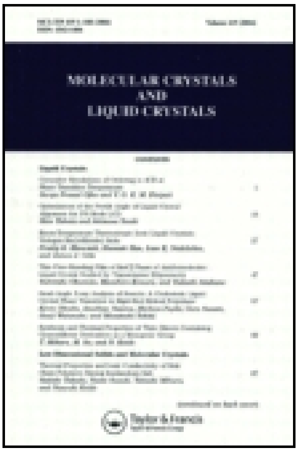

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A Study on the Styrylpyridunium Derivative Monolayer at the Air/Water Interface

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Trans and cis forms of N-alkyl-4-styrylpyridinium derivatives (C_nSP, n = 4, 8, 12, 16) were successfully synthesized and purified. The derivatives of styrylpyridinium cause photoisomerization when they illuminated with UV light. The pressure-area isotherms of C_nSP and their derivative were studied on the effect of alkyl chain length. The photoisomerization of C_nSP monolayers at the air/water interface was indirectly studied by measuring surface potential change with photoirradiation on the water surface. The characteristics of C_nSP were furthermore studied with surface pressure-area isotherm, Brewster Angle Microscopy (BAM) and optical diffraction efficiency.

Keywords: styrylpyridinium; photoisomerization ; Langmuir behavior

INTRODUCTION

The introduction of a nitrogen atom in the ring noticeably affects the photophysical and photochemical behavior of stilbalzol probably because of the invlovemenet of n,π* states in the reaction mechanism.[1] The photoreactive response of alkylstyrylprydinum derivatives at the air/water interface was studied with surface pressure-area isotherm and BAM in the Langmuir trough. The Langmuir-Blodgett (LB) technique offers a convenient way to organize molecules in two-dimensional surface, both at the air/water interface and on the solid substrates. Through the control of variables such as surface pressure, subphase composition, nature of amphiphilic groups and the nature of substrate, it is possible to manipulate the orientation, aggregation and surface density of chromophores in the monolayer and styrylpyridinium derivatives have been studied on the optical diffraction efficiency in the ultrathin film by Langmuir-Blodgett technique.

EXPERIMENT

N-alkyl-4-styrylpyridinium derivatives were synthesized as the procedure described before.[2] For the experimental set-up of UV-vis spectrophotometer for characterization of photoisomerization of purified trans-styrylpyridinium derivative, a 2 mM chloroform stock solutions of styrylpyridinium derivatives were stored in the dark more than 1 day to keep the trans form of styrylpyridinium. The trans isomer composition of 2 mM chloroform stock solutions of styrylpyridinium derivatives were changed into cis isomer with changing the irradiation time of UV light (365 nm, 10 mW, Spectronics Coperation) on the sample solution in quartz cuvette. The concentration of the cis isomer in solution was determined from the absorption spectra. The surface pressure isotherms were measured on the subphase of pure water with KSV 2000 at the subphaes temperature of 5°C. BAM images were recorded with BAM 2 Plus on the trough of KSV 2000 system.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra changes of the styrylpyridinium derivative by photoirradiation of UV light (365 nm). The absorption spectra of styrylpyridinium derivative were characterized by a strong short wavelength (π, π*) band at $220 < \lambda < 250$ nm and long wavelength band at $320 < \lambda < 360$ nm. On increasing irradiation

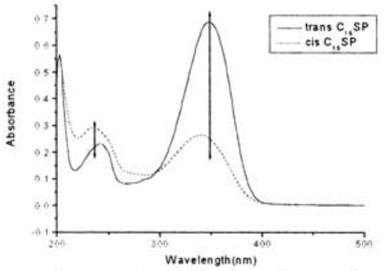
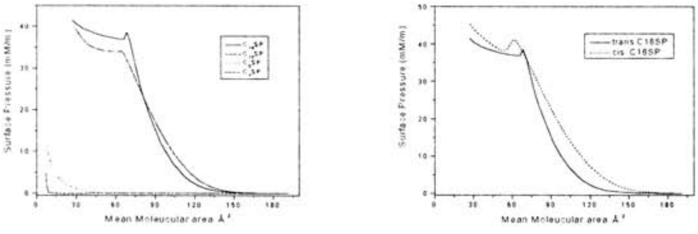


Figure 1. UV-vis absorption spectra of 2×10^{-4} M chloroform solution of C_{16}SP versus UV light (365 nm) irradiation time

time with UV light of 365 nm, the peak intensity at 356 nm (π, π*) decreases and the peak intensity at 240 nm increases. This is due to photoisomerization from trans isomers to the cis isomers. The spectral conversion from trans form to cis form in chloroform solution was completed in 11 s and cis form was not reconverted to trans form at dark state for 5 day.

Figure 2 (a) shows surface pressure-area isotherms of the styrylpyridinium derivative with different alkyl chain length. C_4SP and C_8SP could not form the stable monolayer because of high solubility in the water. But C_{16}SP and C_{12}SP resulted in the stable monolayer at the air/water interface. The limiting areas of monolayers of C_{16}SP and C_{12}SP were 105 Å^2 and 120 Å^2, respectively. Figure 2 (b) shows the surface pressure-area isotherms of cis and trans form of C_{16}SP. The cis and trans monolayers were stable up to 37 mN/m of surface pressure.The difference of limiting area between trans and cis form was about 15 Å^2 as shown in Figure 2 (b). This indicates that the cis form of styrylpyridinium had more expanded surface structure at the air/water interface.

To obtain an insight intrinsic optical properties of the C_{16}SP monolayer,



(a) (b)

Figure 2. Surface pressure isotherm of styrylpyridinium derivatives with different alkyl chain (a) and trans (¯) and cis (˙˙) C_{16}SP monolayer (b) at the air/water interface·

Figure 3. BAM images of trans styrylpyridinium derivative (C_{16}SP) versus increasing of surface pressure at the air/water interface

The dark field background is the surface of water and bright spots is the optically active molecule of C_{16}SP. The trans C_{16}SP monolayer at 0 mN/m exhibited a dark image. As the surface pressure was increased, the BAM images of C_{16}SP monolayer showed a bright image by the enhanced light reflections because of the higher molecular density of C_{16}SP on the water surface. As shown in BAM images of Figure 3, C_{16}SP monolayer tends to be partially aggregated state with each other from the surface pressure of 30 mN/m.

The different optical diffraction of styrylpyridunium derivatives between cis and trans forms was represented by the reversible cis-trans photoisomerization with respect to the C=C double bond of styryl group. The styrylpyridunium derivatives film onto the quartz plate showed fringe contrast in a spatially varying intensity pattern and the maximum diffraction efficiency of 0.12%.

Acknowledgments

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References

1. D. G. Whitten and M. T. Mccall. *J. Am. Chem. Soc.*, **91**, 5097 (1969)
2. K. W. Seo, D. J. Lee, Y. P. Hong and Y. S. Kang. JKIEE, In press (2001)
3. P. Bortolus, G. Favaro, and U. Mazzucato, *Mol. Photochem.*, **2**. 311 (1970)
4. P. Zarnegar, C. R. Bock, and D. G. Whitten, *J. Am. Chem. Soc.*, **95**, 4367(1973)