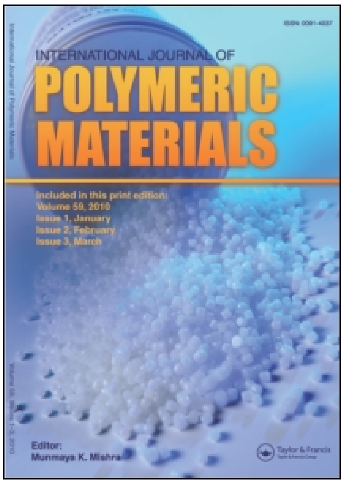

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Standardization of photoresponsive LB films fabricated from simple azobenzene derivative

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STANDARDIZATION OF PHOTORESPONSIVE LB FILMS FABRICATED FROM SIMPLE AZOBENZENE DERIVATIVE

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It is believed that azobenzene amphiphiles tend to be strongly H-aggregated during pure Langmuir-Blodgett (LB) film manipulation and therefore they are unable to photoisomerize. However, we present in this article the manner for destabilizing such aggregation by means of a simple physical treatment process, obtaining finally well photoresponsive amphiphilic azobenzene in the pure LB films. Such LB films are highly suitable for regulating the orientation and photoreactivity of other surface-in touch systems such as nematic liquid crystals and photoreactive monomers to be polymerized. Therefore, we investigated the manipulation of LB films of the azobenzene derivative, 11-(4-(4-hexyl-phenylazo)-phenoxy)-undecanoic acid using different monomeric isomers, by temperature and monolayer transfer methods. The LB films were then exposed to heat treatment process and finally to photophysical processes.

Keywords: azobenzene, photoresponsive, LB film

INTRODUCTION

Langmuir-Blodgett (LB) films of photochromic materials such as azobenzene amphiphiles are of interest as possible high-density information storage media and light switching devices. For this purpose, for more than one decade extensive studies have been conducted on the fabrication of long-chain azobenzene-based LB films with photoresponsive character [1–12]. The fundamental idea was to obtain a long chain-based multilayered structure, which enables the azobenzene moiety to photoisomerize reversibly. The free volume, defined as the volume swept out by the van der Waals area of the

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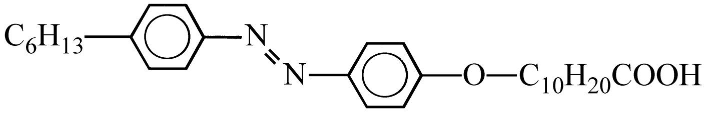
displacement group, required for the photoisomerization of some photoprobes has been determined [13, 14]. In particular, the free volume needed for azobenzene to isomerize was estimated to be 127 Å^3. Hence, for azobenzene with attached alkyl tail groups the sweep volume should be larger and so the intermolecular distance should be much greater than few tens of Angstroms. Therefore, it has been demonstrated that azobenzene guest molecules in host-guest LB films showed photochromic behavior with complete reversibility owing to the free volume of cyclodextrine cavity [12]. On the other hand, Seki et al. have reported that azobenzene derivatives with a variety of long chain lengths are photoisomerizable in the LB film when they are pendants to a polymer such as poly(vinyl alcohol), PVA [10]. However, the drawback was in the fabrication of long-chain azobenzene, which photoisomerizes in the pure LB films. Some authors have reported that the azobenzene units in LB film composed of a carboxylic acid derivative were not photoreactive [4, 11]. They gave a common reason that a clear hypsochromic shift of the absorption spectrum ($\lambda_{max} = 296\,nm$) was observed, as a result of side-by-side aggregation (or H-aggregation). From such a point we started to create the strategy of how to destabilize such aggregation in the LB film, aiming finally to have photoresponsive pure LB films made from simple azobenzene amphiphile.

MATERIALS AND EXPERIMENTAL WORK

The azobenzene derivative, denoted as 6Az10, was synthesized according to a method described elsewhere [16]. The synthesis of the target material, 6Az10, is essentially based on a coupling reaction process. The starting reagents of this reaction are 4-[(4′-hexylphenyl)azo]phenol, 11-bromoundecanoic acid and potassium hydroxide in ethanol refluxing for 6 h at room temperature.

Two solutions have been used in the manipulation of LB films: The first was freshly prepared trans-isomeric solution of 6Az10 in chloroform ($1 \times 10^{-3}\,mol\,dm^{-3}$). The second was a similar solution that was converted into the cis-isomeric analog by exposing 3 ml of it (in a quartz cell) to a 365 nm UV light source 16 cm apart, for one second, as an optimum irradiation time for the photostationary state. Then the LB film manipulation, using a commercial Langmuir-Blodgett balance (Messgratewerk



6Az10

SCHEME 1

Dr. R. Wobser KG, Lauda), has been started by spreading 0.2 ml of each solution either on doubly distilled water or on 4×10^{-4} mol dm^{-3} aqueous $CdCl_2$ (buffered with 4×10^{-5} mol dm^{-3} aqueous $KHCO_3$). The monolayer formation was performed isothermally at three temperatures: 22, 10 and 5°C, using surface pressure of 20 – 30 dyne/cm and compression speed of 50 cm^2/min. Both the vertical and horizontal dipping methods were used to transfer the monolayers.

For the purpose of vertical dipping, quartz substrates were hydrophilically treated as follows: They were pre-washed by chloroform and ethanol, then they were ultraviolet-ozonated and finally rinsed by distilled water in an ultrasonic bath. Hydrophobic quartz substrates were prepared by performing first the procedure mentioned above and then they were treated with 1,1,1,3,3,3-Hexamethyldisilazane (HMDS) for 12 hours to be ready for the horizontal dipping use. The transfer ratio for all transfer processes ranged 0.95 – 1. We have investigated four different samples of 6AZ10 LB films denoted as AzCH (horizontally transferred cis-isomer), AzTH (horizontally transferred trans-isomer), AzCV (vertically transferred cis-isomer) and AzTV (vertically transferred trans-isomer).

Absorption spectra were measured by Shimadzu UV-2500PC spectrophotometer. All irradiation processes were performed using two lights: UV-365 nm and VIS-450 nm powered by the source "500 W super-high pressure mercury lamp, Ushino USH-500 D".

RESULTS AND DISCUSSION

The surface pressure-area (π-A) isotherms of the 6Az10 monolayer at the air-$CdCl_2$ aqueous solution interface are illustrated in Figure 1. In this graph one can observe the effect of the molecular conformation on the aggregation and packing of the molecules. The monolayer of the trans-isomer is formed in an extremely condensed fashion at room temperature (see curve 1). In a separate study, not represented here, the molecular area was shown to slightly increase with lowering the temperature. However, in the case of the cis-isomer, the monolayer frequently collapses rapidly at lower values of the surface pressure owing to the thermodynamic instability of the cis-isomer [10]. In order to avoid such thermoisomerization problem it is important to treat the solution of the cis-isomer carefully as follows: First, we keep that isomeric state frozen-in by quenching the solution rapidly down to – 10°C just after the irradiation with UV light. Second, we cool the subphase down to 5°C so as to create more viscous and adhesive face-to-face interface. The π-A isotherm corresponding to the cis-isomeric solution is illustrated by curve 2 of Figure 1. The molecular area of the cisoid isomer records for about 36.6 Å^2/molecule, which is significantly larger than that determined for the trans-isomer, 22.5 Å^2/molecule prepared at 22°C. It is noteworthy that the onset

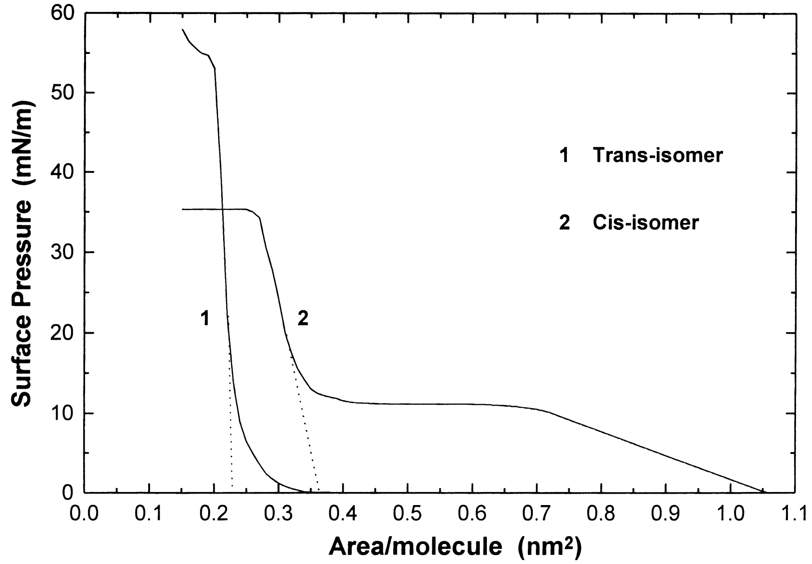


FIGURE 1 Surface pressure (π)-area (A) isotherms of 6Az10 monolayer at the air-$CdCl_2$ aqueous solution interface (see text). Curve (1) corresponds to the trans-isomer at 22°C and curve (2) corresponds to the cis-isomer at 5°C.

surface pressure at about 40 Å^2/molecule implies the formation of a cadmium salt of the 6Az10 monolayer as a result of the complexation of the carboxylate end group with the cadmium ions in the form: COO^-—Cd^{2+}—^-OOC, at the air-subphase interface. That is to say, closely packed dimers are formed. The molecular area difference (ca. 14 Å^2), determined from the two isotherms, sheds some light that the molecules of the latter are tilted with respect to the normal to the surface. The optimum conditions required for highly photoresponsive LB films were investigated through the variation of some manipulation parameters such as surface pressure, LB trough temperature, film transfer method and number of transferred monolayers.

Let us start first with the fabrication of the photoisomerizable LB film manipulated from a spreading trans-isomer at the air-$CdCl_2$ aqueous solution. After the transfer of the condensed monolayer onto the quartz substrate, we verified that heating the substrate at a particular temperature (110°C) followed by quenching it in a dry ice is the best way to relax the packing of the stressed transoid isomers to the normal trans-isomeric conformation. Such mechanism could be understood by monitoring both the intensity enhancement and position red shift of the absorption band (peaked around 300 nm) of the LB films (sample AzTV, $n = 2$ layers, $T =$ 22°C) shown in Figure 2. The new peak position at 320 nm is an evidence that the H-aggregation of the LB film ensemble has been partially

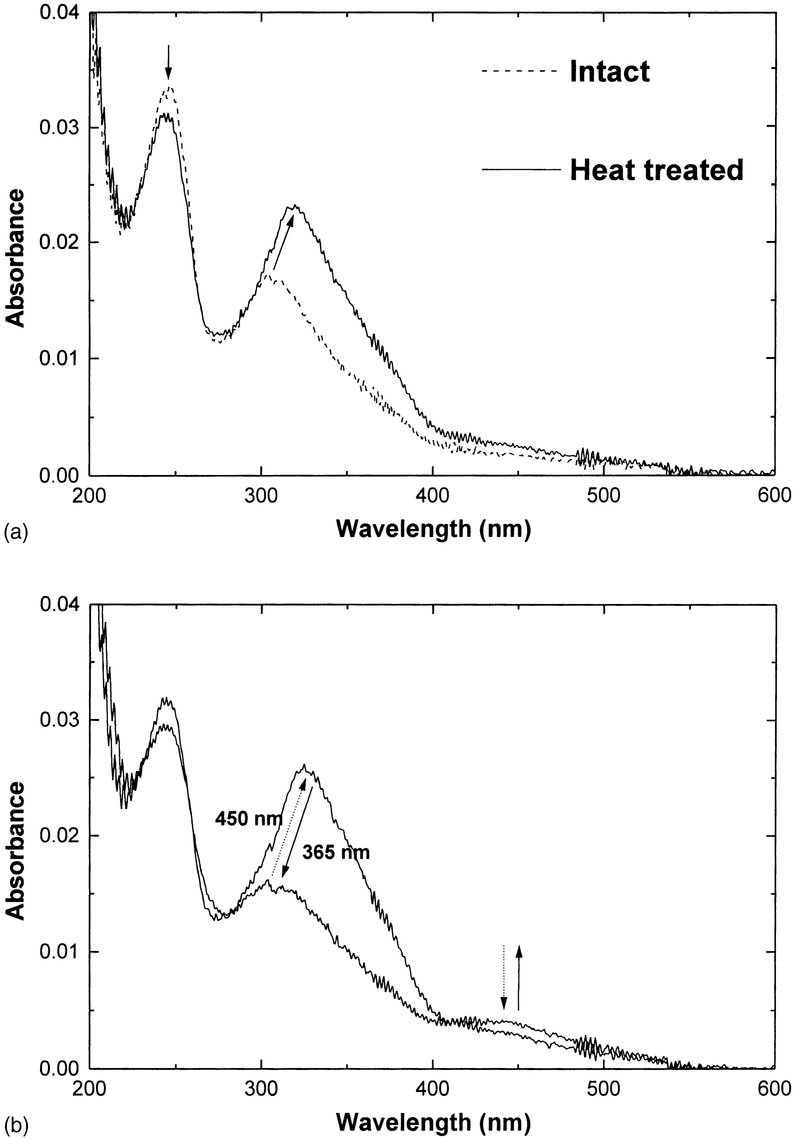


FIGURE 2 Absorption spectra of the LB film (AzTV: single layer on both sides manipulated at T = 22°C and $\pi = 30\,\mathrm{mN/m}$). (a) Effect of heat treatment at $T_H = 110°C$ for $t_H = 60\,\mathrm{min}$. (b) Reversible trans-cis photoresponsive behavior.

destabilized by the heat treatment process. Such loose structure gives rise to the performance of photoresponsive behavior as verified by alternately exposing the LB film to UV and visible light irradiation. This can be typically verified by the observation of the intensity changes of both the π-π^* trans-isomeric and n-π^* cis-isomeric transitions peaked at 320 nm and 450 nm [17], respectively (see Figure 2b). The response times for maintaining the photostationary cis- and trans-isomeric states were determined to be 5 and 15 sec, respectively. With regard to the LB films manipulated horizontally (sample AzTH, n = 1 layer, T = 22°C), no marked change in the overall photoresponsive behavior of the LB film was observed, except for a little more spectral red shift in the later case reflecting, to a slight extent, a higher orientation order in the monolayer transferred horizontally (see Figure 3).

It is important to state that the optimum conditions for manipulating LB films adopting excellent photoresponsive fingerprint were determined using a freshly prepared chloroform solution of the trans-isomeric azobenzene derivative and a surface pressure of 20 dyne/cm applied at 22°C. The heat treatment effect together with photoresponsive behavior of the fabricated LB film (AzTV-type, n = 1) are illustrated in Figure 4. Interestingly, the spectral red shift of the band peaked around 340 nm is typical evidence for the face-to-face dimer formation [2]. Such mechanism leads us to visualize and configure the reasonable ensemble of the LB film structure to be described by the following model (see Figure 5). After the heat treatment, the closely packed side-by-side dimers are forced to adopt face-to-face configuration. That is to say, they avoided the destructive thermal expansion that might occur, creating free volume sites required for the reversible cis-trans photoisomerization. Under such circumstances we may say that the H-aggregation has been significantly destabilized. Indeed, it is difficult to determine, in a quantitative manner, the exact molecular dynamics and driving forces of our model structure. But rather we are satisfied with this qualitative description since our main target is to examine the photoresponsive property of the LB films rather than seeking a detailed study of the molecular and thermodynamical aspects.

Further study was conducted on the fabrication of photoresponsive LB film manipulated by using cis-isomeric azobenzene derivative. The cis-isomer-based solution was prepared by irradiating a freshly prepared trans solution (in the dark) with 365 nm light for one second (optimum time required for maintaining the cisoid photostationary state) as illustrated in Figure 6. In this case there was no need for the heat treatment process and the LB films were manipulated from the air-$CdCl_2$ aqueous solution interface after which they were taken directly to the photophysical process. The photoresponsive profile of the cis-isomer-based LB film (sample AzCH, n = 1, T = 5°C) is represented through the absorption spectra shown in Figure 7. It was found that the response times for the photostationary cis-to-trans and trans-to-cis conversions are 10 s and 2 s, respectively. Such photoresponsive behavior is analogous, to some extent, to that exhibited by the trans-isomeric LB

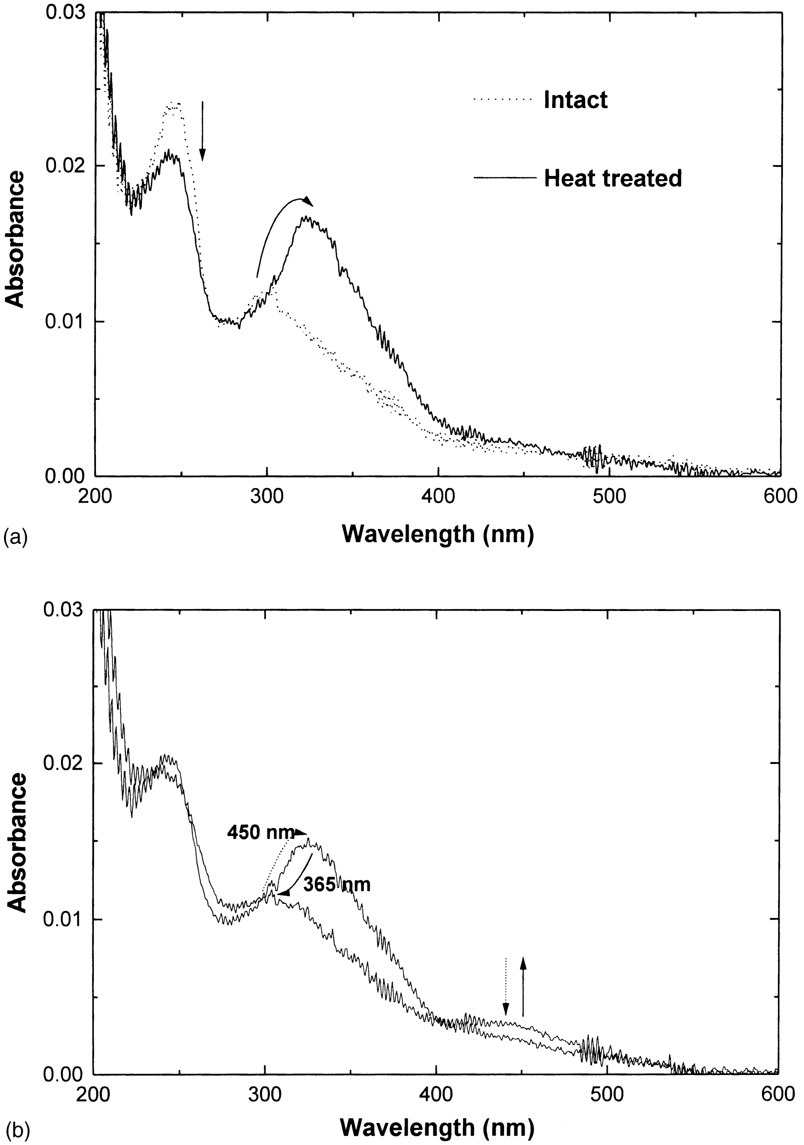


FIGURE 3 Absorption spectra of the LB film (AzTH: single layer manipulated at $T = 22°C$ and $\pi = 30\,mN/m$). (a) Effect of heat treatment at $T_H = 110°C$ for $t_H = 60\,min$. (b) Reversible trans-cis photoresponsive behavior.

films. We should mention also that very poor results were obtained for the latter LB film when manipulated by the vertical dipping method (sample AzCV).

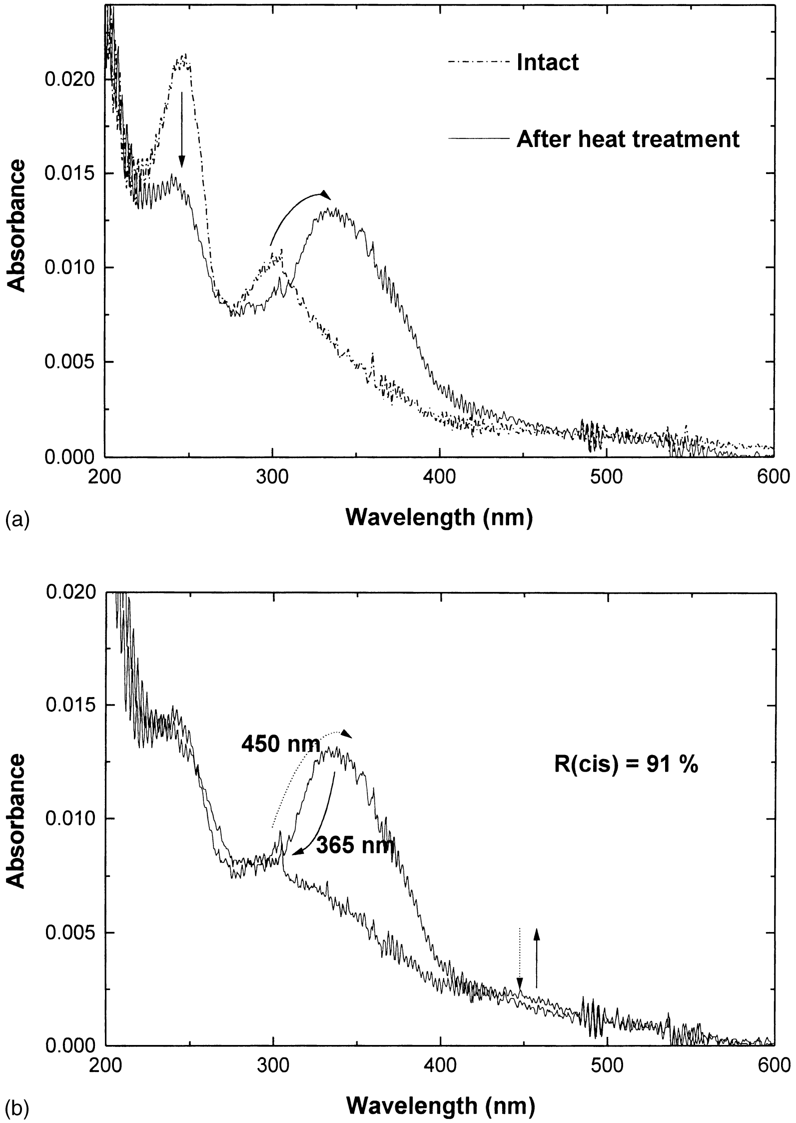


FIGURE 4 Absorption spectra of the LB film (AzTV: single layer on both sides manipulated at T = 22°C and $\pi = 20\,\mathrm{mN/m}$). (a) Effect of heat treatment at $T_H = 110°C$ for $t_H = 30\,\mathrm{min}$. (b) Reversible trans-cis photoresponsive behavior.

Now we turn our attention to an important tool, which can be used for monitoring the orientation order of the azobenzene moiety in the LB film. That is the value of the ratio A_s/A_l: the ratio of integrated absorbances of

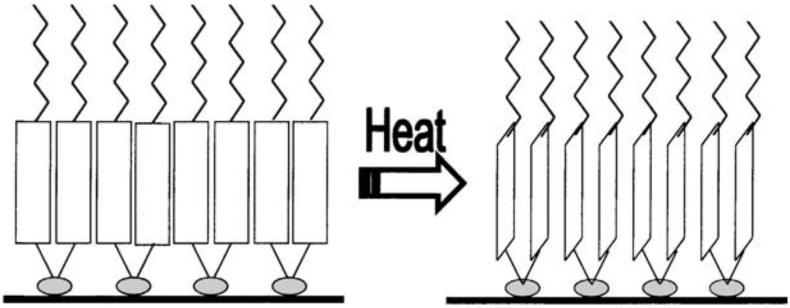


FIGURE 5 Model of the heat treatment effect on the molecular packing of H-aggregated 6Az10 LB film. (a) Packed side-by-side dimers (couple of 6Az10 attached to a single cadmium ion) of intact monolayer. (b) Destabilization of H-aggregation into face-to-face dimerization upon heat treatment.

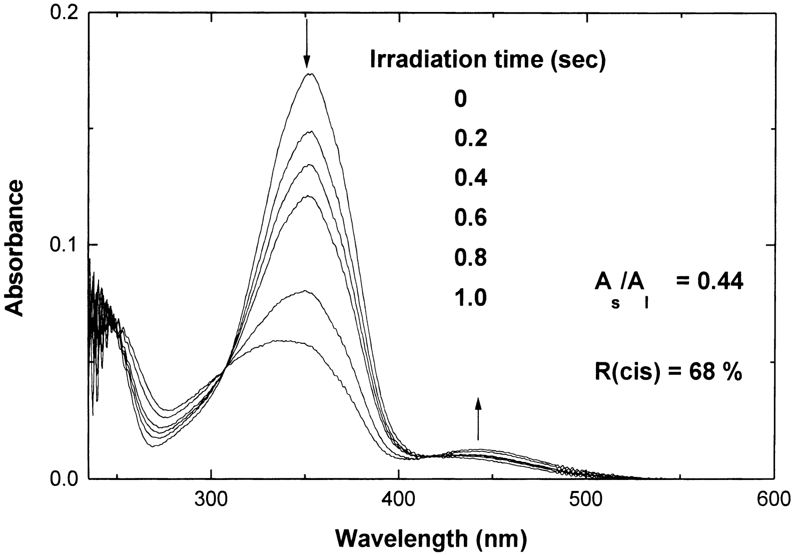


FIGURE 6 Absorption spectra of freshly prepared 6Az10 chloroform solution (10^{-3} mol dm^{-3}) irradiated with 365 nm light.

the maxima peaks at 238 nm and ca. 300 nm, referring to the short (A_s) and long (A_l) axes, respectively. As the spectra were observed with a perpendicular incident beam, upright orientation of the azobenzene long axis to the substrate raises this value. It has been demonstrated that A_s/A_l of azobenzene derivatives in solutions and in LB films have the values of 0.45 and 2.4, respectively. These values could be regarded as an indicator of two

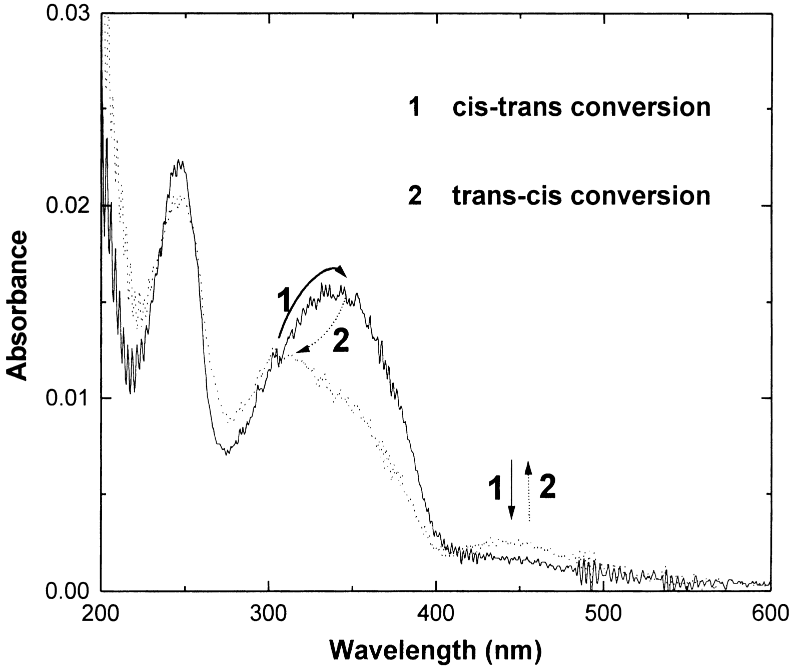


FIGURE 7 Cis-trans photoresponsive behavior of the LB film (AzCH: single layer manipulated at T = 5°C and $\pi = 30\,\text{mN/m}$).

TABLE 1 The photoresponse times and conversion parameters of different LB films

LB film	$T_H(°C)^a$	$\pi(mN/m)$	$R(cis)^b$	A_s/A_l ^{c}	$t_{t\text{-}c}(s)^d$, $t_{c\text{-}t}(s)^e$
AzTV	22	20	0.09	1.00	5,10
	22	30	0.29	1.40	60,15
AzTH	22	30	0.24	1.20	5,10
	10	30	0.46	1.65	10,15
AzCH	5	30	0.53	1.37	2,10

[a] LB trough temperature.
[b] Cis-isomer conversion parameter.
[c] Chromophore orientation ratio (see text).
[d] Photostationary trans-cis response time.
[e] Photostationary cis-trans response time.

extremes, i.e. random and highly oriented systems [15]. Table (1) summarizes the A_s/A_l values of the different LB film types together with the cis-isomer conversion parameter, R(cis) and the response times of the cis- and trans-isomeric photostationary states. We must state that the initial cycle of the trans-cis-trans photoisomerization changes the values of λ_{max} and A_s/A_l, probably because of some disordering of the film structure. After the second cycle was reached, these values were reproducible by repeated cyclic isomerization. Therefore, the data represented here are those including the second cycle. With regard to the values of A_s/A_l, R(cis) and response times, the optimum condition and photophysical properties for a highly photoresponsive LB film may be extracted and summarized again as follows: 1- AzTV; $\pi = 20$ dyne/cm, T = 22°C, $T_h = 110$°C, $t_h = 30$ min., R(cis) = 91%, $A_s/A_l = 1$, $t_{t\text{-}c} = 5$ sec, $t_{c\text{-}t} = 10$ sec. 2- AzCH; $\pi = 20$ dyne/cm, T = 5°C, R(cis) = 46%, $A_s/A_l = 1.37$, $t_{t\text{-}c} = 2$ sec, $t_{c\text{-}t} = 10$ sec.

It is noteworthy that similar results have been obtained for azobenzene pendants on PVA multilayer structured LB film reported elsewhere [18, 19], supporting the quality and processibility of our new method of fabrication. This approach of scientific research utilizes a physical method in order to circumvent the obstacle of complicated chemistry. We must stress that the outcome of this paper encouraged us to investigate the controlling capability of such photoresponsive LB for regulating the nematic liquid crystal orientation and for enhancing the photoreactive kinetics of other systems to appear in other papers [20, 21].

CONCLUSION

The azobenzene derivative could be easily manipulated into LB films in both the transoid and cisoid isomers. A simple heat treatment of LB films fabricated from the trans-isomer proved to bring about the destabilization of the H-aggregation. The observed absorption spectral shift upon the heat treatment process sheds light on the transformation of azobenzene monolayer from a closely packed side-by-side dimer configuration into a face-to-face analogue. We were able to determine the optimum condition for creating highly photoresponsive LB films. Similar data were obtained from the LB films fabricated from the cisoid-isomeric azobenzene-based solution.

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