

# Photoisomerization of Styrylpyridinium Derivatives for Optical Memory

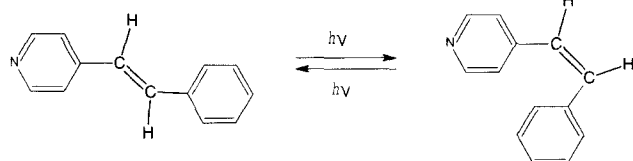
Young-Soo Kang, Kyong-Won Seo, Dong-Jae Lee and Yong-Pyo Hong

**Abstract** - The trans and cis forms of N-alkyl-4-styrylpyridinium derivatives (CnSP:  $n = 4, 8, 12, 16$ ) were successfully synthesized and purified. The derivatives of styrylpyridinium cause photoisomerization when they are illuminated with UV light. We investigated the photoisomerization of the styrylpyridinium derivatives at the air/water interface for holographic memory. The pressure-area isotherms of CnSP and their derivatives were studied to reveal the effect of alkyl chain length. The photoisomerization of CnSP monolayers at the air/water interfaces was indirectly studied by measuring surface tension changes with photoirradiation on the water surface. The characteristics of CnSP were furthermore studied with UV-vis, surface pressure-area isotherms, surface potential-area isotherms, Brewster Angle Microscopy (BAM) at the air/water interface, and optical diffraction efficiency on the ultrathin films.

**Keywords** - styrylpyridinium, photoisomerization, optical memory

## 1. Introduction

The introduction of a nitrogen atom in the ring noticeably affects the photophysical and photochemical behavior of stilbalzol, probably because of the involvement of  $n, \pi^*$  states in the reaction mechanism. Stilbalzol was photoisomerized from trans to cis forms as shown in Fig. 1.



**Fig. 1** Photoisomerization of the cis and trans isomers of stilbalzol.

The Langmuir-Blodgett (LB) technique offers a convenient way to organize molecules in two-dimensional surfaces, both at the air/water interfaces and on the solid substrates. Through the control of variables such as surface pressure, subphase composition, the nature of amphiphilic groups and substrates, it is possible to manipulate the orientation, aggregation and surface density of chromophores in the monolayer. In this paper, styryl-pyridinium derivatives have been synthesized and studied.

## 2. Experimental

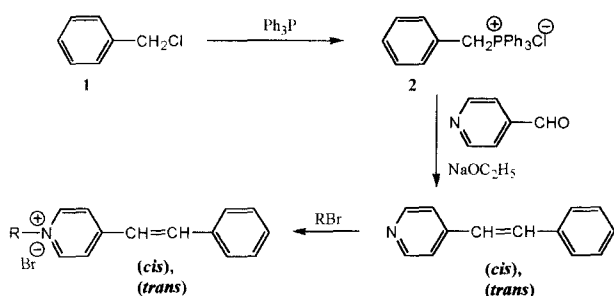
A solution of benzyl chloride (86.9 mmol) in xylene (200 mL) was mixed with  $\text{PPh}_3$  (113 mmol) and followed by refluxing at  $170^\circ\text{C}$  for 7 h. The resulting solution was cooled to  $60^\circ\text{C}$  and then, the white solid was filtered, and washed with xylene (20 mL). The white product was obtained with 92% yield after drying. Continuously, to a mixed solution of benzyltriphenylphosphonium chloride (59.1 mmol) and 4-pyridinecarboxaldehyde (65.0 mmol) in ethanol (100 mL), 65 mL of 1.0 M sodium ethoxide (65.0 mmol) was added and stirred. After stirring for 20 min at room temperature, the solid was filtered off, and the solution was concentrated in vacuo. The residue was purified by column chromatography (silica, 50% of ethyl acetate in hexane) to give cis-4-styrylpyridine (33.2%) and trans-4-styrylpyridine (30.3%). A solution of trans-4-styrylpyridine (5.52 mmol) and 1-bromoalkane (6.63 mmol) in acetone (25 mL) was refluxed at  $70^\circ\text{C}$  for 2 days. The reaction mixture was cooled to room temperature and resulted in a white solid. The solid was collected by filtration, and washed with cold acetone (5 mL). After recrystallization from acetone, 2.1 g (67%) of trans-4-butylstyrylpyridinium was obtained. The cis form of 4-butylstyrylpyridinium was obtained by following the same procedure as the trans form of 4-butylstyrylpyridinium.

In the experimental set-up of the UV-vis spectrophotometer for the characterization of the photoisomerization of purified trans-styrylpyridinium derivatives, a 2 mM chloroform stock solution of styrylpyridinium derivatives was stored in the dark more than 1 day to keep the trans form of styrylpyridinium. The trans isomer composition of the 2 mM chloroform stock solution of styrylpyridinium derivatives was changed into a cis isomer with

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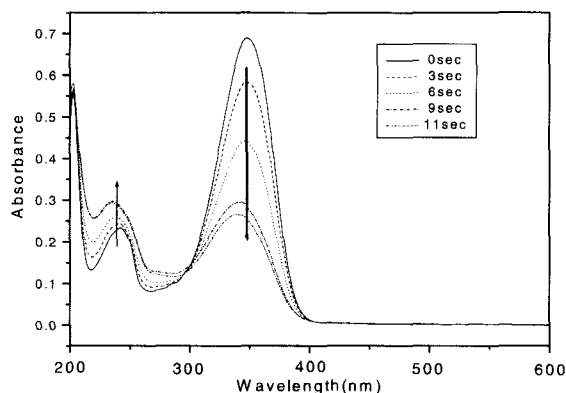


**Fig. 2** Synthetic procedure of styrylpyridinium derivatives.

changing the irradiation time of UV light (365 nm, 10 mW, Spectronics Corporation) on the sample solution in a quartz cuvette. The concentration of the cis isomer in the solution was determined from absorption spectra. The absorption spectra in the solutions were measured using a Varian Cary UV-vis Spectrophotometer. The solutions of styrylpyridinium derivative concentration ( $\epsilon_0 = 2 \times 10^{-4}$  M) was illuminated in a sealed quartz cuvette at room temperature.

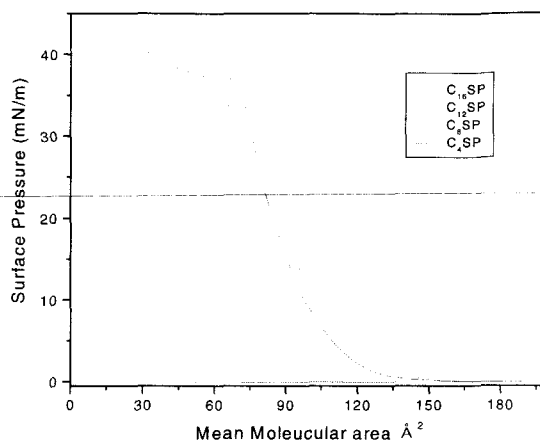
### 3. Results and Discussion

Fig. 3 shows the absorption spectra changes of the styrylpyridinium derivatives by the photoirradiation of UV light (365 nm). The absorption spectra of styrylpyridinium derivatives were characterized by a strong short wavelength ( $\pi, \pi^*$ ) band at  $220 < \lambda < 250$  nm and a long wavelength band at  $320 < \lambda < 360$  nm. On increasing irradiation time with UV light of 365 nm, the peak intensity decreases at 356 nm ( $\pi, \pi^*$ ) and the peak intensity increases at 240 nm. This is due to photoisomerization from trans isomers to the cis isomers. The spectral conversion from trans forms to cis forms in the chloroform solution was completed in 11 s and cis forms weren't reconverted to trans forms in dark state for

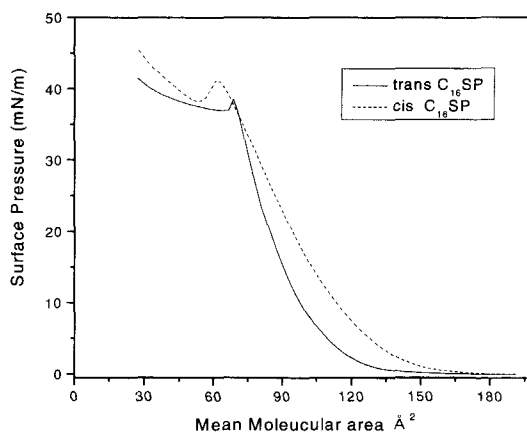


**Fig. 3** UV-vis absorption spectra of the  $2 \times 10^{-4}$  M chloroform solution of  $C_{16}SP$  versus UV light (365 nm) irradiation time.

5 days. In selection rules, the  $n \rightarrow \pi^*$  transition for the trans form of styrylpyridinium is forbidden. But the  $n \rightarrow \pi^*$  transition is allowed for the cis form of styrylpyridinium due to the non-planar distortions and vibrational coupling of the cis form.



(a)



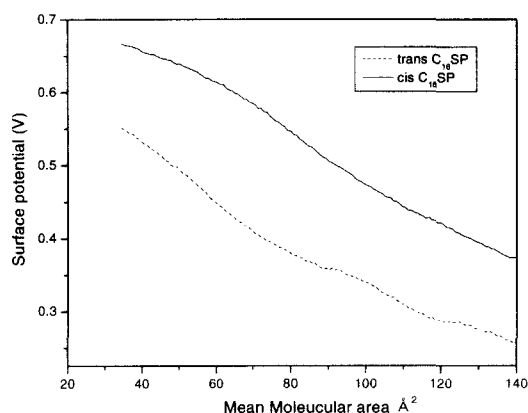
(b)

**Fig. 4** Surface pressure - isotherms of styrylpyridinium derivatives with different alkyl chains (a) and trans (—) and cis (···)  $C_{16}SP$  monolayers (b) at the air/water interfaces.

Fig. 4 shows the monomolecular film organization of the styrylpyridinium derivatives at the air/water interface. Fig. 4 (a) shows the surface pressure-area isotherms of the styrylpyridinium derivatives with different alkyl chain length.  $C_4SP$  and  $C_8SP$  could not form the stable monolayer because of high solubility in water. But  $C_{16}SP$  and  $C_{12}SP$  resulted in the stable monolayer at the air/water interface. The limiting areas of the monolayers of  $C_{16}SP$  and  $C_{12}SP$  was  $105 \text{ \AA}^2$  and  $120 \text{ \AA}^2$ , respectively. Fig. 4 (b) shows the surface pressure-area isotherms of cis and trans form of  $C_{16}SP$ . The cis and trans forms have different conformations at the air/water interface and resulted in the different degrees of

expansion on the water surface because of the monomolecular packing structure. Thus, the trans-cis isomerization process leads to structural changes in the monolayer. The cis and trans monolayers were stable up to 37 mN/m of surface pressure. The limiting area of the trans and cis forms was  $105 \text{ \AA}^2$  and  $120 \text{ \AA}^2$ , respectively. The difference of the limiting area between trans and cis forms was about  $15 \text{ \AA}^2$  as shown in Fig. 4 (b). This indicates that the cis form of styrylpyridinium had more expanded surface structure at the air/water interface.

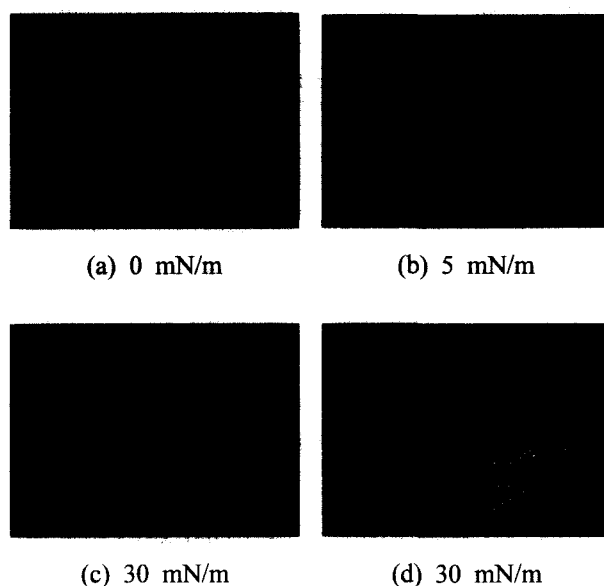
The surface potential of the monolayer at the air/water interface is concerned with the alkyl chain flip of  $C_{16}SP$  from parallel to perpendicular orientation by barrier compression. The surface potential difference by the head group charge and subphase composition was negligible because of the almost same factors between cis and trans isomers. Thus, the difference is due to the dipole moment change of chromophores by the orientation of the alkyl chain. In the initial state of barrier compression, the surface potential of cis isomers was higher than that of trans isomers because of the intrinsic higher dipole moments of cis isomers. This is shown in Fig. 5. After the stock solution is spread,  $C_{16}SP$  forms islands. As the barrier was compressed, the alkyl chain orientation of  $C_{16}SP$  was varied from water surface to the perpendicular alignment to the surface. This alkyl chain orientation change of the trans form of  $C_{16}SP$  showed the higher rate than the cis form of  $C_{16}SP$ .



**Fig. 5** Surface potential-area isotherms of trans (—) and cis (···)  $C_{16}SP$  monolayers at the air/water interface.

To obtain an insight intrinsic optical properties of the  $C_{16}SP$  monolayer, BAM images were taken in correlation with the surface pressure-area isotherms. The dark field background is the surface of water, and bright spots are the optically active molecule of  $C_{16}SP$ . The trans  $C_{16}SP$  monolayer at 0 mN/m exhibited a dark image. As surface pressure was increased, the BAM images of the

$C_{16}SP$  monolayer showed bright images by the enhanced light reflections because of the higher molecular density of  $C_{16}SP$  on the water surface. As shown in the BAM images of Fig. 6, the  $C_{16}SP$  monolayer tends to be partially aggregated with each other from the surface pressure of 30 mN/m. As the barrier was compressed, the size of spots increased and the spots appeared to be brighter in BAM images because of the higher molecular density due to aggregation. The BAM images of the cis  $C_{16}SP$  (Fig. 6 (d)) monolayer showed similar patterns compared with its trans isomers and showed higher optical reflection at the air/water interface than the trans  $C_{16}SP$  monolayer because of the greater dipole moment of cis forms.



**Fig. 6** BAM images of trans styrylpyridinium derivatives ( $C_{16}SP$ ) versus increasing surface pressure at the air/water interface: (a), (b), (c) and cis styrylpyridinium derivatives at 30 mN/m:

The different optical diffraction of styrylpyridinium derivatives between cis and trans forms was represented by the reversible cis-trans photoisomerization with respect to the C=C double bonds of the styryl group. The mechanism of biphotonic holographic storage is attributed by the excitation of both the short-wavelength light and the long-wavelength light. The styrylpyridinium derivatives films onto the quartz plate showed a fringe contrast in a spatially varying intensity pattern and the maximum diffraction efficiency of 0.12%. The styrylpyridinium derivative films showed a rewritable process by the absorption of the selected wavelength light, and the process of photoisomerization was accomplished in the moment of laser irradiation.

#### 4. Conclusions

Styrylpyridinium derivatives were successfully synthesized. They were converted from trans to cis forms by 365 nm UV light irradiation. The cis isomers of styrylpyridinium derivatives at the air/water interface showed higher mean molecular areas than trans isomers at the specific surface pressure because of more expanded structures. The monolayers of the styrylpyridinium derivatives showed different pressure-area isotherms by alkyl chain length of them. After spreading a stock solution to the styrylpyridinium derivatives at the air/water interface, the surface potential of cis isomers was found higher than that of trans isomers because of higher intrinsic dipole moments of cis isomers. The BAM images of the trans styrylpyridinium derivative monolayers showed partial aggregation above 30 mN/m of the surface pressure at the air/water interface. While the BAM images of C<sub>16</sub>SP showed an homogeneous pattern correlation with the surface pressure, the BAM images of the cis isomers of the styrylpyridinium derivative monolayers were to be distinguished with their trans isomers due to higher intrinsic dipole moments of the cis forms of C<sub>16</sub>SP. The spin coated styrylpyridinium derivative films showed the diffraction efficiency of 0.12 %.

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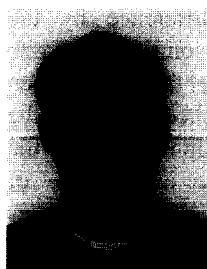


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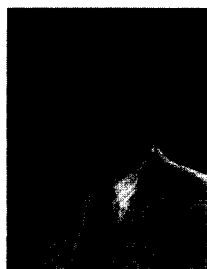
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