a reddish violet pigment characterized by a high tinting strength and an excellent lightfastness as well as good resistivity to heat and solvent.1) Recently, their derivatives have been applied to electronic devices such as organic photoconductors.2) By controlling the orientation of the chromophore in thin films, their functions will be improved. We have synthesized soluble carbazoledioxazine derivatives with a linear3) and an angular type structures4) by introducing long alkyl groups. This paper is the first adaptation of these pigments to the Langmuir-Blodgett (LB) films. Molecular arrangements were studied by surface pressure(π)-area(A) isotherms of the monolayers on water and polarized visible and IR spectra as well as film thickness of the multilayers on solid plates.

Carbazoledioxazines with a linear type structure (**1**) were synthesized by dealkoxylation ring closure of the precursor (**4**) in a solvent of high boiling temperature, while those of an angular type structure (**2**,**3**) were obtained by dehydrogenation ring closure of **4** using electrochemical oxidation. Their structures were identified by ^{1}H-NMR and elemental analysis.

Although carbazoledioxazines with short alkyl chains (R^1=C_2H_5 and C_3H_7) were scarcely soluble in common organic solvents, these compounds having long alkyl chains were soluble in various organic solvents such as chloroform and benzene, among which toluene was most suitable as a spreading solvent (ca.1×10^{-6} mol/l) to obtain the homogeneous monolayers.

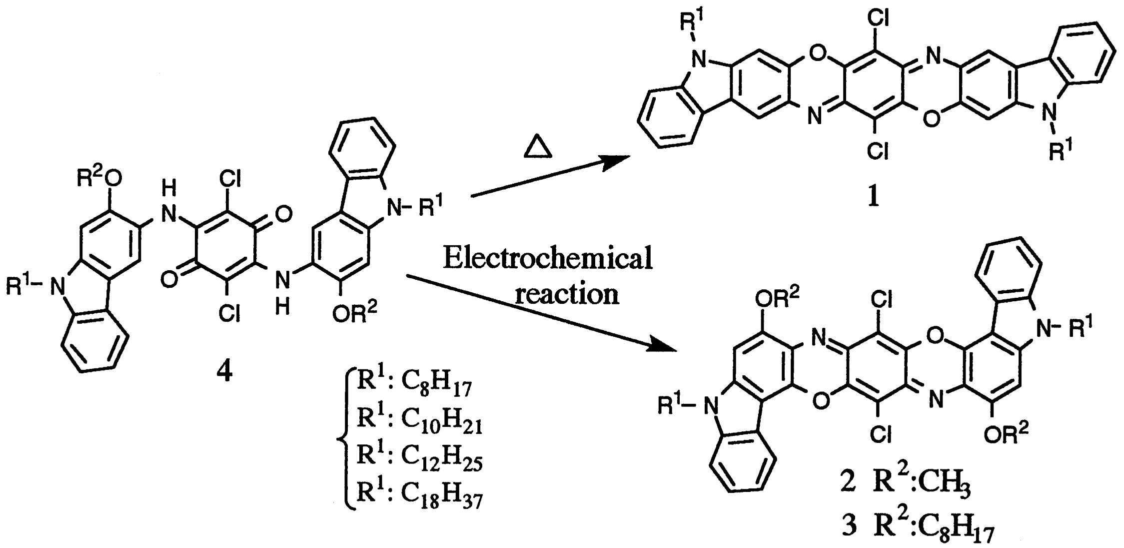

Figure 1 shows π-A isotherms for the monolayers of 1, 2, and 3 having octyl groups as R^1, measured by a Lauda film balance on water at 15 °C. The corresponding derivatives with different alkyl chain lengths of R^1 (C_{10}, C_{12}, C_{18}) gave similar results. Although the chromophore of carbazoledioxazines is very rigid, stable monolayers could be formed since alkyl groups act as a plasticizer. The monolayer of the linear type compound (**1**) exhibited two condensed states through a characteristic phase transition region. In consideration of molecular dimensions as indicated in the top of Fig.1, this result suggests that the chromophore lies flat on water surface at zero pressure region (>100 Å^2/molecule), the short axis of the chromophore stands up in the first condensed region (limiting area 98 Å^2/molecule) and then the long axis stands up in the second condensed region (limiting area 58 Å^2/molecule) through the phase transition. Finally the film becomes very rigid with high collapse pressure due to close packing of the chromophore. The monolayer of the angular type compound (**2**) was similar to the linear type (**1**) exhibiting a phase transition, while compound (**3**) gave a simple condensed type monolayer without any phase transition. The latter is probably due to increasing cohesive interaction of four long substituents, although the limiting area (60 Å^2/molecule) of 3 is too small for the large chromophore with four long alkyl chains.

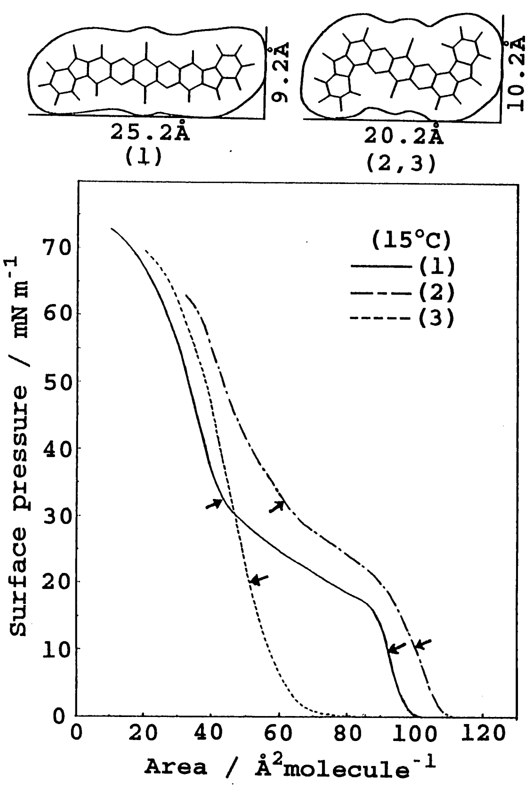

Fig.1. Surface pressure-area isotherms of 1, 2, and 3 at 15 °C and their molecule dimensions: the arrows indicate deposition pressure for the multilayers.

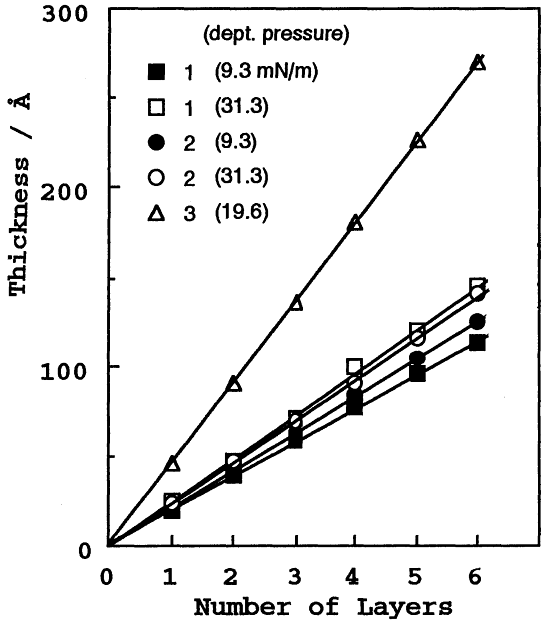

Fig.2. Thickness of multilayers of 1, 2, and 3 with $R^1=C_8H_{17}$ measured by optical interference.

It was difficult to prepare the multilayers using a conventional LB method because of the rigidity of these monolayers. However, the multilayers were able to be prepared by a horizontal lifting method at 9.3 mN/m and 31.3 mN/m for two condensed regions of 1 and 2 and 19.6 mN/m for 3.

In Fig.2, the thicknesses of the multilayers (R^1:C_8H_{17}) measured by optical interference are plotted against the number of layers. The good linear relationship was obtained for each film and the values of thickness per layer were 19.3 and 24.3 Å for the low and high pressure regions of 1, respectively, 21.0 and 23.3 Å for the respective regions of 2 and 45.4 Å for 3. The large thickness for 3 together with the small area in the π-A isotherm suggests that two of four alkyl chains are oriented up and the other two chains down. In addition,the absorbance of visible spectra of each film increased linearly with number of layers which is also indicative of reproducible monolayer depositions.

Figure 3 shows the electronic absorption spectra of the multilayers of 1 deposited at 9.3 and 31.3 mN/m together with that of the toluene solution. The transition moment of visible region can be assigned to the long axis of the chromophore. The relative absorbance of visible region for the high pressure film was weaker than that for the low pressure film. Furthermore, the absorbance of p-polarized visible spectrum at 45° incidence was stronger than that of s-polarized one for the high pressure film as shown in Fig.4, whereas this dichroism

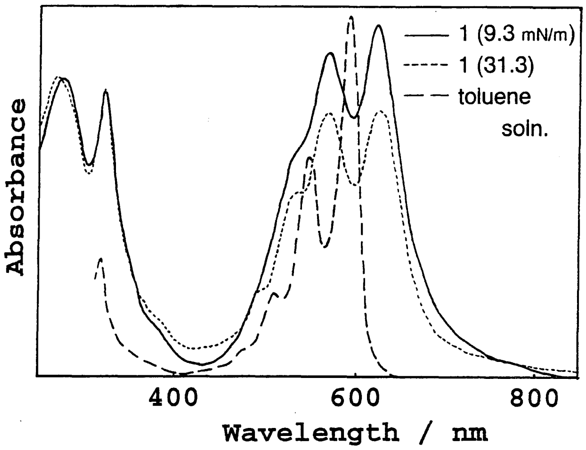

Fig.3. Electronic absorption spectra of multilayers of 1 deposited at 9.3 mN/m (20 layers) and 31.3 mN/m (7 layers) together with the toluene solution.

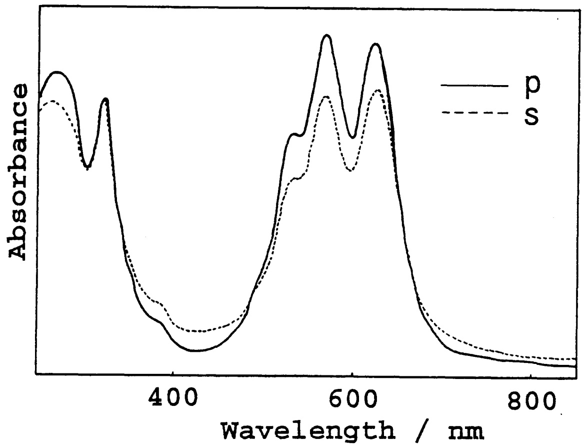

Fig.4. Polarized electronic absorption spectra at 45° incidence for the multilayer of 1 deposited at 31.3 mN/m (7 layers).

was reversed for the low pressure film. These results indicate that the long axis of chromophore of 1 is oriented rather perpendicular to the surface at higher pressure, while it is rather flat at lower pressure. In addition, two dimensional anisotropy of the chromophore orientation in the plane with respect to film compression was detected clearly for the high pressure film.

The electronic absorption spectra of the multilayers of 2 deposited at two different pressures and of 3 are shown in Figs. 5 and 6, respectively, as compared with those of toluene solutions. The solution spectra in visible region of 1(Fig.3), 2(Fig.5), and 3(Fig.6) were very similar, irrespective of different shapes of the chromophores and different substituents. However, their spectra in the multilayers differed markedly from each other, particularly in the relative absorbance of the peak at the longest wavelength. These results seem to reflect characteristic orientation and packing of the chromophore in each film, although directions of the transition moments are not yet clear for 2 and 3 with the angular shape chromophore.

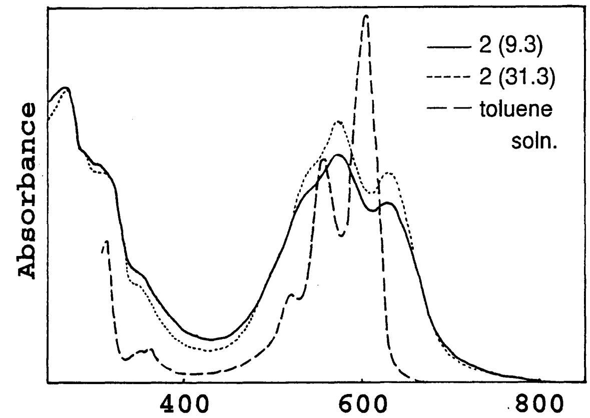

Fig.5. Electronic absorption spectra of multilayers of 2 deposited at 9.3 mN/m (20 layers) and 31.3 mN/m (16 layers) together with the toluene solution.

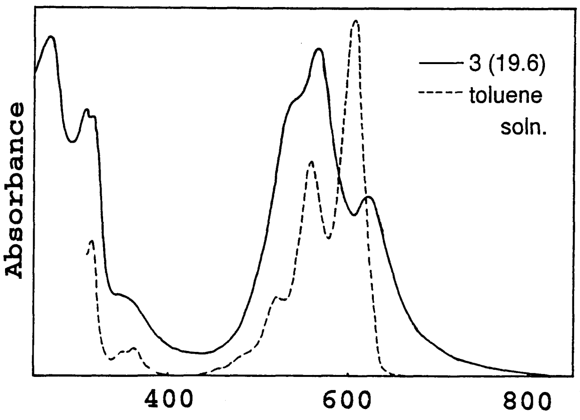

Fig.6. Electronic absorption spectra of multilayer of 3 deposited at 19.6 mN/m (20 layers) together with the toluene solution.

On the other hand, the angular dependence of IR spectra on inclination of the multilayers indicated that the transition moments due to CH_2 stretching were oriented almost parallel to the surface, that is, the hydrocarbon chains were oriented nearly perpendicular.

Thus, it has been found that well oriented LB films of carbazoledioxazine derivatives with the linear and angular type structures can be obtained. Further investigation on the other derivatives is in progress.

References

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