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Fully Reversible Isomerization of Azobenzene Chromophores in Polyelectrolyte Layered Assemblies

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Introduction

The development of photosensitive materials has been a focal subject in polymer science and technology. Azoaromatic polymers that contain azobenzene chromophores in the backbone or side chains are widely used to construct photosensitive molecular assemblies such as dendrimers,[1] monolayers,[2] Langmuir−Blodgett films,[3] and organic−inorganic hybrid films.[4] Recently, much attention has been devoted to the development of multilayer assemblies of thin film based on an alternate adsorption of oppositely charged polyelectrolytes, because of the simplicity of the technique, a wide choice of the materials, and the versatility in the film design.[5−11] In this context, it is interesting to construct polyelectrolyte multilayer assemblies containing azobenzene chromophores and to evaluate their photoresponse. From this point of view, Stroeve and co-workers have prepared polyelectrolyte multilayer films containing azobenzene chromophores by a layer-by-layer deposition of an azobenzene-substituted polyanion, poly(1-(4-(3-carboxy-4-hydroxyphenylazo)benzene sulfonamide)-1,2-ethanediyl) sodium salt (PAZO, Figure 1).[12] X-ray reflectivity measurements revealed that the PAZO films are featured by a well-ordered layer-by-layer structure of PAZO and polycation layers. The azobenzene chromophore in the multilayer films was found to be isomerize from trans form to cis form upon UV light irradiation, while a visible light irradiation did not induce reverse reaction from cis to trans isomer. In addition, the thermal isomerization reaction from cis to trans form was not fully reversible in the multilayer films. On the other hand, polyelectrolyte films composed of azobenzene bolaamphiphiles[13−15] and ionenes[15,16] have been prepared, in which azobenzene residues exhibit a reversible photoresponse.

In the present study, we prepared another type of multilayer assemblies containing azobenzene chromophores using poly(allylamine) derivative bearing a small amount of azobenzene residues as pendant (Az-PAA, Figure 1) and found that the photochemical and thermal isomerization is fully reversible. The different behavior in photoresponse of the Az-PAA multilayer films from PAZO-based films is discussed on the basis of the fact that the azobenzene chromophores in Az-PAA are not involved in ionic interactions in the film.

Experimental Section

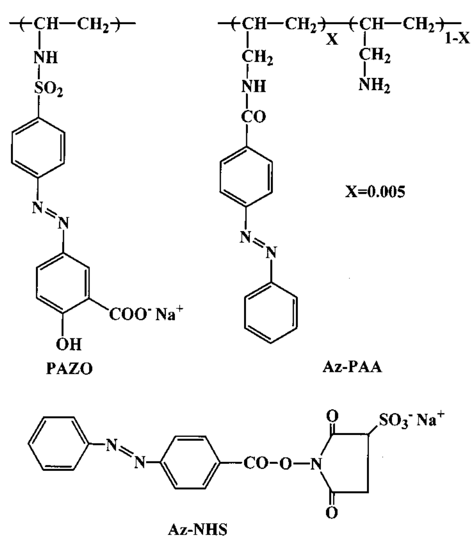

Figure 1. Chemical structures of azobenzene-modified polymers and active ester of azobenzenecarboxylate.

Preparation of Azo-PAA. Az-PAA was prepared by the coupling reaction of poly(allylamine) HCl (average molecular weight: ca. 10 000) and an active ester of 4-carboxyazobenzene (Az-NHS, Figure 1) in water (the ratio of Az-NHS to poly(allylamine) monomer unit was set at 3:100 in the reaction). The reaction mixture was stirred for 24 h at room temperature and then purified by dialysis to water. The content of azobenzene residues in Az-PAA was determined to be 0.5 mol % by UV spectrophotometry.

Construction of Multilayer Assembly. Sodium poly(styrenesulfonate) (PSS, average molecular weight: 70 000) and potassium poly(vinyl sulfate) (PVS, average molecular weight: 243 000) were used as anionic counterpart, because these polyanions have been widely used for constructing multilayer assemblies.[5−10] The Az-PAA multilayer films were prepared on the surface of a quartz slide (50 × 10 × 1 mm) according to the standard protocol.[10] Before use, the quartz slide was treated in a 10% dichlorodimethylsilane solution in toluene overnight to make the surface hydrophobic. The silylated quartz slide was immersed in a PSS or PVS solution in pure water (1 mg mL^{-1}) for 10 min to deposit the first polyanion layer through hydrophobic interactions. After being rinsed in water for 5 min, the polyanion-adsorbed quartz slide was immersed in an aqueous Az-PAA solution (1 mg mL^{-1}) for 10 min to deposit Az-PAA through electrostatic force of attraction. This treatment would provide a polyanion/Az-PAA bilayer on both surfaces of the quartz slide. The deposition was repeated to prepare the multilayer assemblies composed of the desired number of layers. After each deposition, the absorbance of the quartz slide around 330 nm, originating from the $\pi-\pi^*$ transition of the azobenzene chromophore, was monitored. The preparation of the multilayer assemblies was carried out at ca. 20 °C.

Measurements. A 500 W xenon lamp was used as light source for photoirradiation. The UV (320 nm < λ < 380 nm) and visible light (450 nm < λ) was isolated using Corning 7-37 and Toshiba Y-45 glass filters, respectively. The content of cis isomer in the irradiated samples was calculated from the decrease in absorbance at the $\pi-\pi^*$ absorption maximum, assuming that the absorbance of the cis isomer at this wavelength is negligibly small compared with that of the trans isomer.[17]

Results and Discussion

Preparation of Azo-PAA Multilayer Assemblies. The construction of the Az-PAA multilayer films was monitored by measuring UV−vis absorption spectra of the films. Figure 2 shows typical absorption spectra of

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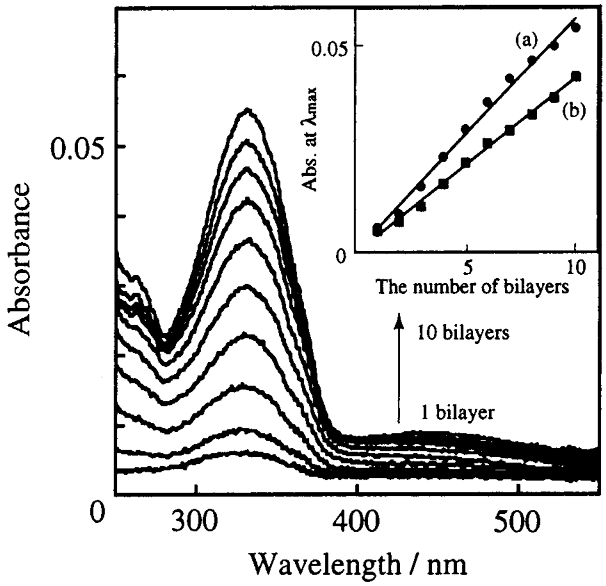

Figure 2. Absorption spectra of Az-PAA/PSS multilayer films as a function of the number of depositions. (inset) Absorbance of the Az-PAA/PSS (a) and Az-PAA/PVS (b) multilayer films at λ_{max} as a function of the number of bilayers.

Az-PAA/PSS multilayer films and the change in absorbance of both Az-PAA/PSS and Az-PAA/PVS films as a function of the number of depositions. The spectra exhibited a clear absorption maximum (λ_{max}) around 330 nm arising from *trans*-azobenzene chromophores, and the intensity of the absorption band was enhanced linearly with increasing number of depositions. These results suggest that a constant amount of Az-PAA is adsorbed in each deposition to form a layered assembly, in a similar manner as for the formation of multilayer assemblies composed of PSS or PVS and unmodified PAA.[5-7,10] In other words, a small amount of azobenzene residues in Az-PAA has no undesirable effect on the regular growth of the multilayer assembly. The loading of Az-PAA on the quartz slide in each deposition was estimated to be 1.2×10^{-6} g cm^{-2} for Az-PAA/PSS film and 0.9×10^{-6} g cm^{-2} for Az-PAA/PVS film from the absorbance data, using a molar extinction coefficient of 2.5×10^4 M^{-1} cm^{-1} for the azobenzene unit.

Photoresponse of Azobenzene Chromophores in the Multilayer Films. It is interesting to evaluate photoresponse of the Az-PAA multilayer films because trans–cis isomerization of azobenzene chromophores in condensed media depends significantly on the local environments such as polarity, viscosity, and free volume distribution around the chromophores.[18-20] Figure 3 shows UV–vis absorption spectra of Az-PAA/PSS film (10 bilayers on both surfaces of the slide) before and after UV light irradiation in air. UV light irradiation induced a decrease in intensity of absorption band originating from $\pi-\pi^*$ transition of the azobenzene chromophore, showing the formation of the trans–cis mixture of the azobenzene chromophores in the film. The trans-to-cis isomerization reaction reached a photostationary state after ca. 30 min irradiation, in which the trans:cis ratio of the azobenzene chromophores was 69:31 in the film, and the resultant cis isomer was converted completely to the original trans form by visible light irradiation for 1 min. Alternatively, the trans form can be fully recovered from the mixture thermally in the dark. The photochemical and/or thermal isomerization reactions of the film can be induced repeatedly several times without any deterioration of the spectra. The Az-PAA/PVS film showed an almost the same behavior in the isomerization reactions as for the Az-PAA/PSS film. Thus, trans–cis isomerization reactions of azobenzene chromophore in the Az-PAA/PSS and Az-PAA/PSV films were demonstrated to be fully reversible and reproducible, in contrast to the irreversible photoresponse of the PAZO-based multilayer films. It was reported that, in the PAZO films, the visible light irradiation did not induce cis-to-trans isomerization, and in the thermal reaction, the recovery of the trans form was incomplete (i.e., 50–85%).[12]

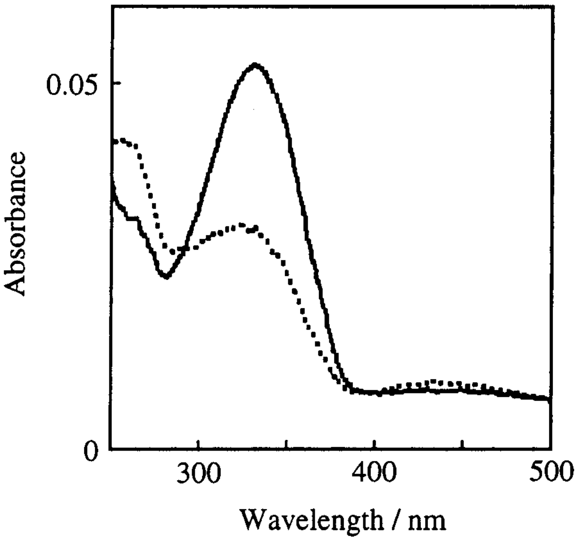

Figure 3. Absorption spectra of Az-PAA/PSS multilayer film (10 bilayers on both surfaces of the quartz slide) before (solid line) and after UV light irradiation for 30 min (broken line).

Table 1. λ_{max} Values and Cis Content in the Photostationary State of Azo-PAA in the Multilayer Films[a]

	dry film		swelled film	
multilayer films	λ_{max}/nm	cis/%	λ_{max}/nm	cis/%
(Azo-PAA/PSS)$_{10}$	333	31	331	50
(Azo-PAA/PVS)$_{10}$	327	31	328	40

[a] The multilayer films used are composed of 10 bilayers. For methanol solution of Azo-PAA, λ_{max} was found at 326 nm, and the content of cis isomer was 64% at the photostationary state.

We studied the photoresponse of the films in air and in water (i.e., swelled film). The cis contents at the photostationary state of the films and the absorption maxima (λ_{max}) are listed in Table 1. The contents of cis isomer at the photostationary state in the films were lower than in the methanol solution. This may be caused by a compact packing of the polyelectrolyte chains in the films, and as a result, the free volume available around the azobenzene chromophores is limited in the films. It has been reported that photoisomerization of azobenzene is suppressed or inhibited in polymer films due to the close packing of the polymer chains and subsequently the lack of free volume.[4,21] In some cases, the formation of H- or J-type aggregates of azobenzene residues is responsible for the suppressed photoisomerization in organized films.[22,23] However, this is not the case for the Az-PAA films in view of the fact that the λ_{max} values in the UV spectra of the films are not shifted significantly from the λ_{max} in solution. It is known that the formation of H- or J-aggregate usually results in a significant shift of λ_{max} value.[22,23] In other words, the

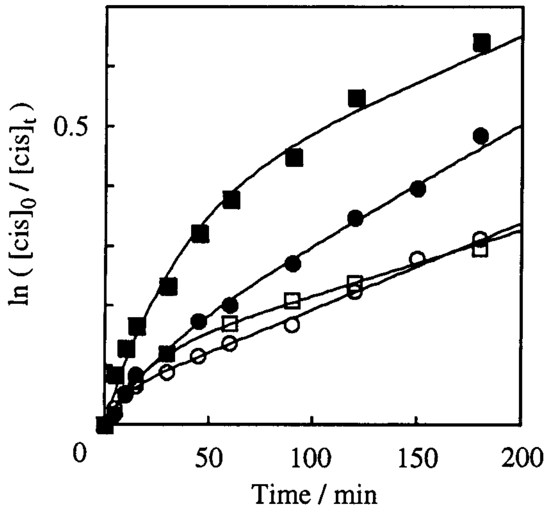

Figure 4. First-order plots for the thermal cis-to-trans isomerization of the azobenzenechromophore in the multilayer films at 40 °C: Az-PAA/PSS film in dry (■) and swelled state (●); Az-PAA/PVS film in dry (□) and swelled state (○).

azobenzene chromophores are isolated from each other in both the dry and swelled Az-PAA films. This is reasonable judging from the low contents of azobenzene chromophores in the polymer chain of Az-PAA (0.5%). The effects of swelling of the films on the photoisomerization were not significant, though the swelled samples gave slightly higher cis contents than those for dry films.[24]

The reversible photoresponse of azobenzene chromophores in the Az-PAA multilayer films should be arising from the fact that, in the Az-PAA films, azobenzene chromophores are not involved directly in the ionic bonding between the cationic and anionic polymers. On the other hand, the azobenzene chromophore in PAZO is substituted with $-COO^-$ residue which is involved inevitably in the ionic bonding with polycations to form the multilayer structure. It can be envisaged that, in the PAZO films, the azobenzene chromophores are captured rigidly in the network of ionic bonding between the cationic and anionic polymers. This is probably the reason for the irreversible photoresponse of the PAZO multilayer films, as suggested also by Stroeve et al.[12] Thus, one should use azobenzene polymers containing no ionizable substituent on the azobenzene residue for constructing photosensitive polyelectrolyte assemblies. Otherwise, judging from the reversible photoresponse reported for multilayer films containing azobenzene bolaamphiphiles and ionenes,[13−16] it is recommended to incorporate a long spacer arm between azobenzene residue and ionic sites in the materials for constructing photosensitive films.

Kinetics of Thermal Cis-to-Trans Reverse Isomerization. The thermal cis-to-trans reverse isomerization was studied in dark by monitoring the recovery of the $\pi-\pi^*$ absorption band around 330 nm after the photostationary state had been obtained under UV light irradiation. It is known that the thermal cis-to-trans isomerization of azobenzene usually follows first-order kinetics in solution. In practice, the first-order plot for the isomerization of Azo-PAA in an aqueous solution gave a straight line, from which the first-order rate constant was calculated to be 0.3×10^{-3} min^{-1} at 40 °C.

Table 2. Kinetics of Thermal Cis-to-Trans Isomerization of Azo-PAA[a]

sample	α[b]	$k_1/10^{-2}$ min^{-1}	$k_2/10^{-3}$ min^{-1}
(Azo-PAA/PSS)$_{10}$			
dry film	0.30	3.5	1.5
swelled film	0.14	2.2	1.7
(Azo-PAA/PVS)$_{10}$			
dry film	0.10	5.0	1.1
swelled film	0.06	7.8	1.3
Azo-PAA solution (in H_2O)	0		0.3

[a] The multilayer films used are composed of 10 bilayers. The reactions were carried out at 40 °C. The average values of two or more preparations are listed. [b] Mole fraction of the component exhibiting fast isomerization.

On the contrary, the first-order plot deviated from the straight line for the film samples (Figure 4). The isomerization proceeded faster than in solution in the beginning and was followed by a slow process. The fast process, which is observed often in film samples, can be attributed to trapping of some portion of cis isomers in a strained environment in the film.[4,17,25] This type of decay kinetics can be described by the biexponential equation

$$[\text{cis}]_t/[\text{cis}]_0 = \alpha \exp(-k_1 t) + (1 - \alpha) \exp(-k_2 t) \quad (1)$$

where $[\text{cis}]_t$ and $[\text{cis}]_0$ are the concentration of cis isomer at time t and zero, α is the fraction of the fast species, and k_1 and k_2 denote the rate constant for the fast and slow processes, respectively.[4,12,26] The parameters obtained by curve fitting are collected in Table 2. For all films, the rate constants for the fast process are more than 1 order of magnitude larger than those for the slow process. The slow isomerization rates are nearly comparable to that in solution. The fraction of the fast process (α) was less than 30%, and the smaller α values were observed for the swelled films. These results confirm that the fast isomerization originates from the small portion of cis isomers entrapped in the strained environment in the films. It should be noted that trans isomers were recovered completely from the trans−cis mixture in the thermal reaction, in contrast to the incomplete recovery in PAZO-based multilayer films.[12]

In conclusion, photosensitive polyelectrolyte assemblies in which azobenzene chromophores exhibit a reversible trans−cis isomerization can be prepared using Az-PAA. To our knowledge, this is the first example for reversible photoresponse in multilayer assemblies composed of polyelectrolyte bearing azobenzene pendant groups. The reversible photoresponse of the films probably originates from the fact that the azobenzene chromophores in Az-PAA are not directly involved in the ionic bonding networks in the film. The photochemical and/or thermal isomerization reactions are fully reversible for swelled films as well as for dry films. This suggests that the Az-PAA multilayer assemblies would be useful for constructing photosensitive systems to be used in aqueous environments such as permselective films for ions and molecules, a surface coating on chromatographic support, and polymer-modified electrodes.

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References and Notes

(1) Archut, A.; Azzellini, G. C.; Balzani, V.; Cola, L. D.; Vögtle, F. *J. Am. Chem. Soc.* **1998**, *120*, 12187.

(2) Seki, T.; Fukuchi, T.; Ichimura, K. *Langmuir* **2000**, *16*, 3564.

(3) Tedeschi, C.; Polli, M.; Fontana, M. P.; Pieroni, O. *Thin Solid Films* **1996**, *284−285*, 174.

(4) Imai, Y.; Naka, K.; Chujo, Y. *Macromolecules* **1999**, *32*, 1013.

(5) Decher, G.; Hong, J. D.; Schmitt, J. *Thin Solid Films* **1992**, *210−211*, 831.

(6) Decher, G.; Lvov, Y.; Schmitt, J. *Thin Solid Films* **1994**, *244*, 772.

(7) Decher, G. *Sciences* **1997**, *277*, 1232.

(8) Clark, S. L.; Montague, M. F.; Hammond, P. T. *Macromolecules* **1997**, *30*, 7237.

(9) Farhat, T.; Yassin, G.; Dubas, S. T.; Schlenoff, J. B. *Langmuir* **1999**, *15*, 6621.

(10) Lvov, Y.; Ariga, K.; Onda, M.; Ichinose, I.; Kunitake, T. *Colloids Surf.* **1999**, *146*, 337.

(11) Shiratori, S. S.; Rubner, M. F. *Macromolecules* **2000**, *33*, 4213.

(12) Dante, S.; Advincula, R.; Frank, C. W.; Stroeve, P. *Langmuir* **1999**, *15*, 193. The polyelectrolyte multilayer films composed of PAZO were first prepared by Lvov et al.[6] However, photoisomerization of the azobenzene chromophore in the PAZO films has not been reported. Recently, nonlinear optical effects were studied using the PAZO multilayer films (Lvov, Y.; Yamada, S.; Kunitake, T. *Thin Solid Films* **1997**, *300*, 107).

(13) Saremi, F.; Tieke, B. *Adv. Mater.* **1998**, *10*, 388.

(14) Hong, J. D.; Park, E. S.; Park, A. L. *Langmuir* **1999**, *15*, 6515.

(15) Toutianoush, A.; Sareme, F.; Tieke, B. *Mater. Sci. Eng., C* **1999**, *8−9*, 343.

(16) Toutianoush, A.; Tieke, B. *Makromol. Rapid Commun.* **1998**, *19*, 591.

(17) Paik, G. S.; Morawetz, H. *Macromolecules* **1972**, *5*, 171.

(18) Nakahara, H.; Fukuda, K. *J. Colloid Interface Sci.* **1983**, *93*, 530.

(19) Anzai, J.; Sugaya, N.; Osa, T. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1879.

(20) Song, X.; Perlsteim, J.; Whitten, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 9144.

(21) Ueda, M.; Kim, H.-B.; Ikeda, T.; Ichimura, K. *Chem. Mater.* **1992**, *4*, 1229.

(22) Seki, T.; Fukuda, R.; Yokoi, M.; Tamaki, T.; Ichimura, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2375.

(23) Petruska, M A.; Talham, D. R. *Chem. Mater.* **1998**, *10*, 3672.

(24) It has been reported that, under ambient conditions, polyelectrolyte multilayer films usually contain 10−20% water.[9] Therefore, the "dry film" does not mean that the films contain no water in air under the present experimental conditions.

(25) Mita, I.; Horie, K.; Hirao, K. *Macromolecules* **1989**, *22*, 558.

(26) Wu, A.; Talham, D. R. *Langmuir* **2000**, *16*, 7449.

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