Characterization of Spironaphthooxazine Derivative Thin Films for Optical Memory

Young-Soo Kang, Sang-Do An, Ju-Seog Jang, Byung-Kyu Kim and Yong-Joo Kim

Abstract - The derivatives of spironaphthooxazine cause photoisomerization when they are illuminated with UV light. We investigated the photoisomerization of spironaphthooxazine derivatives for holographic memory. Langmuir-Blodgett (LB) films contain amphiphile spironaphthooxazine derivatives which can be applied in molecular devices by a change of molecular level energy and a refractive index. In order to investigate the photoisomerization of spironaphthooxazine derivatives at the air/water interfaces, spironaphthooxazine derivatives with side alkyl chains were synthesized. The films of the spironaphthooxazine derivatives were characterized by the measurement of UV/vis spectroscopy, Brewster Angle Microscopy (BAM) and Atomic Force Microscopy (AFM). The monolayers of the spironaphthooxazine derivatives mixed with stearic acid were stable at the air/water interface and visualized by the measurement of BAM. The spironaphthooxazine derivative monolayers on the glass surface showed the maximum efficiency of diffraction as 0.99% by the measurement of holography.
Key Words - organic thin films, optical memory

1. Introduction

The photoisomerization of spironaphthooxazine deriva - tives has received considerable attention over the past few years because of the potential applicability in such areas as high-density optical memory elements and molecular switching devices.[1-2] The isomerization process of the spironaphthooxazine derivatives between the spironaphthooxazine form and merocyanine forms as shown in Fig. 1 has been investigated both in a solution and in thin films on the solid substrate. The langmuir

Spironaphthooxazine Form   Merocyanine Form

Fig. 1 Photoisomerization of spironaphthooxazine deriva - tives.

monolayer technique offers a convenient way to organize molecules in two-dimensional surfaces, both at the air/water interfaces and on the solid substrates. In this paper, amphiphilic spironaphthooxazine derivatives with side alkyl chains have been synthesized and studied by preparing ultra-thin organic films.[3-5]

2. Experimental

2.1 Materials

2.1.1 Preparation of 1-alkyl-3,3-dimethyl-2-methylene indoline

A mixed solution of 2,3,3-trimethyl indoline (0.48g, 3 mmol) in 1 mL of hexane (Fisher's base derivative) and alkyl bromide (0.6g, 3 mmol) was refluxed at 60~70 °C for 3 days. The mixture was cooled and evaporated. The mixture was then filtered, dried and recrystallized from ethanol. Yield: 40%, TLC: Rf = 0.6 with an eluent solution (ethyl acetate: hexane = 1: 1). And 1-alkyl-2,3,3-trimethyl indolenium bromide produced from the mixture was mixed with 4% of an NaOH aqueous solution by dropwise. The solid mixture was then filtered, dried and recrystallized from chloroform. The 1-alkyl-3,3-dimethyl-2-methylene indoline obtained from the solid mixture is a pink colored liquid.

2.2.2 Preparation of spironaphthooxazine derivatives

A mixed solution of 1.14 g (6.6 mmol) of 1-nitroso-2-naphthol in 170 mL of ethanol or hexane was added into the synthesized 1-alkyl-3,3-dimethyl-2-methylene indoline (6.6 mmol) solution by dropwise and refluxed for 3 days. The precipitate was dissolved by acetone and
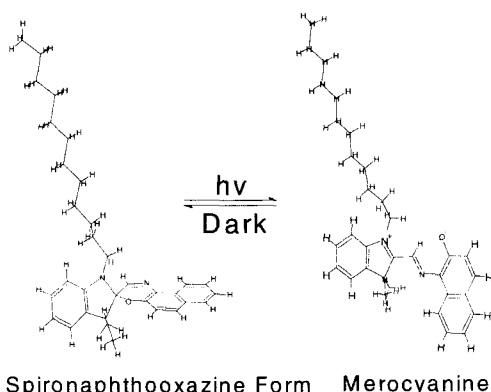
was recrystallized from ethanol.

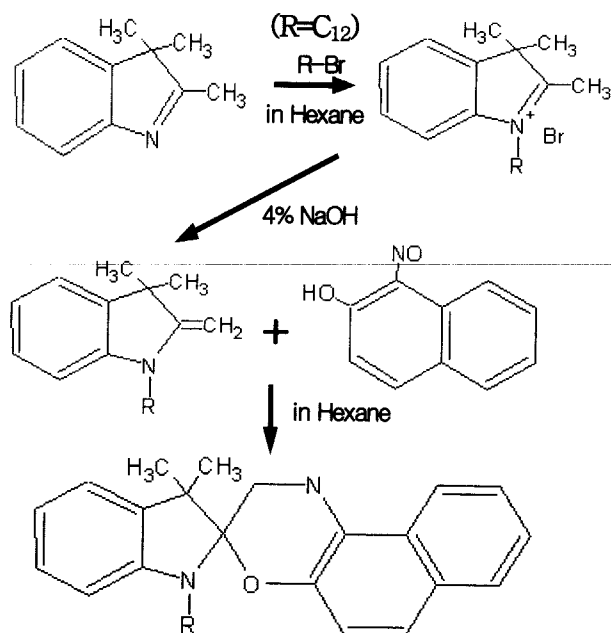The synthetic procedure of the spironaphthooxazine derivatives is shown in Fig. 2.

Fig. 2 Synthetic procedure of spironaphthooxazine derivatives.

2.2 Methods

In the experimental set-up of UV/vis spectrophotometer for the photoisomerization of the spironaphthooxazine derivatives, 1 mM acetone solution of the spironaph-thooxazine derivatives was stored in the dark more than 1 day. The spironaphthooxazine form isomer composition of the 1 mM acetone stock solution of the spironaph-thooxazine derivatives was changed into a merocyanine form isomer with changing irradiation time of UV light (230 < λ < 420 nm, 10 mW, Spectronics Coperation) on the sample solution in a quartz shell. The concen-tration of the merocyanine isomer in solution was determined from absorption spectra. The absorption spectra in the solution were measured by using a Varian Cary UV/vis spectrophotometer. The solution of spironaphthooxazine derivative concentration (ε o = 3 × 10^{-5} M) was illuminated in a sealed quartz shell at room temperature. In the experimental set-up of a Brewster Angle Microscope (BAM; Nanofilm Tech, Germany) for the characterization of spironaphthooxazine derivative monolayers and interfacial processes, the light beam of a pulsed laser (λ = 532 nm, beam diameter: 1 mm) passed a polarizer set for p-polarization and was put on the monolayer of the spironaphthooxazine derivatives at the air/water interfaces at the Brewster angle (53.15°). The reflected beam was detected using a CCD camera. Also the sample deposited on the mica plat by the L-B

technique was measured to get surface images by Atomic Force Microscopy (AFM; MMAFM, Digital Instrument Int, Tapping mode, image size 1,000 nm^2). To measure the induced optical diffraction, thin films of the spironaphthooxazine derivatives were prepared by the spin coating of its acetone solution onto a clean glass slide. The film was allowed to dry at room temperature in a desiccator. The optically induced diffraction was measured by placing the sample between two crossed linear polarizers as shown in Fig. 3. A coherent beam from the laser is divided by a 50% beam splitter into two beams, a reference beam and a signal beam.
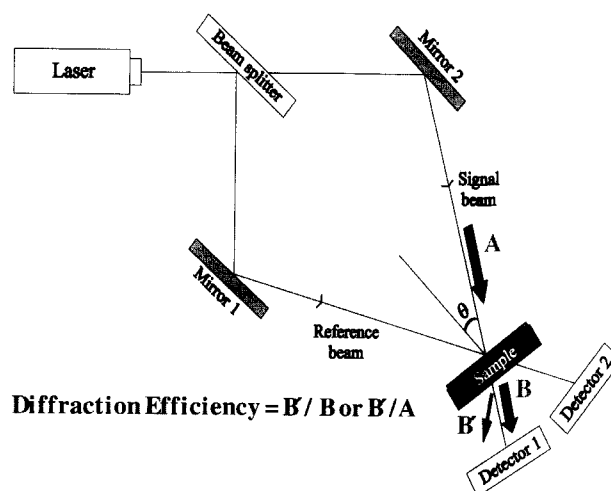

Diffraction Efficiency = B′ / B or B′ /A

Fig. 3 The experimental set-ups for optical diffraction.

The spatially modulated signal beam is focused on the sample on the glass plate so that the reference beam and the signal beam overlap spatially on the sample at the optimum angle of about 5°. In this experimental technique, the reference beam acts as a reading beam to read the holographic information recorded by the interference of the two input as 633 nm beams. Optical diffraction was induced by the spironaphthooxazine derivatives films using a polarization argon beam at 488 nm (intensity of 90 mW/cm^2) to write on. Film thickness is 10 μ m. The photoinduced birefringence was erased by the irradiation of an He-Ne laser at 633 nm.

3. Results and Discussion

Fig. 4 shows the absorption spectra change of the spironaphthooxazine derivatives by photoisomerization. The absorption spectra of the spironaphthooxazine derivatives were characterized by a strong short wavelength (π, π^*) band at the wavelength of 240 < λ < 260 nm. The spironaphthooxazine derivative was converted to the merocyanine form by 230 < λ < 420 nm light irradiation.
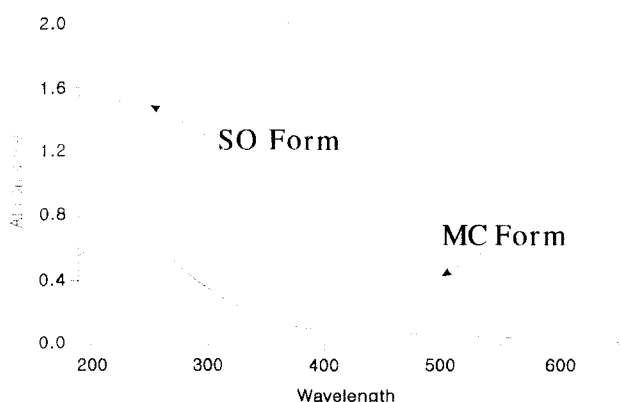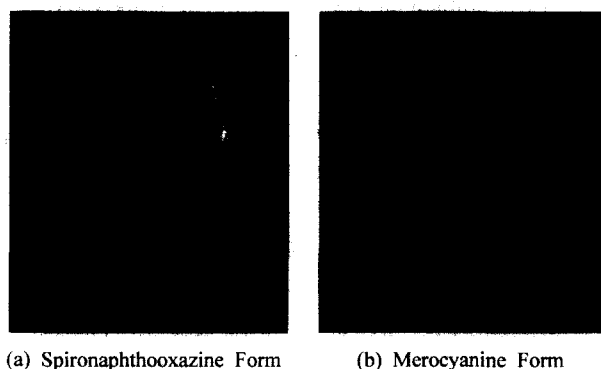
Fig. 4 UV-vis spectra of spironaphthooxazine derivative solutions in CH_2Cl_2. The solid line is the spironaphthooxazine form and dot line the merocyanine form.

The BAM images of the spironaphthooxazine deriva- tives as shown in Fig. 5 were taken in correlation with surface pressure. The BAM images of the spironaph- thooxazine derivative monolayer at the air/water interface showed the homogeneous pattern. Also they showed a brighter pattern with increasing surface pressure up to 15 mN/m. This indicates that the spironaphthooxazine forms an homogeneous stable monolayer well up to approxi- mately 15 mN/m and thereafter the collapsed monolayer disturbs the homogeneous reflection of the laser beam at the air/water interfaces. The monolayer of the spirona- phthooxazine derivatives at the air/water interfaces started to be folded by wrinking above the surface pressure of 46 mN/m.


(a) 0 mN/m   (b) 2 mN/m

(c) 15 mN/m   (d) 46 mN/m
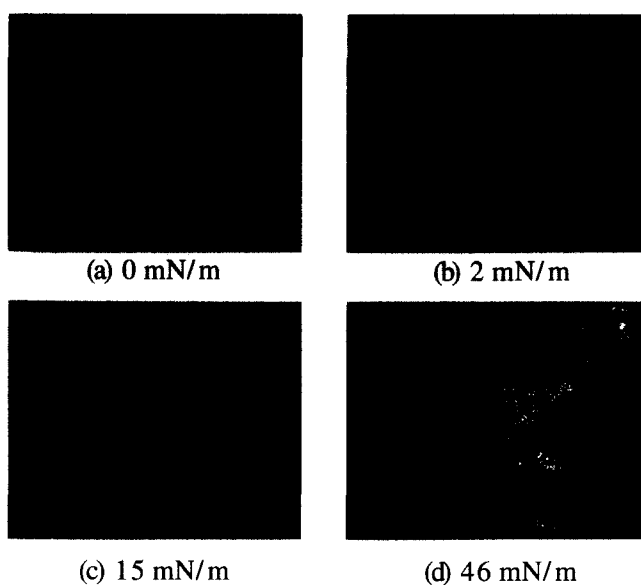
Fig. 5 BAM images of the spironaphthooxazine deriv- ative monolayers versus increasing surface pres- sure at the air/water interfaces (image size: 430 × 320μm).

The BAM images as shown in Fig. 6 were obviously different between the spironaphthooxazine form and the merocyanine form because of their different refractive indexes. As the spironaphthooxazine form was converted to the merocyanine form with UV/vis light (230 < λ < 420 nm, 10 mW, Spectronics Coperation) irradiation, the BAM images of the monolayer became dark. Due to the lower reflectivity of the spironaphthooxazine form than the merocyanine form, the BAM images of the spironaphthooxazine form showed darker images than those of the merocyanine form at the same surface pressure.

(a) Spironaphthooxazine Form   (b) Merocyanine Form

Fig. 6 BAM images of spironaphthooxazine form (a) and merocyanine form (b) at the surface pressure of 2 mN/m. (a) is initial and (b) is after 1 min UV light irradiation (230 < λ < 420nm, 10mW, Spec- tronics Coperation) (image size: 430 × 320 μm).

The three-demensional AFM images of spironaph- thooxazine form and merocyanine form are shown in Fig. 7. The AFM images of the spironaphthooxazine derivative show the more irregular and rough surface structure than the merocyanine form.
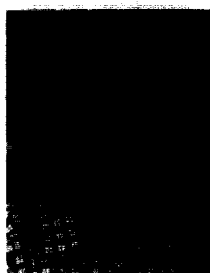

(a) Spironaphthooxazine Form   (b) Merocyanine Form
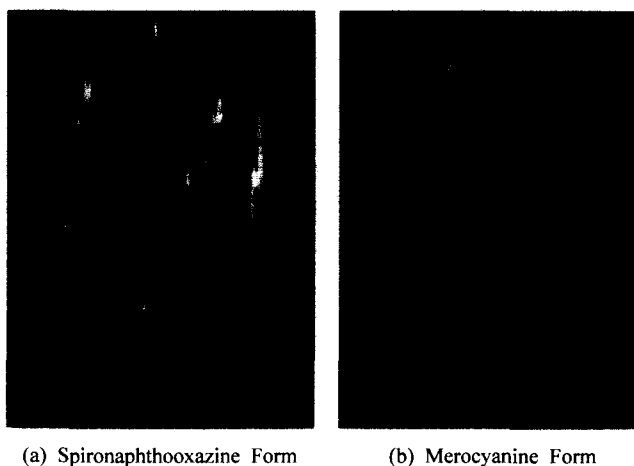
Fig. 7 AFM images of the spironaphthooxazine deriva- tives films. (a) spironaphthooxazine film, (b) merocyannine film on the mica plate deposited by the L-B technicque.

The spironaphthooxazine derivative film on the glass slide showed the maximum efficiency of diffraction as 0.99% by the measurement of holography.

Acknowledgment

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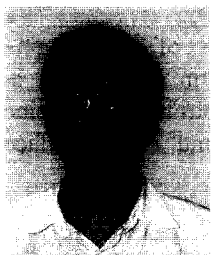
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