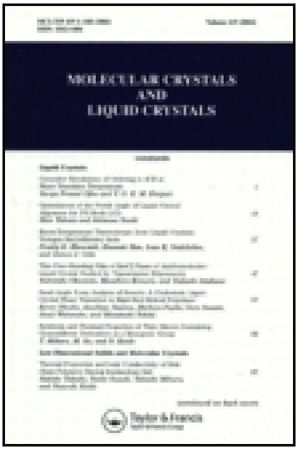

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Studies on Photochemical Isomerization of Azobenzene in Self-Assembled Bolaamphiphile Monolayers

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Studies on Photochemical Isomerization of Azobenzene in Self-Assembled Bolaamphiphile Monolayers

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Photochemical reaction of azobenzene is investigated in systems in which symmetrically substituted chromophores are organized in self-assembled monomolecular film of cationic bolaamphiphiles on fused silica. The bolaamphiphiles consist of an azobenzene chromorphore, attached symmetrically to an alkyl chain on both sides; chain lengths, n, range from 6 to 16 carbons. We have studied the effects of chain length of the bolaamphiphile on an aggregate state in solution and in film, on trans-cis or cis-trans photoisomerization kinetics, and on the degree of dichroism induced upon linearly polarized light irradiation. Our study suggests that the degree of dichroism and the photoisomerization in the self-assembled monomolecular film was strongly dependent on the chain length.

Keywords: Self-Assembly; Photoisomerization; Monolayer; Dichroism

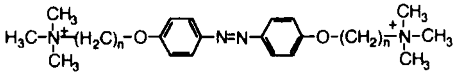
INTRODUCTION

The photoinduced cis-trans isomerization of azobenzene and its derivatives has been widely studied in various media, i.e. solution [1], functionalized glassy polymers [2], Langmuir-Blodgett and self-assembled (SA) films [3]. The most significant developments in the field was the work of Gibbsons et al. about induction of orientation that can be obtained or can be changed with a polarized laser [4].

In this paper, we will describe the cis-trans photoisomerization behavior of azobenzene units in the SA monolayers of the cationic bolaamphiphiles on fused silica precoated with 5 bilayers of polyelectrolytes. We will also discuss the cis-trans photoalignment process of azobenzene in the monolayers and the degree of the film dichroism induced dependent on the alkyl chain lengths.

EXPERIMENTAL

Poly(vinylsulfate, potassium salt) (Mw = 140,000) **PVS** and poly(allylamine hydrochloride) (Mn = 50,000 ~ 65,000) **PAH** were purchased from Aldrich and used without further purification. The synthetic and characterization details of the bolaamphiphiles will be published in a forthcoming paper.



n=6 **(Bola6)**, n=12 **(Bola12)**, n=16 **(Bola16)**

The bipolar amphiphile and polyelectrolytes were deposited onto the negatively charged fused silica as described previously [5]. Firstly, 5 bilayers of **PAH** and **PVS** were deposited by dipping in the **PAH** solution (11 mmolar) and into the **PVS** (6 mmolar) solution for 20 minutes each. Then, a monolayer of **Bola6**, **Bola12**, or **Bola16** was deposited by dipping the substrate into the cationic bolaamphiphile solution (0.1 mmolar), respectively.

The irradiating light source was a high-pressure mercury lamp (Oriel, 500W) equipped with glass filters (ultraviolet: UG1, Spindler & Hoyer: blue: GG10, Spindler & Hoyer) for UV light. The lamp power was adjusted to 2 mW/cm^2 for UV light and to 100 mW/cm^2 for blue light.

RESULTS AND DISCUSSION

Figure 1 shows UV/Visible spectra of the bolaamphiphiles, consisting of an azobenzene chromorphore, attached symmetrically to an alkyl chain on both sides; chain lengths, n, range from 6 to 16 carbons. Comparison of UV/Visible spectra of the bolaamphiphiles in a dilute aqueous solution (0.1 mM) reveals that **Bola6** exists as a molecularly isolated state, reflecting the fact of the maximum absorbance of 4,4'-dihydroxy azobenzene at 358 nm. However, the absorption maximum of **Bola6** is drastically blue-shifted about 17 nm and 37 nm in **Bola12** and **Bola16**, respectively. This suggests that the bolaamphiphile forms a H-aggregate in a dilute aqueous solution (0.1 M), when the alkyl chain contains more that 12 carbons. From the comparison of

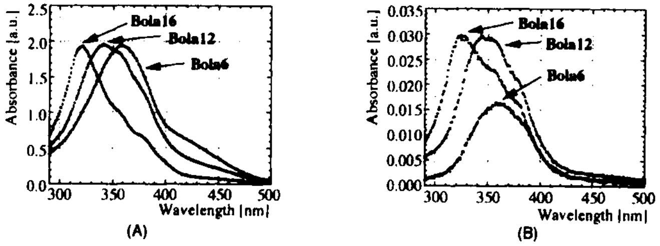


FIGURE 1 UV/Visible spectra of **Bola6**, **Bola12** and **Bola16** in a dilute aqueous solution (A) and in SA monolayer films on fused silica precoated with 5 bilayers of PAH and PVS (B).

aggregate formed in solution was directly adsorbed onto the surface to form the ordered monomolecular film, in the case of **Bola12** and **Bola16**.

Figure 2 shows UV/Visible absorbance of **Bola6**, **Bola12**, and **Bola16** monolayers dependent on the irradiation time with the UV light (365 nm). The kinetics of the photoisomerization in the **Bola6** and **Bola12** monolayers are characterized by a uniform decrease of absorbance at the π-π^* band (360 nm and 344 nm), and an increase of the n-π^* band (445 nm). The different behavior of the photoisomerization, however, is found in the **Bola16** monolayer. The photoisomerization in the **Bola16** monolayers seems to be strongly hindered by the existence of H-aggregates of photochromic moieties in ordered systems.

Birefringence and dichroism can be induced in the monomolecular film resulting from the reorientation of the azobenzene moieties upon irradiating linearly polarized light. This dichroism can be translated into an "order parameter" [6] calculated with the maximum absorbances in the direction parallel and perpendicular to the polarization of the probe light. The order parameters of **Bola6**, **Bola12**, and **Bola16** monolayers were calculated at 352 nm, 340 nm, and 321 nm from the anisotropic spectra as S = - 0.136, - 0.121, and - 0.033, respectively. The results have revealed that the molecular structure or the aggregate state of the azobenzene materials plays also an important role in determining the degree of the maximum dichroism.

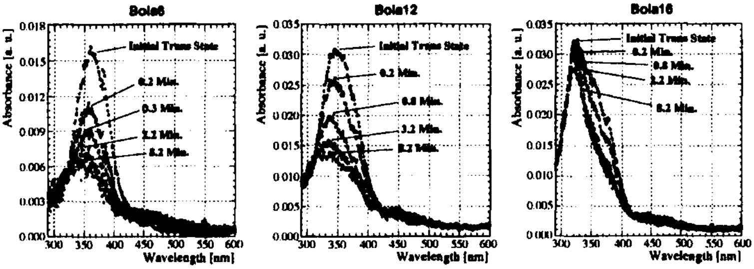


FIGURE 2 Absorbance of **Bola6**, **Bola12**, and **Bola16** monolayers dependent on the irradiation time with UV light (365 nm).

CONCLUSIONS

The UV spectrometry study of the cationic bolaamphiphiles in a dilute aqueous solution (0.1 mM) showed that **Bola12** or **Bola16** forms H-aggregate at r. t. that is adsorbed directly onto the surface for the formation of the well-ordered film on fused silica. Our study has shown that the photoisomerization kinetics and the degree of the dichroism in the SA monomolecular films are strongly dependent on chain length of the bolaamphiphiles.

Acknowledgment.

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