Reversible Morphological Changes Induced by the Photodimerization of Bis (4-Octadecyloxystilbazolium) Isophthalate Films

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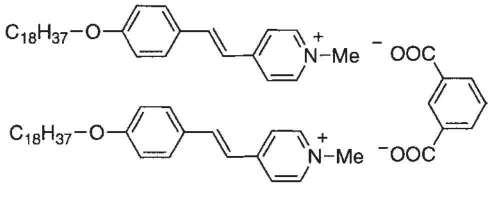
Anti-parallel stacked lamellar films of N-methyl-4-octadecyloxystilbazolium arylcarboxylates (C18O-Stz^+X^-) were found to undergo reversible layer expansion and shrinkage along the c-axis on the glass plates under alternative illumination at $\lambda > 350$ and 254 nm. The stacked lamellar units changed in length according to the phase transition of the lamella structure induced by the photochemical [2 + 2] cyclodimerization and cycloreversion of C18O-Stz^+X^- in the organized assembly.

Photoresponsive materials in organic supramolecular matrices have been the focus of much interest due to their potential in the development of photofunctional devices.[1] Micelles, vesicles, and Langmuir-Blodgett (LB) membranes have been the potent hosts in organizing various functional ion-pair organic materials which can self-assemble into regularly oriented multilayer films on glass slides.[2] In addition to our studies on a series of self-assembled materials in dispersion,[3–8] composite bilayer films made of dioctadecyldimethylammonium bromide and cinnamic acids were investigated in the form of rigid matrices such as thin films on glass slides.[9] In all of these self-assembly systems, divergent reaction pathways subject to *E*-*Z* photoisomerization and [2 + 2] photocycloaddition were dependent on the extent of the packing conformations and the alignment of the olefinic moieties. Stilbazolium ions, as a cationic component of the ion-pair, not only plays an important role as a photochemical probe but also possesses many nonlinear optical properties. Many studies, therefore, have been reported on its photochemistry and second harmonic generation in LB films containing the stilbazole. For example, Mukamel et al. have reported that LB films of hemicyanine derivatives diluted by fatty acid increased their second-order susceptibility.[10] However, for more highly efficient results, it is important to control the orientation of the aggregated structure at the molecular level. In the present paper, we report on a novel photoinduced reversible transformation of the lamella structure of the thin films composed of bis (4-octadecyloxy-*N*-methyl-stilbazolium) isophthalate (C18O-Stz^+X^-, X^-: benzene-1,3-dicarboxylate ion), when isophthalate is used as a counter ion.



C18O⁻Stz⁺X⁻

A 0.3 mM solution of bis(4-octadecyloxy-*N*-methyl-stilbazolium) isophthalate in 10% aqueous methanol was cast on a silica glass slide to give a transparent thin film, the color of which faded away upon irradiation with light longer than 350 nm. The spectral changes in the thin films clearly indicate the disappearance of the olefin, as shown in Figure 1. After a work up of the photolysate film, the head-to-head cyclodimers (*syn*- and *anti*-HH) and *Z*-isomers could be observed by NMR, with yields of 23%, 21%, and 56%, respectively. Regioselective photocyclodimerization was clearly found to require a regular alignment of the olefins in the lamellar films. The XRD spectra of the film under successive irradiation at > 350 nm are shown in Figure 2. The reflection peaks (001) of the starting film at 2.91° decreased with the appearance of new peaks (001) at a lower angle. The lamellar units were estimated to be 3.0 and 4.5 nm before and after UV irradiation, respectively. Polarized IR spectroscopic analysis at 2915 cm^{-1} shows the tilt angles of the *all-trans* CH_2 chain of the octadecyloxy group to be 55° and 43° against the glass slide before and after irradiation, respectively.[1] Morphological changes were evident by the elongation of the lamellar unit length which was found to be one and a half times as long as the molecular length of the ion pair, in spite of a decrease in the tilt

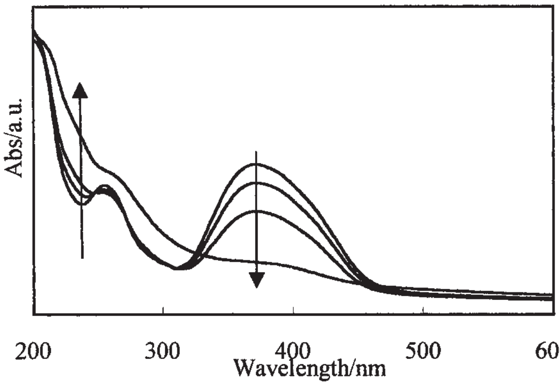


Figure 1. Changes observed in the absorption spectra of the cast film by irradiation at 2 hr ($\lambda > 350$ nm).

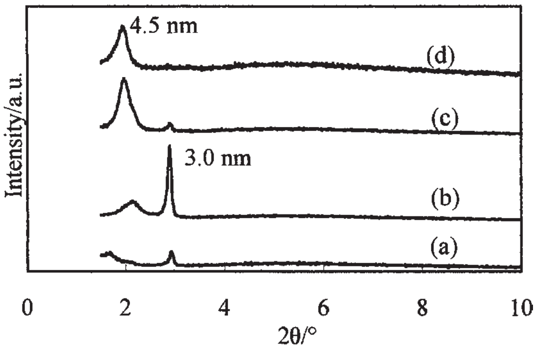
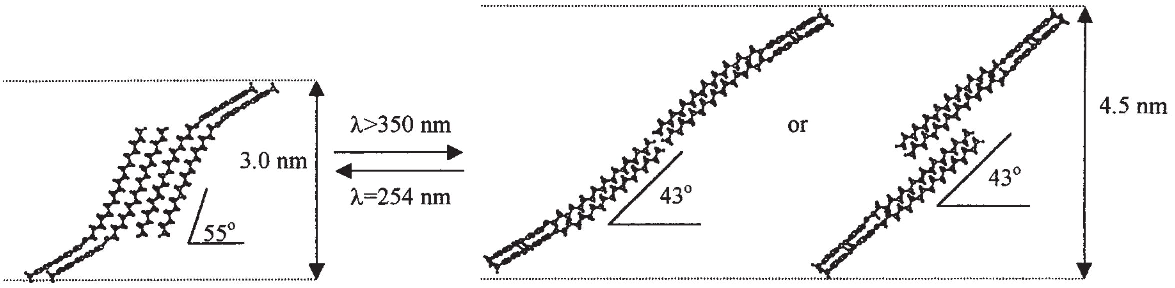


Figure 2. XRD changes in the cast film by irradiation ($\lambda > 350$ nm); (a) 0 min, (b) 30 min, (c) 1 hr, (d) 2 hr.



Scheme 1. The reversible change of the self-assembled structure in cast film by irradiation.

angles of the alkyl chains after UV irradiation. The packing structures before and after 350 nm light irradiation are shown in Scheme 1. At present, either a bilayer (A) or an interdigitated monolayer (B) can be conceived for the lamella unit after irradiation, while the lamella unit before irradiation can reasonably be assumed to be monolayer on the basis of XRD, polarized UV and IR spectroscopic analyses.

It is interesting to note the drastic change from mono- into bilayer structures when only 30% of the olefin is photochemically transformed into the HH dimers. It is well-known in colloid chemistry that corn-shaped molecules form spherical micelles while rod-like molecules with two alkyl chained surfactants make flat multi-layered aggregates. Cyclodimers are thought to be rectangular and more rigid than starting linear shaped olefins. This can be attributed to the morphological changes seen in the lamella films. Studies are now being carried out to clarify the mechanistic origin of this unprecedented structural transformation.

Our previous study disclosed that 254 nm photolysis of *N*-methyl-stilbazolium methylsulfate dimers in water resulted in an efficient cycloreversion to the original olefins. Similarly, this thin film is subject to photochemical cycloreversion by 254 nm light to generate C18O-Stz^+X^-, evidently due to an increase in the absorption of the original olefin at 370 nm.

The olefin was formed with a yield of 30% after two days irradiation at 254 nm. Along with the cycloreversion, the resulting thin film loses its characteristic lamella structure, resulting in a regeneration of the peak at 3.0 nm, as shown in Figure 3.

In summary, thin films of C18O-Stz^+X^- undergo reversible layer expansion and shrinkage along the c-axis on glass plates under alternative irradiation with > 350 nm and 254 nm light. The lamellar units changed in length according to morphological modifications, as shown in Scheme 1, induced by the photochemical cyclodimerization and cycloreversion of C18O-Stz^+X^- in the organized assembly.

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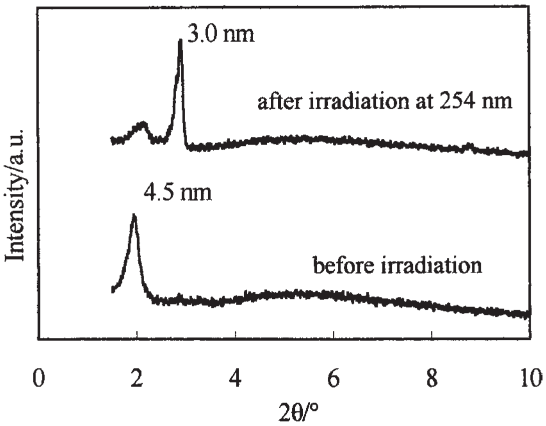

Figure 3. XRD chart of recycloreversion of the cast film by irradiation (λ = 254 nm).

References

1 K. Fukuda, H. Nakahara, and Y. Shibasaki, “The Chemistry of Supra Thin Molecular Organized Films,” Kodan-sha, Tokyo (1993).
2 M. Shimomura, “Immobiled Bilayer Membrane,” Bunshin-sha, Tokyo (1990), pp 96-136.
3 T. Nakmura, K. Takagi, and Y. Sawaki, *Bull. Chem. Soc. Jpn.*, **71**, 909 (1998).
4 K. Takagi, M. Itoh, H. Usami, T. Imae, and Y. Sawaki, *J. Chem, Soc., Perkin Trans.*, 1003 (1994).
5 K. Takagi and Y. Sawaki, *Chem. Lett.*, **1993**, 2103.
6 T. Nakamura, K. Takagi, K. Fujita, H. Katsu, M. Itoh, T. Imae, and Y. Sawaki, *J. Chem. Soc.*, *Perkin Trans.*, **2**, 2751 (1997).
7 K. Takagi, T. Nakamura, H. Katsu, M. Itoh, Y. Sawaki, and T. Imae, *Mol. Cryst. Liq. Cryst.*, **277**, 135 (1996).
8 K. Takagi, K. Aoshima, and Y. Sawaki, *J. Am. Chem. Soc.*, **107**, 47 (1985).
9 O. Osamu, R. Sasai, T. Adachi, K. Takagi, and I. Hatta, *Langmuir*, submitted.
10 D. J. Williams and S. Mukamel, *J. Phys. Chem.*, **96**, 2801 (1992).