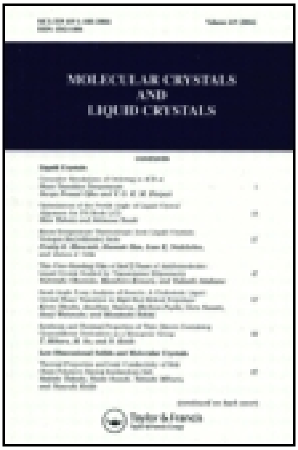

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Hybrid Langmuir and LB Films Composed of Amphiphilic Cyclodextrins and Hydrophobic Azobenzene Derivatives

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Hybrid Langmuir and LB films consisting of amphiphilic cyclodextrins (CDs) and hydrophobic azobenzenes (AZOs) were fabricated. Due to the larger cross-sectional area of the CD core compared with the sum of the cross-sectional areas of the attached alkyl chains, Langmuir and LB films composed of CD have free space in the hydrophobic regions. AZOs having hydrocarbon terminal chains were accommodated in the free space. The average tilt angles of AZO(p-Hexyl) gave minima when the free space was just filled with the AZO. On the other hand, AZO(p-oxy) maintained perpendicular orientation even when the sum of the cross-sectional areas of AZO(p-oxy) exceeded the size of the free space.

Keywords: azobenzene; cross-sectional area; cyclodextrin, photoisomerization; π-A isotherm

INTRODUCTION

Photochromic molecules have attracted considerable interest from the viewpoint of the applications to optical storage, switching devices and

We wish to acknowledge Emeritus Professor W. Tagaki, Osaka City University for providing CDs.

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molecular electronics [1]. Azobenzenes (AZOs) have been extensively studied because of their availability, good photofatigue resistance and ease of preparation. Because trans-to-cis photoisomerization of AZO is accompanied by an increase in cross-sectional area of the molecule, densely packed molecular films are not suitable for photoswitching [2]. In this respect, AZOs in many of the SAMs and LB films are densely packed with very small free space, resulting in a very small degree of photoisomerization.

Cyclodextrins (CDs) are cyclic oligosaccharides consisting of six, seven or eight (α, β or γ, respectively) D-glucopyranose units [3]. Amphiphilic derivatives of α-, β-, and γ-CDs give stable condensed monolayers on the water surface, where amphiphilic CDs can incorporate AZOs without long-alkyl chains in the cavities of their cylindrical structures [4]. The AZOs exhibited excellent photochromic behaviors because the CD cavities provide sufficient free volume [5]. However, these researches assumes that the CD cavity is the only site for the accommodation of AZO though the adsorption of AZO between the CD is pointed out in some cases [5c]. It is to be noted that the cross section of the CD cylinder is much larger than the sum of the cross section of the attached alkyl chains. This indicates the possibility of the presence of additional free space in the hydrophobic region of the Langmuir and LB films.

We have focused on the utilization of the above-mentioned free space located in the hydrophobic region of the Langmuir and LB films of amphiphilic CDs as accommodation sites for guest molecules and have investigated the fabrication of hybrid Langmuir and LB films of amphiphilic CDs and AZOs. Recently, we have found that amphiphilic CDs have the ability to incorporate hydrophobic AZO molecules in the hydrophobic regions of the CDs form homogeneous hybrid Langmuir and LB films [6]. The main driving force of the accommodation of AZO in this case should be hydrophobic interaction. In the hybrid LB films, the tilt angle of the AZO shows a minimum when the free space of the CD is just filled with the AZO. In this study, we examine the formation of hybrid molecular films consisting of amphiphilic CDs and AZOs with variations in the alkyl length of CDs and in the thermal properties of AZOs (Fig. 1). The effect of these factors on the orientation of AZOs in the films is discussed.

EXPERIMENTS

The amphiphilic CDs and the AZOs used in this study were synthesized as reported previously [7]. Measurements of the π-A isotherms were performed on a Lauda FW-II film balance with a subphase of

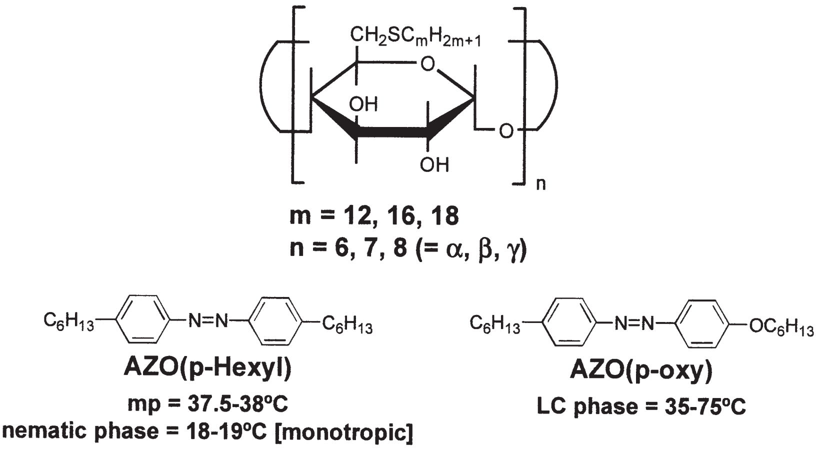

FIGURE 1 Molecular structures of amphiphilic cyclodextrins and azobenzene derivatives used in this study.

pure water (Milli-Q). Spreading solutions were prepared by mixing CDs and AZOs at given molar mixing ratios ([Azo]/[CD] $= r$) using $CHCl_3$ (DOJIN for spectroscopy) as a spreading solvent. The subphase temperature was set at 20°C using a Lauda RSC, RC6 circulator. After spreading, the molecule were left for 10 min for the completion of solvent evaporation and compression at a speed of 1.0×10^{-1} nm^2 mol^{-1} min^{-1} for the measurements of π-A isotherms. The hybrid LB films were transferred at 20 mN m^{-1} onto quartz glass plates with hydrophilic pre-treatments. Polarized absorption spectra of the LB films at an incident angle of 45° were measured on a Cary 500 Scan (Varian UV-VIS-NIR spectrometer). Brewster angle microscope (BAM) equipped with a CCD camera and a video recorder was home-made. Photoisomerization was carried out by using monochromatic light at 365 nm and 436 nm from a 500-W high-pressure Hg lamp. The circular dichroism and absorption spectra of the chloroform solutions were measured using a JASCO J-820 Spectropolarimeter at room temperature. ^{1}H-NMR measurements were carried out on a Varian UNITY at 300 MHz using $CDCl_3$ as solvent.

RESULTS AND DISCUSSION

The interaction between the amphiphilic CDs and AZOs was studied in the chloroform solutions. CDs are known to incorporate many guest molecules in the cavities to form inclusion compounds. The formation of inclusion compounds causes induced circular dichroism [8] and changes in the chemical shifts in the ^{1}H-NMR [9]. In the present study, neither of the above two features were observed for a mixed chloroform solution of β-CDC$_{18}$ (β-CD having octadecyl substituents) and AZO(p-Hexyl). This indicates that the AZO molecules are not incorporated in the cavities of the amphiphilic CDs in the spreading solutions.

The effect of the length of alkyl chains tethered to the CDs on the orientation of AZOs in the hybrid molecular systems was investigated. Amphiphilic β-CDs having dodecyl (β-CDC$_{12}$) and hexadecyl (β-CDC$_{16}$) substituents and β-CDC$_{18}$ were used as the host molecules. AZO

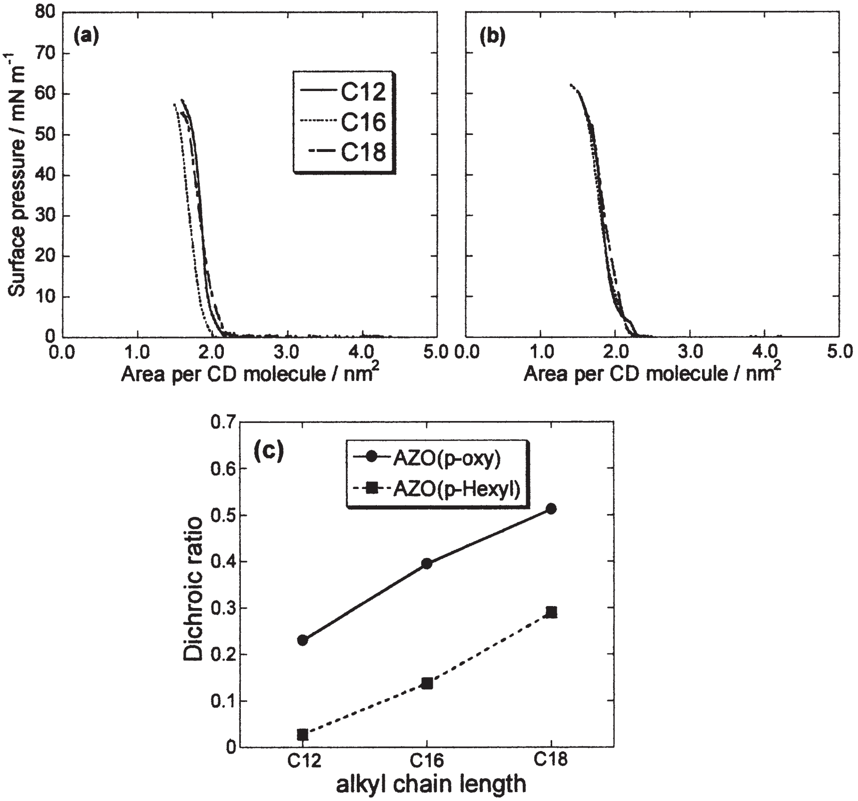

FIGURE 2 π-A isotherms of mixed systems composed of β-CDC$_n$ (n = 12, 16 and 18) with (a) AZO(Hexyl) and (b) AZO(p-oxy) at a mixing ratio of 3 at 20°C and (c) dichroic ratios of the azobenzene derivatives in the LB films as a function of alkyl chain length of β-CD.

(Hexyl) and AZO(p-oxy) having different thermal properties were used as the guest molecules. The molar mixing ratio was fixed at 3 because our previous study showed the average tilt angle of the long axis of AZO(p-Hexyl) in the LB films of β-CDC$_{18}$/AZO(p-Hexyl) is smallest at this mixing ratio [6]. The π-A isotherms are shown in parts (a) and (b) of Figure 2. It is evident that the π-A isotherms show steep rises at *ca.* 2.0 nm^2 and are similar to each other irrespectively of the AZO species and the length of the alkyl chains of the CDs. This result strongly suggests that the molecular areas of the CDs are governed by the sizes of the CD core and that the hydrophobic AZO molecules are incorporated in the Langmuir films without any significant contribution to the areas.

Polarized UV-vis absorption spectroscopic measurements were carried out to obtain information on the orientation of AZO molecules in the hybrid films. Since the polarization of the π-π^* transition of trans-AZO is approximately parallel to the long axis of the molecule, dichroic ratios (DRs) will gives us important information on the orientation of AZO. The DRs are defined by the following equation:

$$\mathrm{DR} = (\mathrm{A_{p45}} - \mathrm{A_{s45}})/(\mathrm{A_{p45}} + \mathrm{A_{s45}}) \tag{1}$$

where $\mathrm{A_{p45}}$ and $\mathrm{A_{s45}}$ denote the absorbance at $\lambda_{\max}$ in the p-polarized and s-polarized spectra at 45° incidence, respectively. Larger value of DRs correspond to smaller tilt angles of the AZO. Figure 2(c) shows the DRs with variation in the AZO species and the length of alkyl chains of the CDs. It is evident that the DRs increase with increasing alkyl

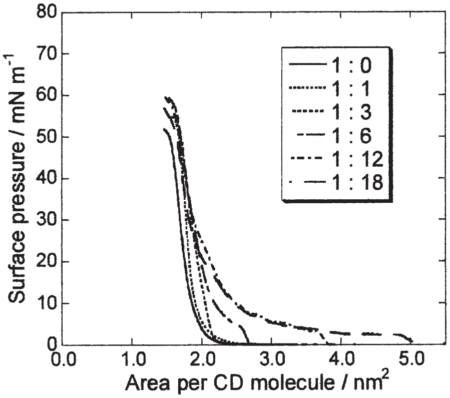

FIGURE 3 π-A isotherms of mixed systems composed of β-CDC$_{18}$ and AZO (p-oxy) at various mixing ratios ($r = 3$, 6 and 12) at 20°C.

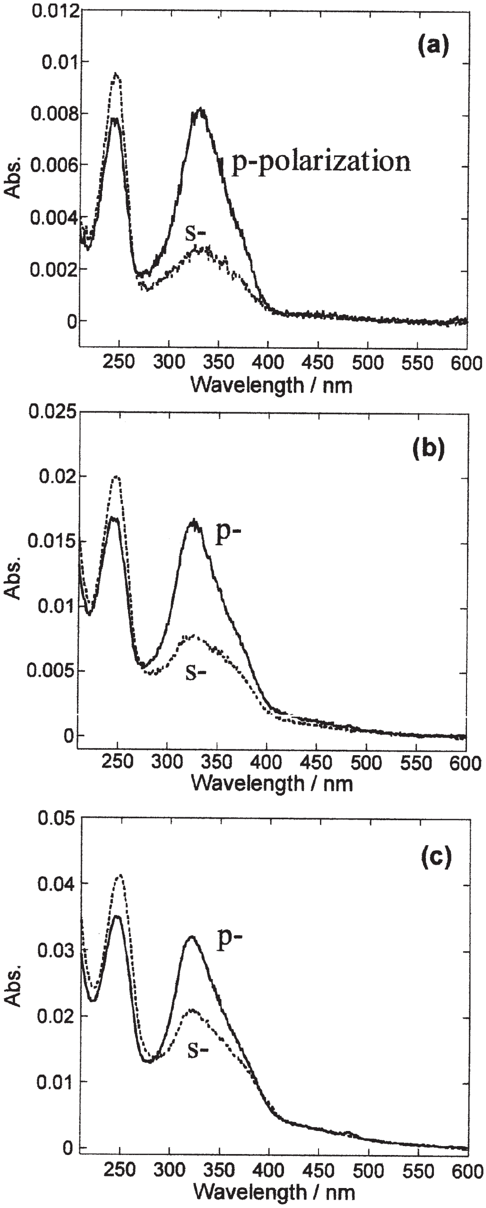

FIGURE 4 Polarized UV-vis absorption spectra of single-layer hybrid LB films of β-CDC$_{18}$ and AZO(p-oxy) at mixing ratios of (a) 3, (b) 6 and (c) 12.

chain length of β-CDs. This means that the tilt angles of the AZOs are smaller when the length of the alkyl chains is longer. Considering the melting points of dodecane (−9°C) and octadecane (28°C) [10], the fluidity of the alkyl chains of β-CDC$_{12}$ is larger than that of β-CDC$_{18}$. The "softer" alkyl chains of β-CDC$_{12}$ tend to hold the guest AZO molecules in an oblique manner in the films while the "harder" alkyl chains of β-CDC$_{18}$ can keep the guest molecules in a more upright orientation. It is also evident that the DRs of the AZO(p-oxy) systems are always larger than those of the AZO(Hexyl) systems. This suggests that AZO(p-oxy) tends to adopt a more upright orientation than AZO(Hexyl).

The structures of the hybrid Langmuir films of β-CDC$_{18}$ and AZO-(p-oxy) were studied at various mixing ratios ($r = 3$, 6, 12). Figure 3 shows the π-A isotherms of the mixed systems. Although the molecular areas at low surface pressure are larger than that of per β-CDC$_{18}$, the area per CD estimated from the steep regions of the isotherms are almost the same and are ~2.0 nm^2. These values roughly correspond to the size of the CD core. This result strongly suggests that the molecular areas of the CD in the condensed phases are governed by the size of the CD core and that the hydrophobic AZO molecules are incorporated in the Langmuir films without any significant contribution to the areas. Furthermore, when the mixing ratios are larger than 3, the isotherms rise at larger areas and condensed phases appear after phase transitions. This suggests that AZO(p-oxy) molecules occupy significant area before the phase transitions. These

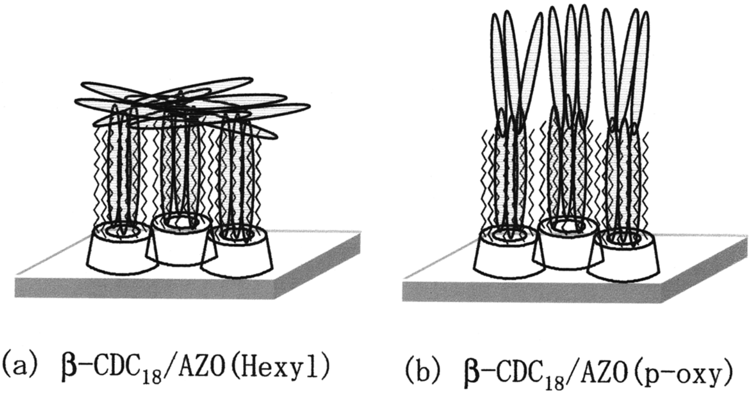
(a) β-CDC$_{18}$/AZO(Hexyl) (b) β-CDC$_{18}$/AZO(p-oxy)

FIGURE 5 Schematic view of the structures of the hybrid molecular films of β-CDC$_{18}$ with AZO(Hexyl) or AZO(p-oxy) at mixing ratios more than 3.

AZO(p-oxy) molecules should be squeezed out on to the β-CDC$_{18}$/AZO(p-oxy) monolayers to form condensed films after the phase transitions.

The structures of the hybrid LB films of β-CDC$_{18}$ and AZO(p-oxy) were studied using polarized UV-vis spectroscopic measurements (Fig. 4). AZO(p-oxy) molecules are oriented almost perpendicularly in the film at a mixing ratio of 3. The orientation does not change significantly when more AZO(p-oxy) molecules are added. This suggests that the additional AZO(p-oxy) molecules are located on the top of the β-CDC$_{18}$/AZO(p-oxy) monolayers with almost perpendicular orientation as schematically shown in Figure 5. This is in contrast to the case of β-CDC$_{18}$/AZO(Hexyl) systems where the additional molecules are oriented almost parallel to the films surface. The reason of the differing behaviors of the two AZO derivatives at high mixing ratios is not clear at present. One of the possible explanations is relevant to the difference in thermal properties of the two AZOs. AZO(p-oxy) has a wide-range of liquid crystalline phase near room temperature in the bulk state, whereas the liquid crystalline phase (monotropic) of AZO(Hexyl) exists only in a narrow temperature region. AZO(p-oxy) may have larger tendency of parallel orientation with each other compared with AZO(Hexyl), which can be reflected in the differing orientation of the two AZOs in the LB films at mixing ratios larger than 3.

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