In situ Observation of the Photochromism in the Langmuir Monolayer of a Non-typical Amphiphilic Spiropyran Derivative at the Air/Water Interface

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In situ photochromic process in the monolayer of a photochromic spiropyran derivative without long alkyl chain, was investigated. The photochromism at the air/water interface under different surface pressures was studied by surface pressure-area isotherms, surface pressure-time curves, area-time curves and Brewster angle microscopy. Both forms of the compound were found to form monolayers at the air/water interface although it does not have long alkyl chain. A large area expansion in the monolayer corresponding to a zero[th] order reaction was found at the initial stage of the UV light irradiation. A series of dynamic investigations revealed that at high pressure after phase transition in the monolayer, the surface pressure changes greatly under alternative irradiation of UV and visible light. An obvious morphological change accompanying with the photochromism was observed *in situ*.

Keywords   photochromism, spiropyran, air/water interface, morphology, BAM

Introduction

Photochromism describes the reversible color changes induced by the photoirradiation. Photochromism has been widely studied due to its potential applications in optical information storage,[1-4] molecular switching devices[5] and other fields.[6] The investigation on the photochromism in the Langmuir monolayer at the air/water interface is of considerable interest in understanding the molecular packing and fabricating well-organized functional ultrathin films. As an important photochromic species, spiropyran derivatives have been studied in various matrices such as sol-gel system,[7,8] polymer dispersions,[9-11] bilayer lipid membranes[12] and Langmuir-Blodgett films.[13-15] However, the photochromic behavior of spiropyran derivatives at the air/water interface has been less studied in recent years.[16-18] These studies of photochromic spiropyran at the air/water interface were mostly concerned about the long chain substituted spiropyran[19,20] or polymer having the side groups of spiropyran[21,22] in order to form stable monolayers. However, the photochromic process itself takes place in the photochromic part, which is less affected by the long alkyl chain. In contrast, the existence of long alkyl chain caused the indirect observations of the changes accompanied by the photochromism. In this paper, the photochromism in the Langmuir monolayer of a novel spiropyran was investigated, which has no long alkyl chain substituents. Their structural and morphological changes accompanying with the photochromism at different surface pressures have been studied by surface pressure-area (π-A) isotherms, relaxation (A-t) and kinetic (π-t) curves and *in situ* Brewster angle microscopy (BAM) under the alternative irradiation of UV and visible light.

Experimental

The synthesis of 1-[2-(3,5-ditertbutyl-4-hydroxy)-benzenpropionyloxy] dimethylene-3, 3-dimethyl-spiro [2H-1-benzopyran-2,2'-(2H) indole] (abbreviated as **SP**, depicted in Scheme 1) was based on the condensation of 1-hydroethyl-3, 3-dimethyl-5'-nitro-spiro [2H-1-benzopyran-2,2'-(2H) indole] and a 3,5-ditertbutyl-4-hydroxy-benzenepropanoic.[23] 1-Hydroethyl-3,3-dimethyl-5'-nitro-spiro [2H-1-benzopyran-2, 2'-(2H) indole] was obtained by the reported method.[24] M.p. 184—186 ℃; ^{1}H NMR δ: 1.15 (s, 3H, CH$_3$), 1.24 (s, 3H, CH$_3$), 1.41 [s, 18H, C(CH$_3$)$_3$], 2.58 (t, J = 8.42 Hz, 2H, CH$_2$), 2.81 (t, J = 8.42 Hz, 2H, CH$_2$COO), 3.45 (t, J = 7.8 Hz, 2H, NCH$_2$), 4.23 (t, J = 7.8 Hz, 2H, NCH$_2$CH$_2$), 6.5—8.2 (m, 11H, ArH);[25] MS m/z: 612 (M$^+$). Surface pressure π-area (A)

Scheme 1 Photochromic reaction of spiropyran and their ball-stick models

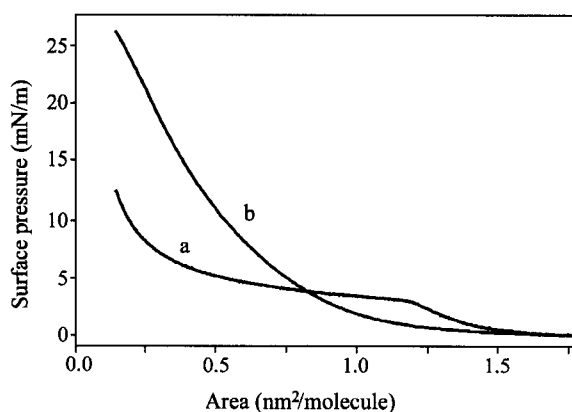Spiropyran (**SP**)   Photomerocyanine (**PMC**)
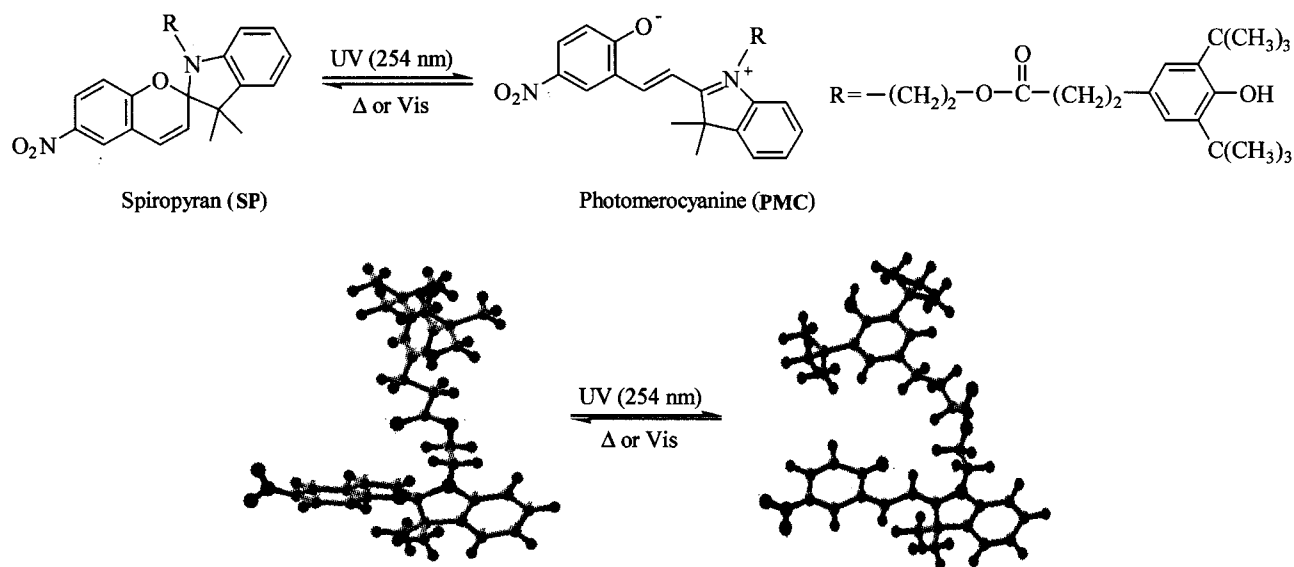
isotherms, relaxation and kinetic curves were measured by KSV mini trough (Finland). A chloroform solution of spiropyran (1×10^{-3} mol/L) was spread on pure water (Millipore, 18 M$\Omega \cdot$ cm) at 20 ℃ under the nature conditions. After 10 min of evaporation, π-A isotherms were obtained by compressing the barrier at a speed of 10 mm/min. To measure the π-A curve of its photomerocyanine form, an UV lamp (254 nm, 20 W) set 20 cm above the monolayer was used to irradiate the monolayer all through the monolayer compressing process after spreading the spiropyran. A halogen lamp (100 W) set 20 cm above the monolayer was used as visible light source in kinetic and BAM studies. BAM observation was carried out with a home built apparatus, which has a He-Ne laser (632.9 nm, 5 mW) source and a CCD camra as a image receiver. Images were recorded on a videotape and transferred to digital images by a computer software.

Results and discussion

Surface pressure-area (π-A) isotherms

Fig. 1 shows the π-A isotherms of the "spiro" and photomerocyanine forms of the spiropyran. Great changes are observed before and after UV light irradiation. The limiting area obtained by extrapolating the steepest rising part of the isotherm is 0.70 nm^2/molecule for photomerocyanine form. For the "spiro" form, a phase transition is observed at 2.9 mN/m. From the CPK model, it is estimated that the area of the di*tert*butyl and hydroxyl substituted benzene group is about 0.36 nm^2 and the planar photomerocyanine structure has the surface area of about 0.71 nm^2. From the isotherms, it can be found that the limiting areas of the "spiro" and photomerocyanine form of spiropyran are 0.35 nm^2 and 0.70 nm^2, respectively. Therefore, it could be concluded that the limiting area of the "spiro" form is mainly decided by the

bulk tail of di*tert*butyl and hydroxyl substituted benzene group while the limiting area of the photomerocyanine form is mainly decided by the planar of merocyanine structure. It is also noticed that the onsets of the isotherms of the two forms are both at 1.5 nm^2/molecule indicating that the molecules lie flat at their initial spreading stage. In comparison with those reported for the monolayer of long-chain spiropyran derivatives,[26] which showed the onset of surface pressure at around 0.8 nm^2/molecule, it can be regarded that true monolayer is formed for both forms of the spiropyran at the air/water interface.

Fig. 1 Surface pressure π-area isotherms of spiropyran (a) and its photomerocyanine form (b).

Molecular area-time (A-t) curves

To investigate the molecular area change of spiropyran at the air/water interface under UV irradiation, photo-induced A-t curves of the monolayer at various surface pressures were performed as shown in Fig. 2, where A/A_0 is the ratio of the

area change. It is found from Fig. 2 that all the curves exhibited a linear relaxation process at the initial stage and a nonlinear process at the succeeding stage of the photoirradiation. For high surface pressure after phase transition at 5 and 7 mN/m, the linear area expansion process was attributed to the photoreaction from the "spiro" form to the photomerocyanine form, because the area of the photomerocyanine form of spiropyran was larger than the "spiro" form at high surface pressure while smaller than the "spiro" form at low surface pressure indicated by the π-A isotherms. For low surface pressure near or below phase transition at 2 and 3 mN/m, the short area expansion process was attributed to the relaxation of the spiropyran before photoreaction including the conformation or the aggregation change of the molecules.
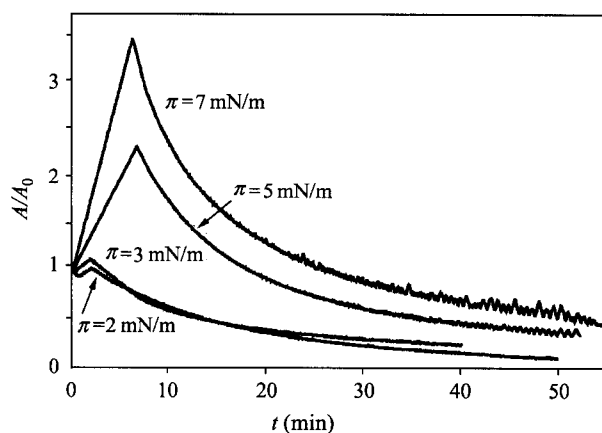

Fig. 2 Molecular area-time (A-t) curves of spiropyran monolayer at different surface pressures.

It is noticed that the incline of the line increased from 5 mN/m to 7 mN/m, indicating the expanding speed is faster at high surface pressure. From the isotherm of the "spiro" and the photomerocyanine form of spiropyran in Fig. 1, it can be seen that the molecular area change from "spiro" form to photomerocyanine form at 7 mN/m is larger than that at 5 mN/m. Moreover, the "free volume" are quite small at high surface pressure and the surface area increases due to the cleavage of the C—O bond are more obvious than at low surface pressure (see Scheme 1). From the incline of each line, the reaction speed at special surface pressure can be calculated.

$$A/A_0 = K_t + y_0 \qquad (1)$$

$$[\mathrm{sp}]A_{\mathrm{sp}} + (1 - [\mathrm{sp}])A_{\mathrm{mc}})/A_{\mathrm{sp}} = K_t + y_0 \qquad (2)$$

$$[\mathrm{sp}] = K_t/(1 - m) + (y_0 - m)/(1 - m) \qquad (3)$$

where K and y_0 are the slope and intercept of the line, respectively. A_{sp} and A_{mc} are the molecular areas of "spiro" form and photomerocyanine form in the monolayer. [sp] is the concentration of **SP** at interface. $m = A_{\mathrm{mc}}/A_{\mathrm{sp}}$. We as-

sume that at $t = 0$ min the species on monolayer are all the "spiro" form. We proposed here that the area expansion is mainly caused by the photoreaction from **SP** to **PMC** at 5 and 7 mN/m. It can be found from Eq. (3) that the concentration of spiropyran is linear with time, which is characteristic of a zero[th] order reaction. It is reasonable to conclude that the reaction speed is not related with the concentration of spiropyran in such a two dimensional surface reaction since many surface reactions have a zero[th] order.

It is also noticed that after an area expansion process, the monolayer area was contracted after successive UV light irradiation. It is proposed that at low surface pressure at 2 and 3 mN/m, the area constriction mainly caused by the photoreaction from the "spiro" form of spiropyran to the merocyanine form. While at high surface pressure after phase transition at 5 and 7 mN/m, the area constriction process was mainly attributed to the aggregation of the merocyanine[27,28] or the relaxation of the monolayer. The area constriction curves can be plotted as Eq. (4).

$$- \ln(A/A_0) = K_t + \text{constant} \qquad (4)$$

The K values were fitted to be 0.046, 0.036, 0.037 and 0.034 for 2, 3, 5 and 7 mN/m, respectively. These values indicate the speed of area constriction after UV irradiation. It is noticed that the area constriction speed at 2 mN/m was faster than that at 3 mN/m. This is reasonable since the area change from the "spiro" form to photomerocyanine form was larger at 2 mN/m than at 3 mN/m in the π-A isotherms. A slight decrease of area constriction speed was observed from 5 mN/m to 7 mN/m indicating that low surface pressure favors the molecular aggregation.

Surface pressure-time (π-t) curves

In order to investigate the photochromism at different surface pressure, π-t curve was measured at constant area under alternative irradiation of UV and visible light. After compressed to a high pressure after phase transition, the pressure change under alternative irradiation of UV and visible light was obvious, as shown in Fig. 3. As the relaxation (A-t) curve revealed, the UV light irradiation caused the area expansion at first. It can be observed in kinetic curve that the first stage of the UV light irradiation increases the surface pressure. A steady reaction cycle was realized after 50 min of relaxation for the molecules to change their conformation and aggregation state. UV light irradiation causes the decrease of the pressure and the visible light irradiation causes the increase of the pressure. As the later stage of the A-t curves, the UV light caused the decrease of the area which corresponding to the decrease of the surface pressure in π-t curve. The steady photochromic cycle can be repeated for at least twenty times without decreasing the surface pressure obviously in air. But at low surface pressure (near or before phase transition), the surface pressure changes under alternative irradiation of UV and visible light are not so obviously than at high pressure. This is because the surface pressure did not change

greatly near the phase transition state or the molecules have more room to adapt the stimulation of the light but to change the pressure.
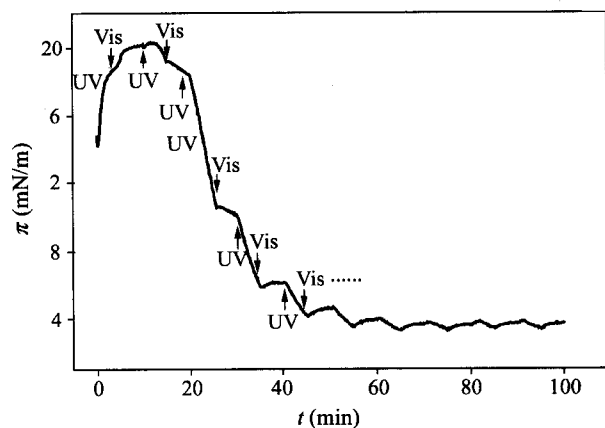

Fig. 3   Surface pressure-time (π-t) curve of the spiropyran monolayer at high surface pressure under alternative irradiation of UV and visible light.

Brewster angle microscopy study

Both Brewster angle microscopy and fluorescence microscopy are powerful techniques to observe the morphological changes in monolayers at the air/water interface. But BAM is more useful in the *in situ* observation of photochromic monolayers for it avoids the introduction of fluorescence probes.[29] Seki *et al*.[30] reported the real time observation of morphologi-

cal changes in monolayer of a photosensitive polymer containing an azobenzene side group. However, *in situ* observations of morphological changes have not been studied in the photochromic spiropyran monolayers. Fig. 4a shows the BAM image at 7 mN/m after UV light irradiation. Tightly packed domains are clearly seen. The morphology did not have much change before and after UV light irradiation. That is to say, the photoreaction did not change the morphology of the film dramatically at the beginning. But the successive visible light irradiation made the film homogeneous and fluid, as shown in Fig. 4b. The tightly packed domains disappeared and the monolayers became more fluid. Then the UV light irradiation made the monolayer return to the tightly packed morphology reversibly (shown in Fig. 4c). Then the succedent visible light irradiation made the film return to the homogeneous and fluid morphology (shown in Fig. 4d) and this kind of morphology change circle can be repeated many times. The photoreaction took place instantly after the UV light irradiation, butthe aggregation morphology change was retarded. The UV light irradiation caused the area expansion as revealed by surface pressure-area isotherms and relaxation curves, which makes the domain structure more tightly and more rigid at first. But visible light irradiation made the molecular area shrink, which caused the fluidity of the monolayer. The successive UV light makes the domain aggregate again indicate a reversible photoreaction took place at high surface pressure after phase transition. However, no obvious morphology change was observed at low surface pressure before phase transition state as revealed by the kinetic study.

Conclusions

A novel kind of spiropyran without long alkyl chain was synthesized and the photochromism in the Langmuir monolayer at the air/water interface was investigated by π-A isotherms, relaxation, kinetics and Brewster Angle Microscopy. π-A isotherms revealed the area expansion of the photomerocyanine form under UV light irradiation. Relaxation and kinetics study indicate that the surface pressure influenced the photochromism of spiropyran. The "spiro" form of spiropyran has more free volume at low surface pressure and the photochromism did not change the surface pressure or morphology greatly. However, obvious surface pressure and morphological changes were observed at high surface pressure after the phase transition where the molecules were packed tightly. BAM observations revealed clear differences in the morphology under the alternative UV and visible light irradiation. In addition, the relaxation study also revealed a zero[th] order kinetic process at the initial stage of photoreaction.
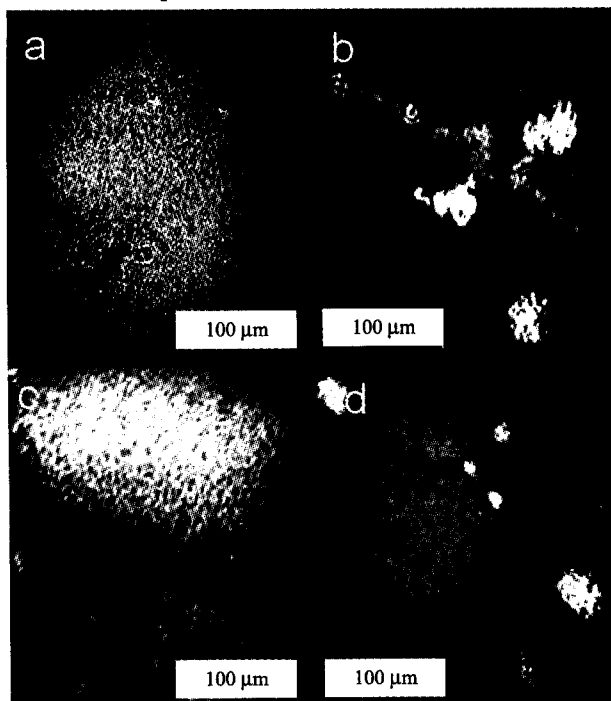

Fig. 4   BAM images of the **SP** at high surface pressure. (a) The image of **SP** monolayer at 7 mN/m after UV light irradiation; (b) after successive visible light irradiation; (c) after UV light irradiation; (d) after visible light irradiation.

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