Photochromic Reaction of Spirobenzoselenazopyrans with Long-chains in Monolayers on Water Surface

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For long-chain derivatives of spirobenzoselenazopyran the photochromic reactions in monolayers on water surface have been investigated and effects of the molecular packing upon the reaction were clarified in comparison with the reactivities at different surface pressures as well as those in the solution.

Spiropyrans have been extensively studied on photochromic reactions in solutions and thin films.[1] Spiropyran derivatives containing selenium instead of sulphur were previously synthesized,[2,3] which show negative photochromic behaviors in solutions. Recently, control of photochemical reactions in monolayers or monolayer assemblies formed by the Langmuir-Blodgett method has been an interesting subject for optical memory devices.[4,5] In the present work, using spirobenzoselenazopyrans with long alkyl chains we have investigated the effects of the molecular packings upon the photochromic reactions in monolayers on water surface.

Long-chain derivatives of spirobenzoselenazopyrans and their colored merocyanine forms together with the abbreviations used in this work are shown in Figure 1, which were synthesized according to the method previously reported.[3] These structures were characterized by ^{1}H-NMR, IR and elemental analyses. Monolayers were spread from the benzene solutions onto the distilled water surface and the surface pressure - area (π - A) isotherms were measured by using a Lauda film balance.

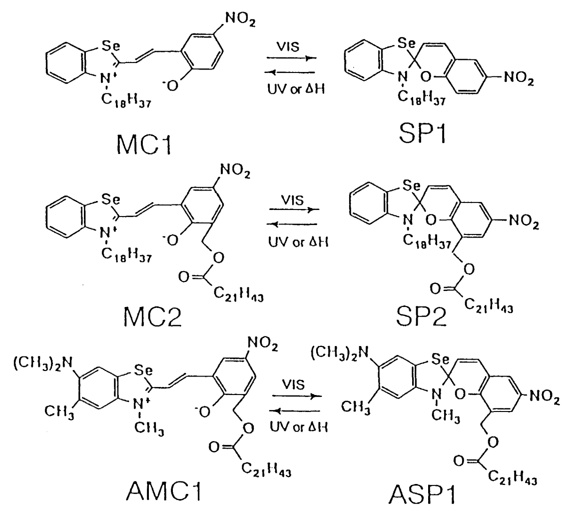

Figure 1. Spirobenzoselenazopyrans with long-chains and their merocyanine forms together with the abbreviations.

UV-Vis. absorption spectra of the solution and the monolayer were measured with a spectrophotometer (Hitachi, U-3210) and multichannel photodetector (Otsuka Electronic Co., MCPD-1), respectively.

Spectral changes accompanied with the photochromic reaction of MC1 $\rightleftarrows$ SP1 in the solution (mixture of ethanol and hexane, 3 : 2 v/v) under irradiation of light (500 W Xe lamp at a distance of 40 cm) above 500 nm or dark and thermal condition, are shown in Figure 2. With the other derivatives the similar spectral changes with the photochromic reactions of MC2 $\rightleftarrows$ SP2 and AMC1 $\rightleftarrows$ ASP1 in the solutions, were observed. From change of the absorbances at the visible band, the rates of the MC $\rightarrow$ SP reaction under the photoirradiation at 0 °C and the

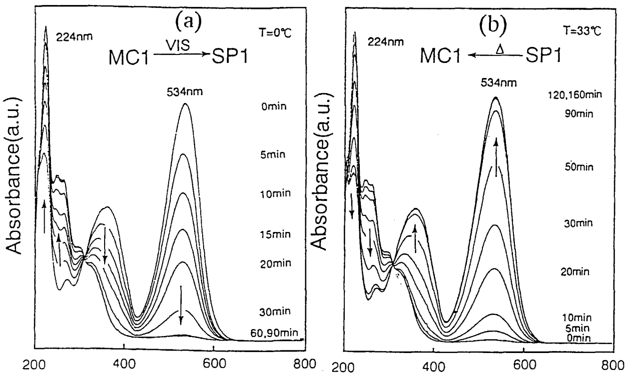

Figure 2. Spectral changes in solutions accompanied with (a) the MC1 $\rightarrow$ SP1 reaction at 0 °C under photoirradiation and (b) the SP1 $\rightarrow$ MC1 under dark and thermal condition.

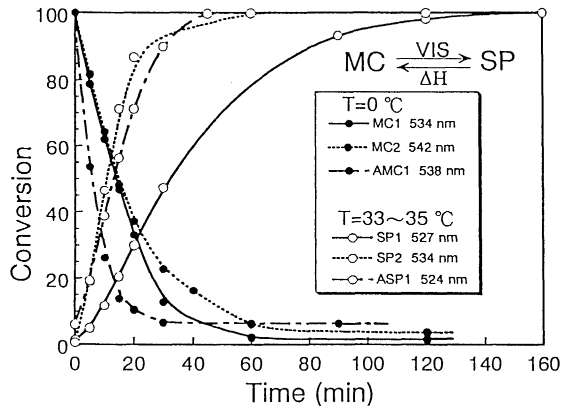

Figure 3. Rates of the photochromic reactions of MC $\rightleftarrows$ SP in solutions followed by the absorption change at the visible bands.

SP→MC reaction under the dark and thermal mode at 33 - 35 °C in the solution were obtained, as shown in Figure 3. For the reactions in the solution it has been found that introduction of the dimethylamino group gives a slightly fast rate for the MC → SP, whereas the long-chain ester at the chromene ring enhances the rate for the SP → MC.

The π - A isotherms at 10 °C for the monolayers of each MC type under the dark condition and each SP type under irradiation of light above 500 nm, are shown in Figure 4. The MC1 with one alkyl chain forms the most condensed monolayer with a limiting area of 40 Å^2/molecule, the MC2 with two chains takes a limiting area of 60 Å^2/molecule, and the AMC1 with one chain as well as a hydrophilic dimethylamino-group exhibits a phase transition point from the expanded to the condensed monolayer with a limiting area of 30 Å^2/molecule. In any cases, the SP types form rather expanded monolayers than the MC films. These facts seem to be ascribed that the MC molecule has a planar structure of a π-conjugated system, whereas the SP takes a twisted structure of the ring formation. The increase of the molecular area due to the structual change of the MC→SP is found to be the largest for the AMC1 monolayer.

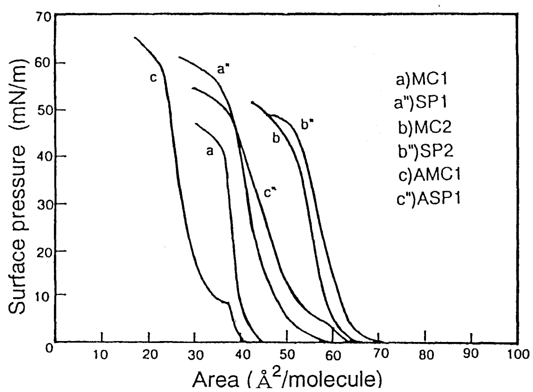

Figure 4. Surface pressure – area isotherms at 10 °C of the MC's under dark condition and the SP's under photoirradiation.

From spectral changes accompanied with the MC → SP reaction in the monolayers on water surface under irradiation of the visible light (500 W Xe lamp at a distance of 40 cm from the water surface) at 10 mN/m and 10 °C, the rates of the reaction were obtained. As shown in Figure 5, the MC1→SP1 reaction in the monolayer is complete for about 40 min, while the AMC1 → ASP1 slightly occurs under the same condition. It should be noted that the MC→SP reaction preferentially occurs and the reverse SP→MC reaction is suppressed in the monolayer on water surface, i.e., these reactivities are considerably different from those in the solution. The former seems to be dependent upon the molecular orientation and packing as well as the difference between the MC and the SP forms in the films. In addition, the surface pressure dependence of the MC1 ⇄ SP1 reaction in the monolayer at 10 °C is shown in Figure 6. The reactivity of the MC1 → SP1 under the photoirradiation in the monolayers at 10 °C is found to be retarded with increase of the surface pressure. The rate of the SP1 → MC1 under the dark condition at 30 °C is considerably slow and the half-recovery was attained at about one hour at even 10 mN/m. From these results, it is considered that the molecular packing just below the transition from the expanded to the condensed monolayer is the most effective for the reaction, and the molecules closely packed in the condensed state are unfavorable to the structual change. Study on control of the photochromic reactions in the L-B films with various molecular environments is in progess.

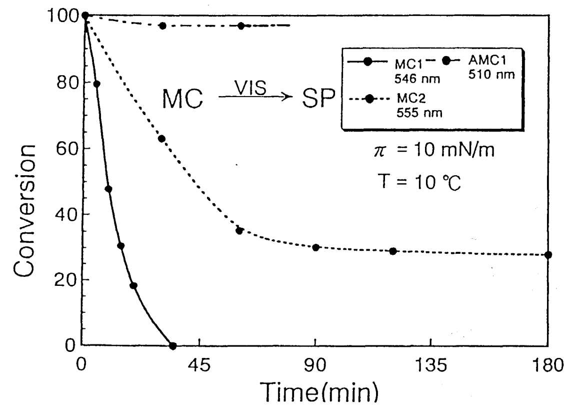

Figure 5. Rates of the MC → SP reaction in the monolayers on water surface under photoirradiation at 10 °C and 10 mN/m.

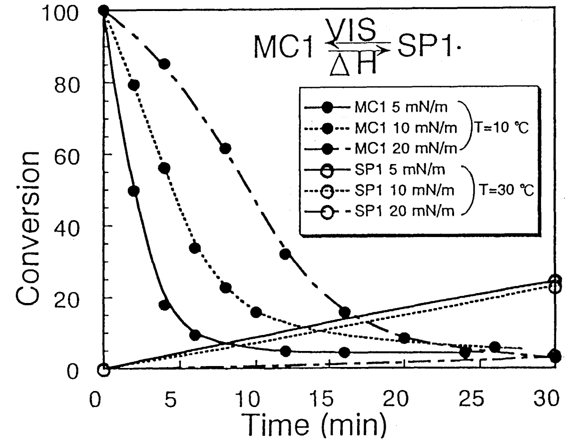

Figure 6. Surface pressure dependence of the MC1 ⇄ SP1 reactions in the monolayer.

References and Notes

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