

Articles

Reversible Optical Information Storage of Self-Assembled Alternating Multilayer Films: Bipolar Amphiphile-Polyelectrolyte

Jong-Dal Hong*, Eung-Soo Park, and Ae-Li Park

Dept. of Chemistry, Incheon University, 177 Dohwa-dong Nam-ku, Incheon 402-749, Korea

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Alternating multilayer films of a cationic bipolar amphiphile and an anionic polyelectrolyte were prepared by a self-assembly method based on electrostatic attraction between opposite charges. The bipolar amphiphile contains an azobenzene unit in order to allow for a *trans-cis* photoisomerization to take place. Optical birefringence or dichroism was induced in the self-assembled film upon linearly polarized light irradiation. This dichroism could be reversibly written and erased by irradiation with light of an appropriate wavelength.

Introduction

It is well-known that azobenzene derivatives undergo *cis-trans* photoisomerization upon light irradiation.¹ A remarkable consequence is the Weigert effect, in which birefringence or dichroism is induced on irradiation with polarized light.² This has great potential specifically for polarization holography³ and more generally for optical information storage and switching applications.⁴⁻⁸ There are a number of reports in the literature on the optical response of organized thin films containing an azobenzene moiety. Reversible photoresponsive alignment changes of the nematic liquid crystals are demonstrated to be dependent on the molecular structure of the azobenzene units in the monomolecular film, which was prepared on the quartz surface by the chemisorption.⁷⁻⁸ Similar photoalignment has also been reported using Langmuir-Blodgett (LB) films of poly(vinyl alcohol) derivative with azobenzene side chains.⁹ Kakimoto and coworkers have studied photochemically inducible and erasable dichroism in which an azobenzene pendant unit in a polyimide LB film is molecularly reoriented.¹⁰ Knoll and coworkers have reported dichroism that is induced in an azosilane monolayer that is self-assembled on a quartz glass substrate.¹¹ There are a few recent reports on the Weigert effect in organized molecular structures.¹²⁻¹³

The self-assembly technique based on electrostatic attraction between opposite charges has now been extensively utilized and shown to allow the preparation of ultrathin organic films with excellent control over thickness and molecular architecture.¹⁴⁻¹⁵ We have constructed assemblies composed of a cationic bipolar amphiphile and an anionic polyelectrolyte on the pretreated substrate surface, shown schematically in Figure 1. The bipolar amphiphile, 4,4'-azobenzene-bis(12-trimethylammonium-N-yl dodecyloxy) dibromide, henceforth referred to as BA-12, is given in Figure 1.

In this article, we report the photochemical switching behavior of a new type of the photochromic material contain-

ing BA-12, the multilayer assemblies, in which the photoactive layers are sandwiched between oppositely-charg-

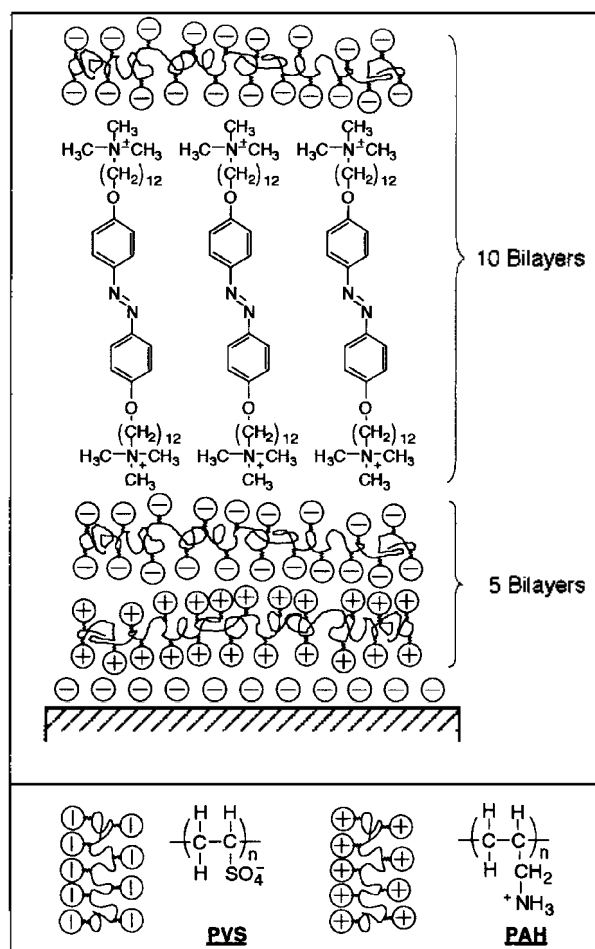


Figure 1. Idealized schematic view of a self-assembled alternating multilayer film composed of a bipolar amphiphile BA-12 and an anionic polyelectrolyte PVS on a precoated fused silica substrate. The precoated substrate contains 5 bilayers of PAH and PVS to obtain the maximum ionic concentration on the surface.

*To whom all correspondence should be addressed.

ed polyelectrolyte layers. We also discuss a photoinducible and erasable dichroism in the self-assembled multilayer film on a fused silica substrate.

Experimental

Materials. Poly(vinylsulfate, potassium salt) PVS and poly(allylamine hydrochloride) (Mn=50,000–65,000) PAH were purchased from Aldrich and used without further purification. The bipolar amphiphile, 4,4'-azobenzene-bis(12-trimethylammonium-N-yl dodecyloxy) dibromide BA-12 was synthesized and the molecular structure is given in Figure 1.

The bolaamphiphile, BA-12 was synthesized in three steps. First, a reductive coupling of *p*-nitrophenol with KOH leads to the 4,4'-dihydroxy azobenzene. Second, the 4,4'-dihydroxy azobenzene was converted to 4,4'-bis(12-bromododecyloxy) azobenzene by the Williamson reaction with 1,12-dibromododecane. Third, the 4,4'-bis(12-bromododecyloxy) azobenzene was quaternized with trimethylamine in toluene.

4,4'-Dihydroxy Azobenzene. The reaction was carried out according to the literature.¹⁶ Yield: 11.4%. Melting point: 216.5 °C. Anal. Calcd: C, 67.3; H, 4.7; N, 13.1. Found: C, 66.8; H, 4.7; N, 12.8. ¹H NMR (DMSO, 60 MHz, ppm): δ 6.9 (d, phenyl ring, 4H_s), δ 7.8 (d, phenyl ring, 4H_s), δ 10.0 (s, phenyl-OH, 4H_s).

4,4'-Bis(12-bromododecyloxy) Azobenzene. 4,4'-dihydroxy azobenzene (4.9 g, 23 mmol) and 1,12-dibromododecane (30 g, 90 mmol) in ethanol were refluxed for 48 h. One mini-spatula of KI was added for the catalyst. When the mixture was cooled, the product precipitated as yellow powder. The precipitates were filtered, and washed with H₂O, and with ethanol, respectively. The crude product was recrystallized. Yield: 52%. Melting point: 109.5 °C. Anal. Calcd: C, 61.0; H, 8.0; N, 3.9; O, 4.5. Found: C, 63.0; H, 8.0; N, 3.9; O, 7.0. ¹H NMR (CHCl₃, 200 MHz, ppm): δ 1.2 (m, $-(\text{CH}_2)_8\text{CH}_2\text{CH}_2\text{-Br}$, 40H), δ 1.9 (m, $-\text{O-CH}_2\text{CH}_2(\text{CH}_2)_8-$, 4H), δ 3.2 (t, $-(\text{CH}_2)_8\text{CH}_2\text{CH}_2\text{-Br}$, 4H), δ 4.0 (t, $-\text{O-CH}_2\text{CH}_2-$, 4H), δ 7.1 (d, phenyl ring, 4H_s), δ 7.8 (d, phenyl ring, 4H_s).

4,4'-Azobenzene-bis(12-trimethylammonium-N-yl dodecyloxy) Dibromide. 4,4'-bis(12-bromododecyloxy) azobenzene (1.4 g, 2 mmol) in toluene was allowed to react with 0.5 g (4 mmol) of trimethylamine in an ampoule at 100 °C for 144 h. The product precipitated as yellow needles. The precipitates were filtered, and washed with warm toluene. Yield: 80%. Melting point: 261 °C. Anal. Calcd: C, 61.0; H, 9.0; N, 6.8. Found: C, 58.0; H, 9.2; N, 6.9. ¹H NMR (DMSO, 250 MHz, ppm): δ 1.3 (m, $-(\text{CH}_2)_8\text{-CH}_2\text{CH}_2\text{-NMe}_3$, 40H), δ 1.7 (m, $-\text{O-CH}_2\text{CH}_2(\text{CH}_2)_8-$, 4H), δ 3.1 (m, $-\text{CH}_2\text{-CH}_2\text{N}(\text{CH}_3)_3$, 22H), δ 4.1 (t, $-\text{O-CH}_2\text{CH}_2-$, 4H), δ 7.1 (d, phenyl ring, 4H_s), δ 7.8 (d, phenyl ring, 4H_s).

Film Construction. The ultrapure water used for all experiments and all cleaning steps was obtained by ion-exchange and filtration unit (Milli-Q, Millipore GmbH). The resistivity was better than 18.0 M Ω -cm. The substrates for all adsorption experiments were fused silica slides of size 25 \times 50 mm². They were cleaned by ultrasonication in the mixture of H₂SO₄/H₂O₂ (7/3) and then heated in the mixture of H₂O/H₂O₂/NH₃ (5 : 1 : 1) at 80 °C for 1 hr. The substrates were thoroughly washed with ultrapure water after both steps.

The bipolar amphiphile and polyelectrolytes were deposit-

ed onto the negatively-charged substrate as described previously.^{14–15} After each adsorption step the surface of the film was thoroughly rinsed and then blown dry with a stream of nitrogen.

Self-assembled multilayers were prepared by dipping a fused silica alternately into aqueous solutions of the cationic bolaamphiphile BA-12 and the anionic polyelectrolyte PVS. In order to adsorb BA-12 as homogeneously as possible, the substrate was precoated with five bilayers of PAH and PVS. The precoating provided a more homogeneous charge distribution on the substrate. After the precoating, the substrate was dipped into the BA-12 solution (0.2 mM). In the next step, the substrate was dipped into the solution of PVS (6 mM). Thus, the substrate was coated with ten bilayers of BA-12 and PVS. The quantity of material deposited at each step was determined from its absorption spectrum, which was generated on a Perkin-Elmer Lambda 4B UV/Visible spectrophotometer.

Photoisomerization. Photoisomerization of the azobenzene was induced by UV light (360 nm) for the *trans-cis* reaction and by visible light (blue, 450 nm) for the *cis-trans* back isomerization. The irradiations were carried out using a high-pressure mercury lamp (Altech, 1 kW) equipped with glass filters (ultraviolet: UG1, Spindler & Hoyer, blue: GG10, Spindler & Hoyer). The lamp power was adjusted to 2 mW/cm² for UV light and to 100 mW/cm² for blue light. The surrounding temperature on the sample was adjusted to be ca 30 °C using a cold plate (Stir-Kool Model SK12, Aldrich Chem. Co.) to prevent thermal back isomerization during UV irradiation.

Polarized UV/Visible spectra of the film before and after polarized UV irradiation were recorded on a Hewlett Packard diode array spectrophotometer (Model 8452A) with dichroic sheet polarizers. Dichroism measurements were performed by irradiating the samples with a linearly polarized UV light and immediately recording absorption spectra with the probe light polarization parallel (Abs_{||}) and perpendicular (Abs_⊥) to the initial UV polarization.

Film Morphology. The film thickness of multilayered films on a silicon wafer was determined with an optical ellipsometer (Rudolph/Auto EL) equipped with a 632.8 nm line of He/Ne laser incident upon the sample at 70°. The orientation of the azobenzene chromophore in BA-12/PVS multilayer was estimated from the polarized UV spectra obtained at 45° incidence angle.

Results and Discussion

Although we have only performed this experiment using polyelectrolytes which are either purely anionic (PVS, poly(vinylsulfate, potassium salt)) or purely cationic (PAH, poly(allylamine hydrochloride)), we believe that in principle all polyelectrolytes can be used in this experiment. The precoating of the fused silica substrate with 5 bilayers of PAH and PVS prior to the deposition of the active layers was designed to provide the maximum surface charge.

Figure 2 shows the UV absorbance of azobenzene chromophores at 351 nm as a function of the number of bilayers deposited. The adsorption occurs essentially uniformly, the same amount being deposited on each cycle. A linear fit of data yields an average increase of the optical

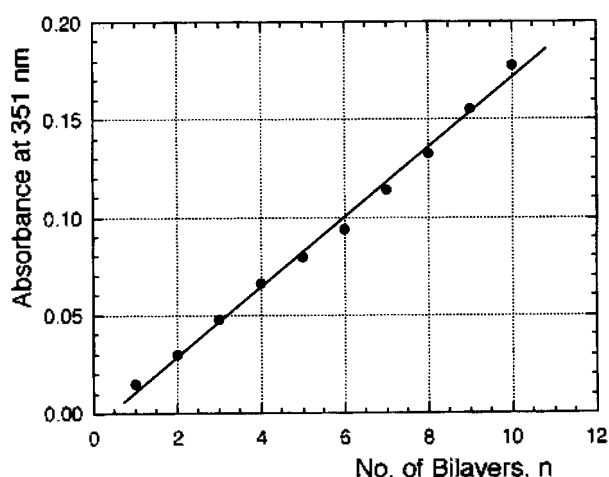


Figure 2. Optical absorbance of 4,4'-azobenzene-bis(12-trimethylammonium-N-yl dodecyloxy) dibromide BA-12 layers at 351 nm depending on the number of the deposited layers.

density of 0.0177 (correlation coefficient $R=0.997$) per layer of BA-12.

Measurement of the polarized UV absorption spectrum of the films shows no preferred in-plane orientation of the azobenzene chromophores. In addition, no difference was observed between the solution UV spectrum of BA-12 and that of the adsorbed layer, indicating no change in chromophore aggregation.

We obtained the thickness of $136 \pm 4 \text{ \AA}$ for the precoated 5 bilayers of PAH/PVS and that of $358 \pm 12 \text{ \AA}$ for 10 bilayers of BA-12/PVS, which were determined with an optical ellipsometer. Since the true refractive indices are unknown, we assumed a film refractive index to be 1.54 to analyze the ellipsometry data. The average thickness of each polymeric layer is $13.6 \pm 0.4 \text{ \AA}$ which is in the same order of magnitude as once reported for an adsorbed polyelectrolyte monolayer adsorbed on silicon substrate.¹⁷ Also, we have obtained $35.8 \pm 1.2 \text{ \AA}$ for the average thickness of a bilayer of BA-12/PVS. If the thickness of PVS monolayer in the multilayer film is assumed to be $13.6 \pm 0.4 \text{ \AA}$ of the thickness of polymer monolayer in the precoated multilayer film, the thickness of BA-12 monolayer accounts for $22.2 \pm 1.6 \text{ \AA}$. From a molecular modeling calculation, the molecular length of BA-12, as a full-stretched form, is estimated to be 46.2 \AA . Based on this, the average tilt angle of a BA-12 molecule with respect to the surface normal is 61.3° from the geometrical calculation.

We have also attempted to estimate the orientation of azobenzene chromophore in the BA-12/PVS film based on the polarized UV spectra obtained at 45° incidence angle. The estimation was made by using the optoelectric equations reported by Vandevyver *et al.*¹⁸ The infinite dilution hypothesis was applied, and the $\pi\pi^*$ transition dipole is assumed to be aligned along a long molecular axis. The refractive indices of fused silica and BA-12 are taken to be 1.47 and 1.43, respectively.¹⁸ The average tilt angle of the azobenzene was computed to be 63.7° with respect to the surface normal. This is approximately consistent with the value obtained from the geometrical calculation. The detailed molecular structure of these films is under investigation exploiting other techniques such as small angle

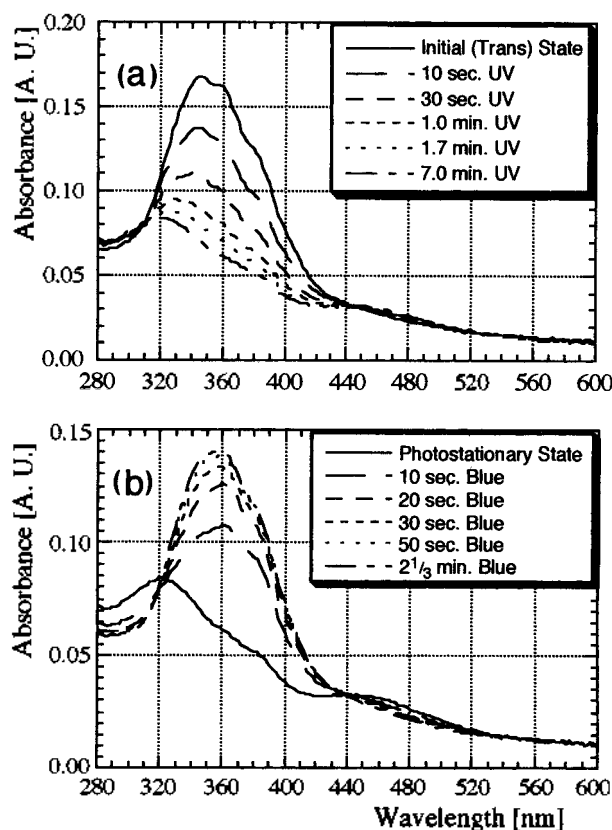


Figure 3. (a) UV/Vis-absorption spectra of a multilayer assembly composed of BA-12 and PVS on a fused silica precoated with 5 bilayers of PAH and PVS: (a) before and after various timed doses of linearly polarized UV (360 nm) irradiation, (b) before and after various amounts of unpolarized blue (450 nm) irradiation. The probe light was linearly polarized and oriented parallel to the exciting UV irradiation.

x-ray scattering, atomic force microscopy and reflection-absorption infrared spectroscopy.

Figure 3 shows the absorption spectra recorded with the linearly polarized probe light oriented parallel to the irradiating UV light polarization. Figure 3a shows the absorption spectra of the multilayer assembly composed of BA-12 and PVS, before and after various UV irradiation times. The change in spectral shape and the existence of the isosbestic points at 308 nm and at 440 nm clearly demonstrate the *trans-cis* photoisomerization reaction. The kinetics of the photoisomerization is characterized by a uniform decrease of absorbance at the $\pi\pi^*$ band (at 346 nm) and an increase of the $n\pi^*$ band (at 450 nm). Before irradiation, only one absorption band with a maximum at 346 nm is observed. It corresponds to the $\pi\pi^*$ transition of the *trans* isomer. The absorption band at 320 nm observed upon UV irradiation can be assigned to the $\pi\pi^*$ transition of the *cis* isomer. The irradiation of the multilayer assembly with the UV light (360 nm) for 7.0 min. establishes a photostationary state.

When the photostationary state is attained, the *cis-trans* reverse isomerization that is induced by irradiation with unpolarized blue light (450 nm), can bring the azobenzene molecules back to the initial state. In Figure 3b, the recovery of the initial, *trans* state, spectra and the existence of the

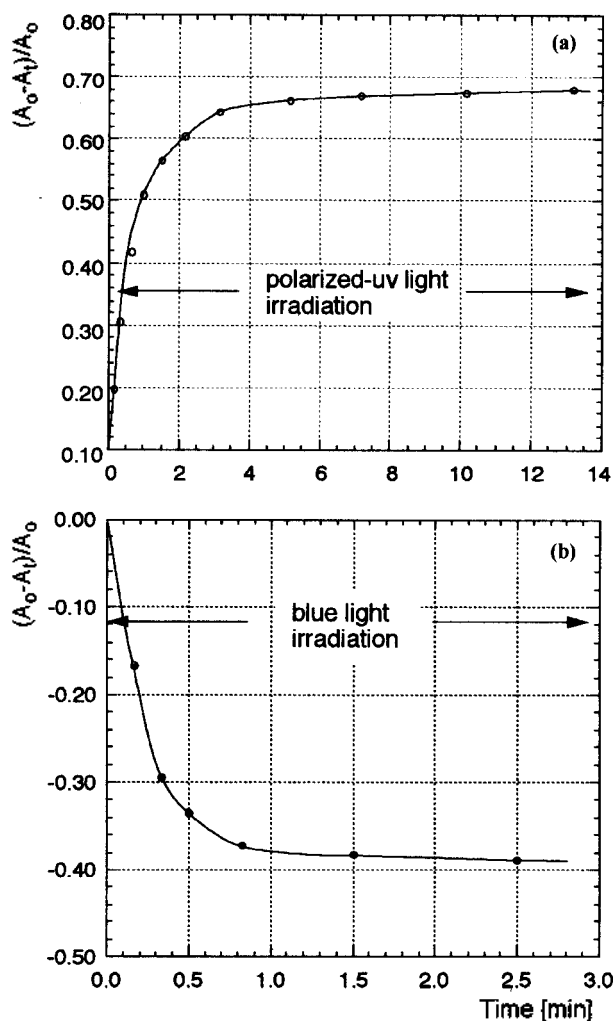


Figure 4. In-plane photoisomerization of the self-assembled 10 bilayers, BA-12/PVS on fused silica substrate. (a) the time dependence of the azobenzene *trans-cis* photoisomerization, (b) the time dependence of the azobenzene *cis-trans* photoisomerization, with respect to the parallel planes of the initial UV polarization. A_0 and A_t are absorbance before ($t=0$), and after UV or blue light irradiation (t minutes), respectively.

isosbestic points clearly demonstrate that the blue light induced *cis-trans* back isomerization. The initial spectra prior to UV irradiation was restored after only $2\frac{1}{2}$ min. of blue light irradiation.

Different mechanisms are discussed for photoorientation process caused by irradiation with linearly polarized light.¹⁹⁻²⁰ In the case of azobenzene moieties it is mainly accepted that the repeated angular-dependent photoselection, photoisomerization cycles, and rotational diffusion within the steady state results in a photochemically induced directed reorientation of the photochromic moieties.^{4-6,19} The probability for the excitation of an individual *trans* azobenzene chromophore follows to $\cos^2 \omega$, where ω is the angle between the electric field vector of the incident light and the transition moment of the photochromic moiety which coincides approximately with its long molecular axis. Thus, molecules oriented parallel to the electric field vector preferably undergo the photoreaction (angular-dependent photoselection). The established steady state between both isomers depends on

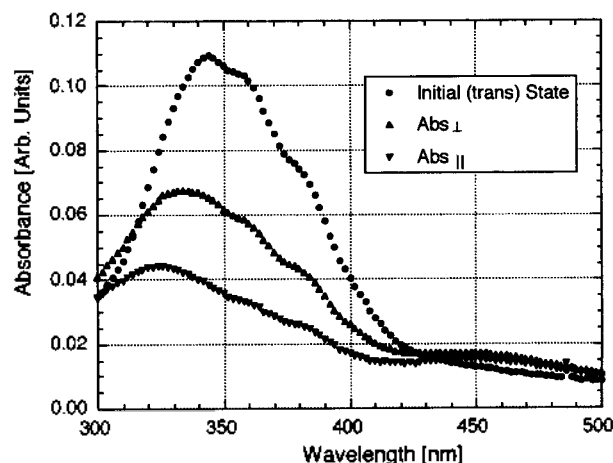


Figure 5. Polarized UV/Vis-absorption spectra of the self-assembled 10 bilayers, BA-12/PVS on the fused silica before (\bullet) and after 5 min. (∇ , \blacktriangle) of linearly polarized UV (360 nm) irradiation. Spectra are obtained for both parallel, ∇ and perpendicular, \blacktriangle , to the initial UV light polarization. For reasons of clarity, only Abs_{\perp} (\bullet) of the initial *trans* azobenzene in the multilayer assemblies is shown.

the ratio between the absorbance coefficients of the *trans* and *cis* isomers at excitation wavelength as well as on the molecular environment of the chromophores. Figure 4 shows the time dependence of the azobenzene *trans-cis* (Fig. 4a) and *cis-trans* (Fig. 4b) photoisomerization with respect to the parallel planes of polarized UV light. As described above, the maximum absorbance value of *trans* form azobenzene unit is found at 346 nm, where A_0 and A_t are absorbance before ($t=0$), and after UV or blue light irradiation (t minutes), respectively. Spectral measurements were made immediately after photoirradiation. The *trans-cis* photoisomerization of the azobenzene unit occurs mainly within 2 min. and completed after 5 min. with the attained steady state between both isomers, while rapid spectral change of the *cis* to *trans* isomeric conversion ($2\frac{1}{2}$ min.) is observed after irradiation of visible light. The *trans-cis* and *cis-trans* photoisomerization are repeated in 5 cycles without appearance of any fatigue in the multilayer film. Thermal back reaction in the dark requires *ca* 10 hours at room temperature. However, the complete thermal recovery required more than 2 days.

Figure 5 shows the dichroism observed in the self-assembled multilayer film. These spectra are obtained after 5 min. of irradiation with linearly polarized UV light. The polarized spectra are measured in the directions both parallel and perpendicular to the initial UV light polarization. It can be clearly seen that the absorption (Abs_{\perp}) is higher than the absorption (Abs_{\parallel}). This suggests that a significant number of *trans* azobenzene are reoriented and realigned perpendicular to the plane of photoirradiation after the *trans-cis* isomerization. This behavior is consistent with the photochemical reorientation of the azobenzene unit previously reported in the literature.^{11,21} As indicated in the Introduction, the optical anisotropy is an induced birefringence and dichroism in the self-assembled film resulting from a reorientation of the azobenzene moieties. This dichroism can be translated into an "order parameter" (as defined in ref. 5).

The order parameter $S = (\text{Abs}_{\parallel} - \text{Abs}_{\perp}) / (\text{Abs}_{\parallel} + 2 \text{Abs}_{\perp})$ calculated at 338 nm from the anisotropic spectra in Figure 5 is $S = -0.033$ and is 8 to 16 times smaller than that obtained in azobenzene dye containing bulk polymer films (about 1 mm thick).²²⁻²⁴ This is indicated to the point, that the azobenzene moieties in this self-assembled film are higher aligned than in the bulk film. It has been known that the levels of the birefringence attainable in polymer system are significantly higher than in amorphous polymer film, if the polymer is crystalline or liquid crystalline. The UV-induced dichroism could be erased on irradiation with unpolarized blue light (450 nm) for 1 min. and the initial spectra of both Abs_{\parallel} and Abs_{\perp} were recovered.

Conclusions

The molecular orientation and the photoresponse properties of the azobenzene units were determined for the new type of the photoresponsive material, the multilayer assemblies, in which the photochromic layers are sandwiched between the oppositely-charged polyelectrolyte layers. We have also shown that dichroism can be photo-induced in the alternating multilayer film composed of 4,4'-azobenzene-bis(12-trimethylammonium-N-yl dodecyloxy) dibromide and poly(vinylsulfate, potassium salt). This dichroism can be reversibly written and erased in the self-assembled film for several cycles without any observance of defect formation. Finally, we believe that this photoinduced reorientation process in the multilayer assembly may be useful for anisotropically altering the structure and/or optical properties of ultrathin supramolecular structures containing azobenzene molecules.

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