2,2,2-Trideuterio-1-phenyldiazoethane (1b): IR (Ar, 15 K) 3110 w, 3088 w, 3063 w, 3035 w, 2210 w, 2138 w, 2128 w, 2050 s, 1601 s, 1575 w, 1503 s, 1380 w, 1455 m, 1351 m, 1341 m, 1332 m, 1268 w, 1189 w, 1098 m, 1080 w, 1059 m, 993 w, 984 w, 889 w, 788 w, 747 s, 701 m, 690 m, 608 m, 508 w, 481 m, cm^{-1}; UV (Ar, 15 K) λ_{max} 312, 302, 298 sh, 280, 245, 235, 228 222 nm. The deep red diazo compound was sublimed at −23 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

1-Diazo-1-phenyl-2-propanone (16): prepared by the method of Regitz;[32] IR (Ar, 15 K) 2098 m, 2070 vs, 1679 s, 1660 w, 1611 w, 1503 m, 1369 s, 1331 m, 1290 m, 1245 s, 1148 w, 1036 m, 1008 w, 908 m, 752 s, 691 m, 618 m, 494 w cm^{-1}. The sample was sublimed at 8 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

[2.2]Paracyclophane (17). [2.2]Paracyclophane (**17**; Aldrich) was purified by sublimation (120 °C, 0.1 Torr) prior to use: IR (Ar, 15 K) 3115 w, 3082 m, 3045 m, 3025 m, 3000 w, 2960 s, 2943 s, 2902 m, 2862 s, 1885 w, 1602 m, 1507 m, 1488 w, 1457 w, 1438 m, 1417 m, 1412 m, 1247 m, 1183 w, 1090 w, 932 m, 892 s, 815 m, 809 s, 765 m, 721 s, 629 s, 509 s cm^{-1}. The sample was sublimed at 95 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

Benzocyclobutene (7a): prepared by thermolysis of *o*-(chloromethyl)toluene.[33] We thank Dr. U. E. Tsou for providing a sample: IR (Ar, 15 K) 3083 m, 3078 m, 3065 w, 3048 w, 3032 w, 3018 w, 2978 m, 2950 s, 2943 s, 2870 w, 2840 w, 1897 w, 1790 w, 1463 s, 1460 s, 1449 w, 1440 m, 1425 m, 1346 w, 1278 m, 1207 m, 1193 m, 1181 w, 1150 w, 1131 w, 1075 w, 1002 m, 929 w, 894 w, 847 w, 780 s, 716 s, 540 w, 410 w, 390 w cm^{-1}; UV (Ar, 15 K) λ_{max} 270, 264, 258 nm. The sample was sublimed at −56 °C (10^{-6} Torr) and codeposited with argon to form a matrix.

Acknowledgment. We gratefully acknowledge the financial support of the National Science Foundation (Grant CHE8404949) and National Institutes of Health (Grant GM24427). The National Science Foundation (1980–1983) and IBM Corp. (1983–1984) provided predoctoral fellowships (R.J.M.). We thank Dr. U. E. Tsou for a sample of benzocyclobutene (**7a**) and M. D. Miller for NMR and GC–FTIR characterization of trideuteriobenzocyclobutene (**7b**).

Photochromism of Salicylideneanilines Incorporated in a Langmuir–Blodgett Multilayer

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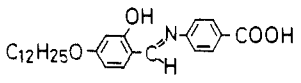
Contribution from the Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University, Fukuoka, Kasuga, 816 Japan, and Dojindo Laboratories, Kumamoto, 862 Japan. *Received April 22, 1987*

Abstract: The photochromic behavior of an amphiphilic salicylideneaniline derivative, *N*-(4-dodecoxysalicylidene)-4-carboxyaniline (DSA), incorporated in a Langmuir–Blodgett film was studied. DSA formed a stable and condensed monolayer at an air–water interface, and the monolayer was transferred on quartz substrates. The built-up multilayer was found to possess a highly ordered and densely packed structure. Reversible photochromism of a salicylideneaniline group was observed in built-up DSA films on repeating irradiation with UV light. The rate of thermal decoloration was proved to be suppressed by the ordered molecular environment in the multilayer.

N-Salicylideneanilines (SA) have been known to exhibit photochromism in their crystalline states or in rigid solid solutions. In their fluid solutions, however, their photochromic behavior is not observable owing to a fast thermal back-reaction.[2-4] The rates of thermal back-reaction of the photocolored SA species are markedly dependent on the regularity and rigidity of their environment. Therefore, one expects that incorporation of the photochromic SA group in highly ordered and densely packed structures will cause the suppression of its thermal back-reaction.

In the present paper, we propose the use of the Langmuir–Blodgett (LB) technique for the control of the molecular environment of the photochromic SA group. An amphiphile that possesses the SA group in its hydrophobic portion, *N*-(4-dodecoxysalicylidene)-4-carboxyaniline (DSA), was adopted. At first, we describe the preparation and characterization of the LB multilayer from the amphiphile and show that the LB films thus obtained possess a well-defined layered structure. Then, the photocoloration and thermal decoloration (reversible photochromism) of the SA group in the multilayer is demonstrated.



DSA

Experimental Section

Materials. An amphiphile DSA was prepared by the condensation of 4-dodecoxysalicylaldehyde and 4-carboxyaniline:[5] mp 204 °C. Anal. Calcd from $C_{26}H_{35}N_1O_4$: C, 73.38; H, 8.29; N, 3.29. Found: C, 73.41; H, 8.20; N, 3.23. Arachidic acid was used as received from Aldrich Chemical Co.

Preparation of LB Films. A conventionally available Langmuir trough with a Wilhelmy-type film balance (Kyowa Kaimenkagaku Co., HBM-AP) was used for both surface pressure–area isotherm measurements and LB film preparations. The subphase was pure water from a Milli-Q system (Millipore Ltd.) containing 10^{-3} M $BaCl_2$. Monolayers on the subphases were deposited on quartz substrates at the surface pressure of 20 mN m^{-1} at 15 °C by the usual vertical dipping method.

Optical Absorption and X-ray Diffraction Measurements. The optical absorption spectra of the multilayers were obtained by use of a conventional spectrophotometer (Hitachi 330). Small-angle X-ray diffraction patterns were obtained on the multilayers deposited on polyester films by use of a focused monochromatic beam X-ray diffractometer (Stoe & Cie Co., STADI/P) using Cu Kα radiation at the Center of Advanced Instrumental Analysis, Kyushu University.

Observation of Photochromism. For the photocoloration of the multilayers, 308-nm UV pulses from a XeCl excimer laser (Lambda Physik, EMG-50E) with the intensity of about 2 mJ cm^{-2}/pulse were used. For the detection of the colored species, the time trace of the absorbance at 480 nm was monitored by use of the monochromatized 480-nm light from a halogen lamp and a photomultiplier.

Results and Discussion

DSA formed a stable well-behaved condensed phase at an air–water interface. Figure 1 shows the surface pressure–area

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(1) On leave from Japan Synthetic Rubber Co. Ltd.

(2) Cohen, M. D.; Schmidt, G. M. J. *J. Phys. Chem.* **1962**, *66*, 2442.

(3) Cohen, M. D.; Schmidt, G. M. J.; Flavian, S. *J. Chem. Soc.* **1964**, 2041.

(4) Cohen, M. D.; Hirshberg, Y.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 2051.

(5) We thank M. Honma (Ajinomoto Co., Inc.) for his helpful advice on the preparation of 4-dodecoxysalicylaldehyde.

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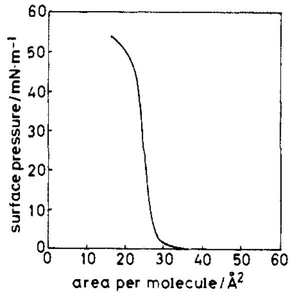

Figure 1. Surface pressure–area isotherm of DSA on aqueous $BaCl_2$ solution (1 × 10^{-3} M) at 15 °C.

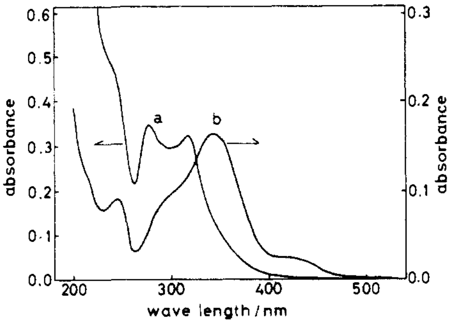

Figure 2. Absorption spectra of DSA: (a) multilayer on a quartz plate (40 layers on both sides of the plate); (b) solution in methanol (5 × 10^{-5} mol/L).

isotherm of DSA at 15 °C. Above 15 mN m^{-1}, a condensed monolayer was formed, and the limiting area was found to be 27–28 Å^2/molecule, which was very close to the cross-sectional area perpendicular to the long axis of the SA nucleus. Several tens of monolayers were neatly deposited on quartz substrates with the transfer ratio being nearly unity (Y-type deposition).

In Figure 2, the absorption spectrum of the built-up multilayer of DSA (40 layers on both sides of a quartz plate) was compared with that of a methanol solution. The major band centered at 350 nm that was observed in the solution disappeared, and new bands appeared at around 300 nm in the multilayer. This spectral change is attributable to the interaction of electronic transition moments of the chromophore in the multilayer. According to the simplified molecular exciton model, an electronic transition band shifts to the shorter wavelength, when chromophores are arranged with their transition moments parallel and ordered perpendicular to the stacking direction (H-aggregate structure). Very similar spectral changes have been reported in some molecular assemblies with chromophores, such as stilbene[6] and azobenzene.[7,8]

The surface pressure–area isotherm and the absorption spectrum of the multilayer clearly demonstrated that the amphiphiles in the multilayer are ordered and packed with the long axis of the chromophore approximately perpendicular to the layer plane. In addition, a small-angle X-ray diffraction experiment gave further evidence of regular stacking of the long-chain molecules. Well-defined first- and second-order reflections from layered structures were observed, and the long spacing was calculated to be 5.56 nm. This spacing is a little smaller than twice the calculated molecular length of 2.97 nm. Then the long-chain molecules in the Y-type arrangement should be assumed to tilt about 20° away from the perpendicular direction of a layer plane.

To cause photochromic reactions, the multilayer on a quartz plate was irradiated with the UV pulses, and the variation of the absorbance at 480 nm, where the absorption of colored species of the SA group had been reported to appear,[2,4] was observed. Figure 3 shows a typical time trace of the absorbance change at 480 nm under repetitive irradiation of UV pulses. The absorbance instantaneously jumped with UV irradiation and then gradually decreased with time, indicating the occurrence of rapid photocoloration of the SA group followed by slow thermal decay of colored species. The photocoloration and thermal decoloration cycles can be repeated for dozens of times. This clearly shows that we are really dealing with the reversible photochromism of the SA group.

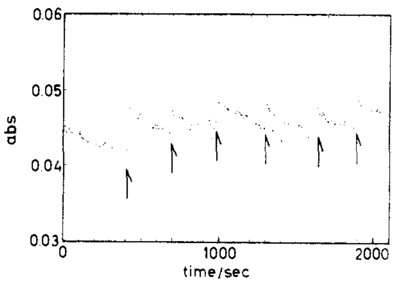

Figure 3. Absorbance change of the DSA multilayer at 480 nm on laser irradiation (308 nm). The laser was flashed at the arrow points.

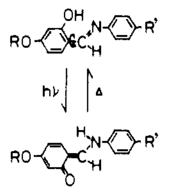

Figure 4. Photochromism of amphiphilic salicylideneanilines.

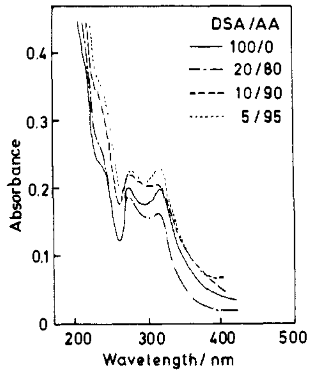

Figure 5. Absorption spectra of the DSA/AA mixed multilayers.

The rate of thermal decay did not follow a simple first-order kinetics, suggesting the presence of a strong influence of the molecular environment.[9] Then, for a rough assumption, we evaluated the rate constant of thermal decoloration *k* from the initial slope of the first-order kinetics plot. The rate constant of the thermal decay thus obtained was around 10^{-3} s^{-1} at the temperature range between 280 and 320 K. This value is comparable with those reported on some SA derivatives in their crystalline states (1 × 10^{-4} – 2 × 10^{-3} s^{-1}) and far smaller than those in solutions ($>10^3$ s^{-1}).[3,9,10]

It should be noted that relatively small changes in molecular shapes are required for the photochromic reaction of the SA group, compared with the cases of other photochromic substances, such as spiropyrans and azobenzenes. The photocoloration process of the SA group consists of proton transfer (enol–keto tautomerization) and a rotation of a phenylene ring (conversion from cis-keto form to trans-keto form) (Figure 4). This possibly is one of the principal reasons why the photoreactions are possible in the stacked multilayers as well as in crystals.

In order to make the relation between the aggregated structures of multilayers and the photochromic behaviors clearer, we performed several additional experiments.

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(6) Mooney, W. F.; Brown, P. E.; Russel, J. C.; Costa, S. B.; Pederson, L. G.; Whitten, D. G. *J. Am. Chem. Soc.* **1984**, *106*, 5659.

(7) Fukuda, K.; Nakahara, H. *J. Colloid Interface Sci.* **1984**, *98*, 555.

(8) Shimomura, M.; Kunitake, H. *Ber. Bunsen Ges. Phys. Chem.* **1983**, *87*, 1134.

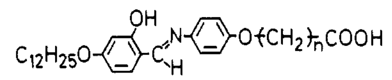
(9) Nakagaki, R.; Kobayashi, T.; Nakamura, J.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1909.

(10) Ottolenghi, M.; McClure, D. S. *J. Chem. Phys.* **1969**, *46*, 4620.

First, several multilayer samples were prepared under the conditions of different surface pressures. Neither the optical absorption spectra nor the long spacings from X-ray diffraction depended on the surface pressure at the multilayer preparation. Moreover, the rates of the thermal decoloration possessed little dependence on the surface pressure.

Second, the multilayers were prepared from the mixed monolayers of DSA and arachidic acid (AA). The monolayers with the DSA/AA mixing ratios of 20/80, 10/90, and 5/95 were spread on a subphase. The mixed multilayers (20–60 layers of Y-type films) could be deposited on quartz plates from every mixed monolayer. As was shown in Figure 5, the same optical absorption peaks were observed in every DSA/AA mixed multilayer as in the pure DSA multilayer. Even in the mixed multilayer with the DSA content of 5 mol %, the peak wavelengths were not affected by the dilution with arachidic acid. Then, we assumed that microphase separation occurred in the mixed monolayers, and therefore, the aggregated structure of DSA molecules in the mixed multilayers turned out to be the same as those in the pure DSA multilayer. The rate constants of the thermal decoloration of the mixed multilayers were exactly the same as that of the pure DSA multilayer.

Then, we finally tried to change the aggregated structures of the SA groups in the multilayers by modification of the chemical structure of the amphiphile. We prepared two amphiphiles in which spacer methylene sequences were inserted between the SA group and the hydrophilic head group. In this case, the aggregated structures of the multilayers were found to depend on the chemical structures of the amphiphiles. The rate constants of the thermal decoloration were also governed by the structures of the amphiphiles. The details of this aspect will be described separately in a subsequent publication.



n=3 DSA-3

n=10 DSA-10

In conclusion, the ordered molecular multilayer that consists of an amphiphilic salicylideneaniline derivative could be prepared by the LB method, and reversible photochromism has been detected in the multilayer. The rate of thermal back-reaction was the same order of magnitude as those in crystalline salicylideneanilines, suggesting the aggregated structures in the multilayer was very regular. This work, we believe, gives the first step for the designed control of photochromism in organic solid films by use of the LB technique.

Acknowledgment. We thank Prof. T. Kunitake of Kyushu University for his interest on our work. This work was partly supported by the Grant-in-Aid on Special Project Research for "Organic Thin Films for Information Conversion" from the Ministry of Education, Science, and Culture, Japan.

Registry No. DSA, 111772-61-3; DSA-3, 111793-76-1; DSA-10, 111793-77-2; 4-dodecoxysalicylaldehyde, 111772-62-4; 4-carboxyaniline, 150-13-0.

Use of a Photoreversible Fulgide as an Actinometer in One- and Two-Laser Experiments[1]

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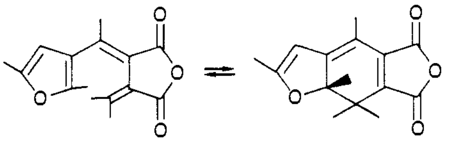
Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6. *Received June 10, 1987*

Abstract: The photoreversible fulgide Aberchrome-540 has been tested and developed as an actinometer for one- and two-laser experiments. In the former, the technique allows the determination of extinction coefficients for short-lived reaction intermediates by a method that requires substantially fewer assumptions than other techniques in the literature. In the case of stepwise two-photon processes, the Aberchrome-540 method allows the determination of quantum yields for photoreactions of short-lived reaction intermediates. For this particular application the technique is the only one of its kind.

This report deals with two closely related problems. The first is the development and testing of an actinometer for use in laser photolysis experiments, including its comparison with other available techniques. The second is the development of a technique for the measurement of quantum yields for the photodecomposition of short-lived reaction intermediates. This technique, which is particularly useful in two-laser, two-color experiments, is, to the best of our knowledge, the only one of its kind available at present.

Heller et al. have calibrated fulgide I for use as an actinometer in solution.[3,4] I, which is commercially available under the name of Aberchrome-540, has an absorption maximum at 344 nm ($\epsilon_{344} = 6400$ M^{-1} cm^{-1}). Upon UV irradiation it interconverts to II with a quantum yield of 0.20 in toluene at room temperature (eq 1).



(1)

The forward quantum yield was examined between 313 and 366 nm and found to be wavelength independent.[3] Reaction 1 is photoreversible; for the photobleaching process (i.e., II → I) the quantum yield was found to be temperature and wavelength dependent.[4] In toluene at 21 °C it follows a remarkable linear dependence between 436 and 546 nm, according to eq 2. This

$$\Phi_{II \rightarrow I} = 0.178 - 2.4 \times 10^{-4}\lambda \text{ (nm)} \qquad (2)$$

expression leads to $\Phi_{II \rightarrow I} = 0.059$ at 494 nm, the absorption maximum for II ($\epsilon_{494} = 8200$ M^{-1} cm^{-1}). We have used this reaction as an actinometer for studies of the photochemistry of short-lived reaction intermediates (e.g., $Ph_2\dot{C}OH$, see following paper in this issue).[5]

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[1] Issued as NRCC-28014.

[2] NATO Fellow, on leave from Laboratoire de Photochimie Solaire, ER-241/CNRS, 94320 Thiais, France.

[3] Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.

[4] Heller, H. G., private communication.

0002-7863/88/1510-0511$01.50/0