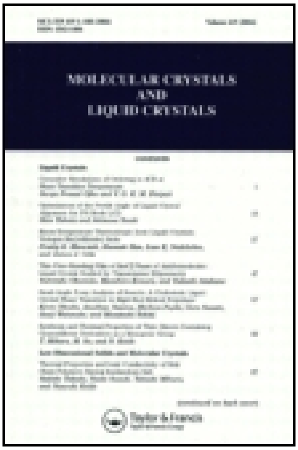

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Photoisomerization of Azobenzene Derivatives at the Air/Water Interface

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Photoisomerization of Azobenzene Derivatives at the Air/Water Interface

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The photoisomerization of azobenzene derivative on the substrate requires a sufficient area to prevent stacking by the aggregation of azobenzene chromophores. In order to overcome such a close stacking of azobenzene chromophores, the azobenzene derivative (8-[4-[4′-octylphenyl]azo]phenoxy]decyl pyridinium salt, 8Az10py) with positively charged head group was synthesized and used after purification. The photoisomerization of 8Az10py was investigated with pressure-area isotherms, surface potential-area isotherm curves and BAM images of a 1:2 mixture of 8Az10py and cholesterol at the air/water interface.

INTRODUCTION

Langmuir-Blodgett(LB) films containing amphiphile azobenzene derivatives can be applied in molecular electronics devices. The conversion efficiency of azobenzene derivatives between cis and trans forms by photoinduced cis-trans isomerization is critical factor for the application to optical recording and switching. In this paper, photoisomerization of N-[[(4-(4-octyl-phenyl)azo)phenoxy] decyl] pyridinium bromide (8Az10py) was characterized by irradiation of UV-vis light (365 nm) from trans to cis isomer and thermal equlibrium by thermodynamic control from cis to trans isomer.

EXPERIMENTAL

Azobenzene derivative 8Az10py of which structure is shown in Figure 1 was synthesized according to the literature method [1]. The cis isomer composition of the 1 mM 8Az10py stock solution of chloroform was modified with changing the irradiation time of 365 nm UV light (10 mW, Spectronics Corporation) on the sample solution in the quartz cuvette. We measured surface pressure-area isotherms, surface pontential-area isotherms, and Brewster Angle Microscopy(BAM) images by spreading 1 mM 8Az10py stock solution of chloroform on the water surface of rectangular Teflon trough from KSV(KSV 2000).

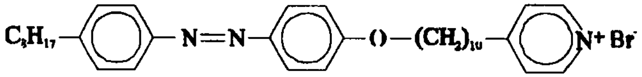


FIGURE 1. The structure of N-[[(4-(4-octylphenyl)azo)phenoxy] decyl]pyridinium bromide (8Az10py)

The surface pressure-area and surface potential-area isotherms are obtained by compressing barriers to control surface concentration of monolayer. The surface potential was contributed from the orientation of the hydrophobic tail of the monolayer molecules by the change of group dipole moment. BAM(Nanofilm Tech., Germany) is a microscoy technique based upon the characteristics of the reflection of the light at the Brewster angle. The refraction index changes abruptly by interfacial properties such as the molecuar density and the orientation of monolayer molecules in the interfacial layer. The experimental sef-ups are shown in Figure 2.

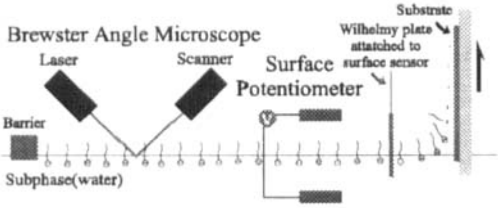


FIGURE 2. Experimental techniques.

RESULTS AND DISCUSSION

The surface potential of 8Az10py monolayer at the air/water interface is dependent on the dipole moment difference between cis and trans forms and the alkyl chain orientation as shown in Figure 3. In the initial state of barrier compression, the surface potential of cis isomer was higher than that of trans isomer because of higher intrinsic dipole moment of cis isomer due to bent structure. The surface potential of cis form starts to decrease at 70 Å^2 of the mean molecular area (MMA). This is possibly interpreted as partial entanglement of the alkyl chain can occur. Therefore, monolayer of cis isomer is more unstable than trans isomer

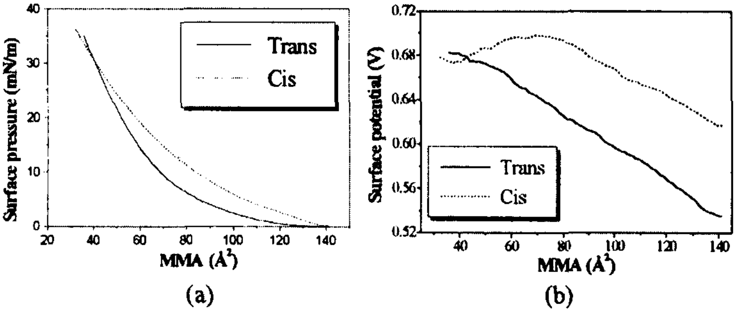
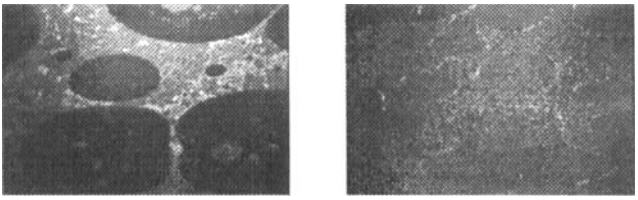


FIGURE 3. Surface potential-area isotherms of 8Az10Py at air/water interface. (a) Surface pressure-area isotherm of 8Az10py (b) Surface potential-area isotherm of 8Az10py.

because of bent structure of cis form. On the other hands, the surface potential of trans form was linearly increased according to the π -A isotherm by packing of molecules with increasing surface concentration of the monolayer. The monoayer of 8Az10py is not stable enough for the preparation of L-B films and to be distinguished between cis and tran isomer by BAM. To get a clear distinction of BAM images between as and trans isomers, 8Az10py was mixed with cholesterol. BAM images of a mixed monolayer of 8Az10py with cholesterol (molar ratio 1:2) at the 10 mN/m of surface pressure are shown in Figure 4. The dark disk regions are made up of cholesterol and the other regions indicate 8Az10py images. Due to intrinsic higher reflectivity of trans form than cis form, BAM image of trans form showed a brighter image than that of cis form at same surface pressure[2]. The image intensity increases or decreases versus the ratio of trans and cis form content which is investigated by BAM image with different molar ratios.



(a) Trans (b) Cis

FIGURE 4. BAM images of a 1:2 mixture of 8Az10py and cholesterol at the air/water interface (surface pressure: 10 mN/m, room temp).

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