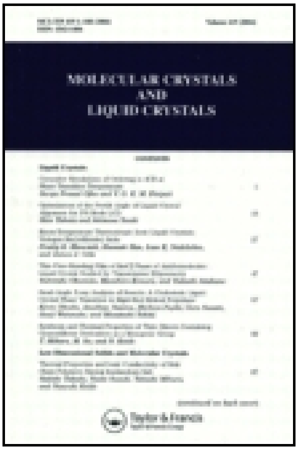

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ORIENTATION CONTROL AND PHOTOPHYSICAL BEHAVIORS IN LB FILMS OF LONG-CHAIN DERIVATIVE OF AMINO ACID CONTAINING AROMATIC RING

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Abstract *Using a long-chain derivative of amino acid containing* naphthalene, the arrangement of the chromophore in the LB films has been examined by circular dichroism (CD) together with UV absorption and fluorescence spectroscopies. The monolayer of N-stearoyl-L-lysyl-L-1-naphthylalanine methylester exhibits a transition from expanded to condensed states. For the LB films prepared at the surface pressures below and above the transition, polarized UV spectra suggest different orientations of the chromophore and also the CD spectra vary significantly of types and magnitude of a Cotton effect. These results were reflected in the fluorescence decay curves for the LB films.

INTRODUCTION

It is current topics in frontier science and technology to investigate on physical and chemical behaviors of molecular assemblies with well-defined orientation and packing of functional groups. Monolayer assemblying techniques have been widely extended to construct supramolecular systems for information-processing and biomolecular electronic devices.[1] Priviously, various orientations of chromophores were produced depending on the number and position of long-alkyl substituents[2,3] and also photo-active J-aggregates of long-chain dyes were formed in the mixed monolayers with various matrices.[4] And further, effects of the orientation and aggregation of chromophores on energy transfer in monolayer systems were clarified.[5,6] In addition, we have reported that the polycondensation of long-chain esters of amino acids proceeds easily in Langmuir-Blodgett (LB) films at room temperature without any initiation.[7] In this paper, using long-chain derivative of amino acid containing naphthalene, arrangements of the chromophore in the LB films have been examined by circular dichroism (CD) together with UV absorption and fluorescence spectroscopies, and these results were found to be reflected in the fluorescence decay curves for the LB films.

EXPERIMENTAL

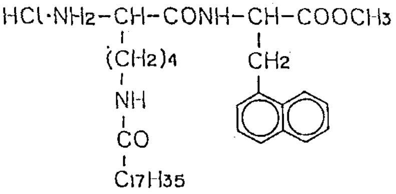
[Materials]

N-Stearoyl-L-lysyl-L-1-naphthylalanine methylester used in this work was synthesized as previously reported.[8]

$$\text{Boc-Lys(Z)} + \text{NapAla-OMe} \longrightarrow \text{Boc-Lys(Z)-NapAla-OMe}$$

$$\xrightarrow[\text{H}_2/\text{Pd}]{} \text{Boc-Lys-NapAla-OMe} \xrightarrow[\text{C}_{17}\text{COOH}/\text{DCC}]{} \text{Boc-Lys(C}_{18}\text{)-NapAla-OMe}$$

$$\xrightarrow[\text{HCl}/\text{DOX}]{} \text{HCl}\cdot\text{Lys(C}_{18}\text{)-NapAla-OMe}$$



[Procedures]

Monolayers of the long-chain derivative of amino acid were spread from chloroform solutions on double-distilled water, and surface pressure area (π- A) isotherms were measured by a Lauda film balance. UV absorption spectra of the monolayers on water were measured by a multichannel photodetector (Otsuka Electronics, MCPD-100) with reference to a spectrum obtained without the monolayer.

Multilayers of these compounds were deposited onto quartz or CaF_2 plates, precoated with a monolayer of ferric stearate, using the conventional LB method and the horizontal lifting method at various surface pressures. Mixed monolayers of the long-chain derivative of amino acid with stearic acid were also prepared by the LB method.

Polarized UV absorption spectra of the multilayers were measured with a Hitachi spectrophotometer (model 340) equipped with a Glan-Thomson prism. Fluorescence and polarized IR spectra of the multilayers were measured with a Hitachi fluorescence spectrometer (MPF-3) and a JEOL FT-IR spectrometer (JIR-100), respectively. CD spectra were obtained using a Jasco J-500A spectropolarimeter at room temperature. For CD measurements of the multilayers and cast films, the sample plates were rotated about the polarized light to remove the influence of linear dichroism. Fluorescence decay curves were measured by means of a picosecond time-correlated single photon counting system at room temperature.

RESULTS AND DISCUSSION

Figure 1 shows the π - A isotherms for the monolayer of the long-chain derivative of amino acid containing naphthalene, together with UV spectra of the monolayer at various surface pressures (in the insert). A phase transition from expanded to condensed states can be observed in the isotherms at a molecular area of 60 - 50 Å^2 and a surface pressure of about 25 mN/m. Taking into account the molecular dimension about(9.1 x 7.2 x 3.6 Å), the naphthalene ring seems to lie nearly flat in the expanded region, whereas on compression through the transition the chromophore stands up vertically to the water surface in the condensed state. In the UV spectra of the monolayer, the absorbance increases with the surface pressure, although band shifts are not observed with the monolayer compression.

The polarized UV spectra at 45° incidence for the LB films, prepared at 40 mN/m for an example, are shown in Fig.2 as compared with the solution spectrum. The bands at 228 nm and 286 nm which can be assigned to the electronic transitions along the long-axis (^1B_b) and the short-axis (^1L_a) of naphthalene, respectively, are slightly shifted from those of the solution. As indicated in the insert table, the dichroic ratios of the ^1B_b band with p- and s-

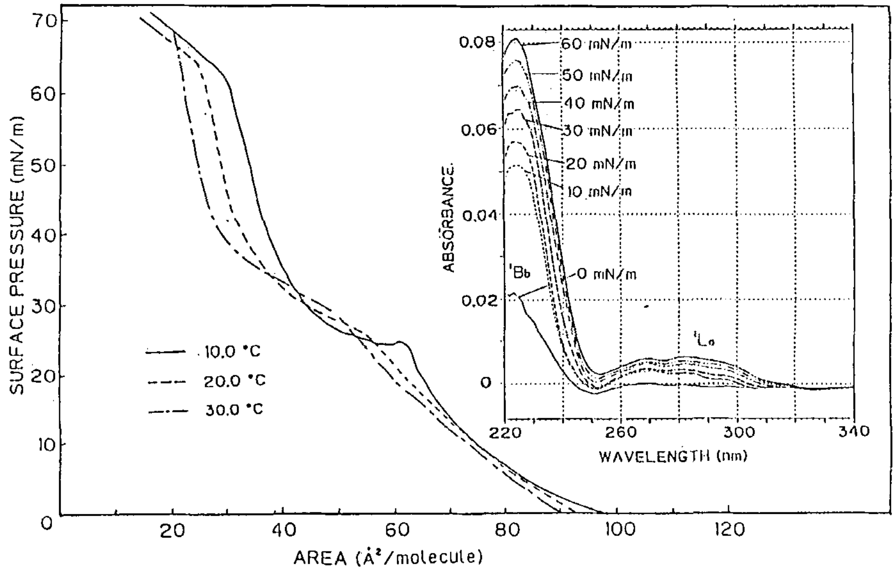
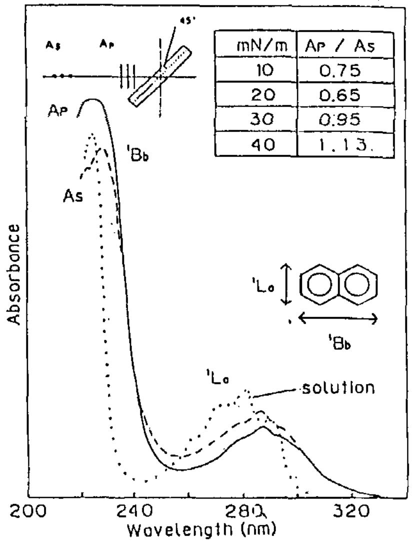


Fig.1. π- A isotherms and UV spectra for the monolayer of $HCl\cdot Lys(C_{18})$-NapAla-OMe.

polarized light are about 0.7 and 1.0 - 1.1 for the films prepared at the surface pressures below and above the phase transition, respectively. This result reflects that the chromophore is oriented with the long-axis parallel to the surface at the lower pressures, and it becomes perpendicular to the surface with increasing the surface pressure, as predicted from the π- A isotherms.



mN/m	Ap / As
10	0.75
20	0.65
30	0.95
40	1.13

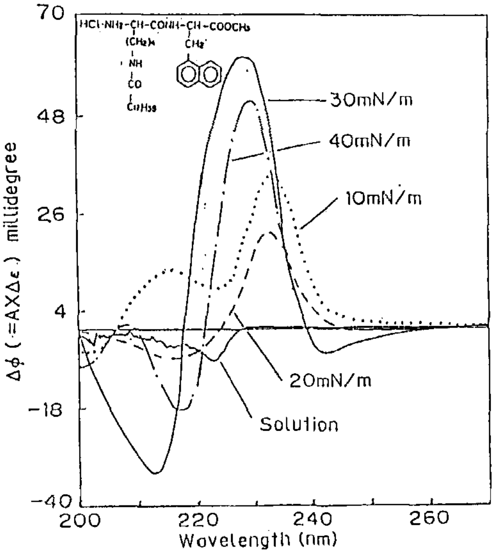


Fig.2. Polarized UV spectra of the LB film and the dichroic ratio at different deposition pressures.

Fig.3. CD spectra of the LB films prepared at different surface pressures.

Figure 3 shows the CD spectra of the Y-type LB films with a head-to-head structure, prepared at various surface pressures, in which a Cotton effect due to dipole-dipole interactions depends significantly on the deposition pressure. In the LB film prepared at 10 mN/m, weak Cotton effects associated with the amide band and the ^1B_b band of naphthalene are observed; in the film prepared at 20 mN/m a weak split Cotton effect is obtained. In the films prepared at 30 and 40 mN/m, strong split Cotton effects associated with the ^1B_b band are observed. This indicates that the molecular arrangement at the higher pressures differs from that at the lower pressures, and close-packing of the chromophores with strong interactions can be produced in the condensed region.

And further, as shown in Fig.4-a the X-type multilayer with a head-to-tail structure, prepared by the horizontal lifting method at 30 mN/m,

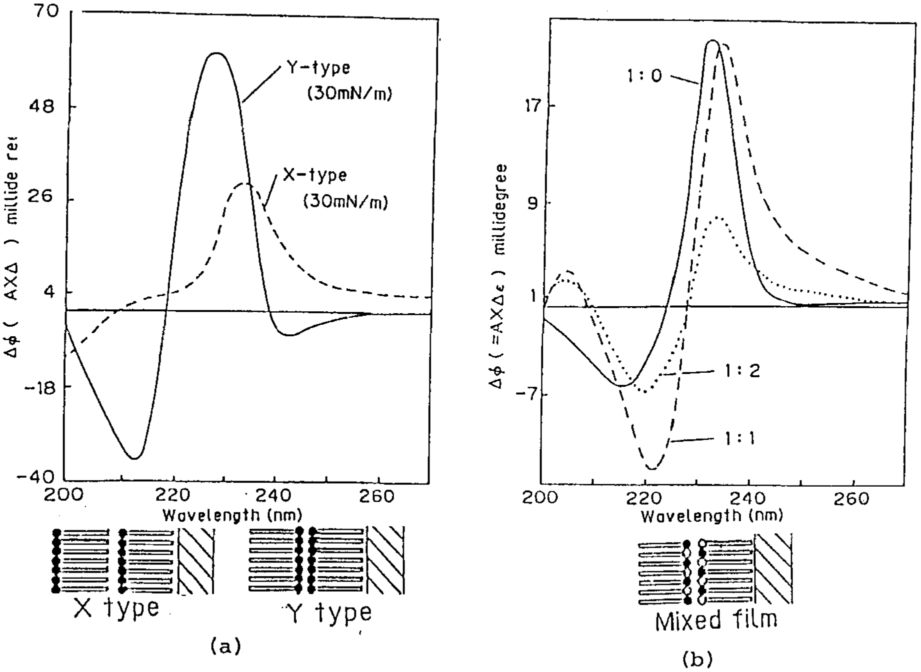


Fig.4. Effects of deposition types (a) and mixtures (b) on CD spectra of the LB films.

shows a weaker Cotton effect without splitting in comparison with the Y-type film despite of the similar UV spectra. It is considered that the Cotton effect in the Y-type films can be ascribed to the strong interlayer interaction of the π-electron system in addition to the intralayer interaction. In the mixed Y-type LB films with stearic acid, prepared at 20 mN/m, the Cotton effect is weakened except for the mixing ratio of 1:1, as shown in Fig.4-b. By mixing with stearic acid the chromophores are separated each other, but the equimolar mixture seems to induce the chromophores to be condensed by interaction of the long hydrocarbon chains.

The results of the polarized IR spectra indicated that the long hydrocarbon chains were oriented nearly perpendicular to the film plane. Consequently, it has been found that the orientation and packing of the chromophore can be controlled in the LB films by introducing a long alkyl chain into lysyl naphthylalanine. For an example, the molecular arrangement in the films prepared at the higher pressures is shown schematically in Fig.5.

Figure 6 shows the fluorescence decay curves observed at 335 nm for the LB films prepared at various surface pressures. In the films prepared at the higher pressures the lifetimes are obtained to be about 600 and 3500 ps. The more rapid component of 120 ps is found to be added to the above for the films at the lower pressures. The different arrangements of the chromophore have been well reflected in the photo-induced relaxation process for the layered systems.

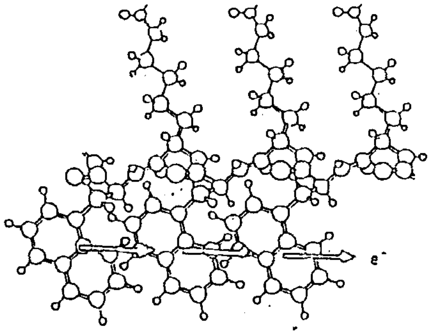


Fig.5. Molecular orientation of Lys(C_{18})-NapAla-OMe in LB films.

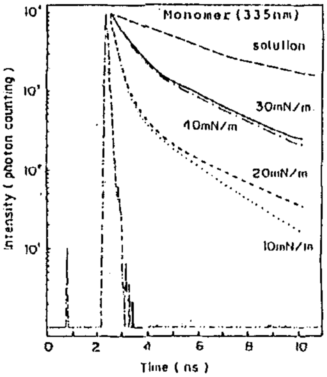


Fig.6. Fluorescence decay curves of the LB films prepared at different surface pressures.

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REFERENCES

1) H.Kuhn, Thin Solid Films, 178, 1 (1989).
2) H.Nakahara, K.Fukuda, J. Colloid Interface Sci., 69, 24 (1979).
3) H.Nakahara, K.Fukuda, J. Colloid Interface Sci., 93, 530 (1983).
4) H.Nakahara, H.Uchimi, K.Fukuda, N.Tamai, I.Yamazaki, Mol. Cryst. Liq. Cryst., 183, 345 (1990).
5) H.Nakahara, K.Fukuda, Thin Solid Films, 99, 45 (1983).
6) H.Nakahara, K.Fukuda, D.Möbius, H.Kuhn, J. Phys. Chem., 90, 6144 (1986).
7) K.Fukuda, Y.Shibasaki, H.Nakahara, Thin Solid Films, 160, 43(1988).
8) H.Nakahara, H.Endo, K.Fukuda, M.Sisido, Thin Solid Films, 178, 355 (1989).