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Self-Assembled Multilayers of Photochromic Bolaamphiphile and Ionene-type Oligomer: Relation of Aggregate State and Photoisomerization

Ae-Li Park and Jong-Dal Hong*

Dept. of Chemistry, Inchon University, 177 Dohwa-dong Nam-ku, 402-749 Inchon (sKorea)

SUMMARY: Photoisomerization process of azobenzene has been studied in the multilayer assemblies of poly(vinylsulfate, potassium salt) and two different layer-elements; 4,4'-azobenzene-bis(12-trimethylammonium-N-yl dodecyloxy) dibromide (BA-12, **1**) and an ionene oligomer, poly(4,4'-azobenzene-bis(12-dimethyl-ammonium-N-yl dodecyloxy) bromide) (PAZ-12, **2**). The change of the photoactive layers from BA-12 to PAZ-12 was found to dramatically influence the photoisomerization characteristics of the azobenzene in the multilayer. Surprisingly, we have observed that the chromophore interaction in PAZ-12 is stronger than that in BA-12 in self-assembled (SA) film (λ_{max} = 320 nm compared to 341 nm), although the aggregate formation is considered to be hindered by the strains of the polymer chains. For BA-12/PVS and PAZ-12/PVS multilayers, the steady state between cis and trans isomers reached after ca 20 min. and 48 min. of UV irradiation, respectively. It was also found that after first one trans-cis-trans cycle of the photoisomerization, the trans to cis isomerization was completed in 30 sec of irradiation in the following 10 cycles without appearance of any fatigue in the multilayer film.

Introduction

During past several years, the layer-by-layer self-assembly technique based on electrostatic attraction between opposite charges1) has been devoted to realization of the variety of the multilayer heterostructures on a solid substrate. The assembly of cationic and anionic polyelectrolytes2) has been extended to the polyelectrolytes and DNA3), polyelectrolytes and latex particles4), polyelectrolytes and proteins5), polyelectrolytes and delaminated clay platelets6-9), polyelectrolytes and colloidal metal particles10-12), polyelectrolytes and dyes13-18), polyelectrolytes and electrically conductive or the electroluminescent conjugated polymers19). Bolaamphiphiles have been used as components of this technique1, 20). The layer formation by these bipolar molecules produces charged surfaces upon their adsorption and allows the alternate assembly to continue. As can be also seen from the precedents of bolaamphiphiles and bilayer-forming amphiphiles, small molecules that tend to aggregate in water have been assembled as molecular layers in combination with oppositely-charged polyions. Very recently, photoisomerization was demonstrated in the multilayer assemblies, in which the photoactive

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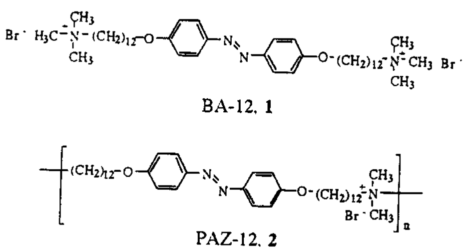
layers sandwiched between oppositely-charged polyelectrolyte layers consist of bolaamphiphiles bearing azobenzene chromophores[21-23].

Scheme I



BA-12, 1

PAZ-12, 2

The reversible cis-trans photoisomerization is of great interest for application in optical information storage systems. The azobenzene molecules undergo "trans-cis" reversible photoisomerization under irradiation of photoactive light with an appropriate wavelength. These changes of the molecular structure result in modified intermolecular interactions and in a modification of the supramolecular order of the SA multilayers. So, the periodicity of the lamellar architecture and the in-plane order is affected. Laschewsky and his coworkers[24] reported about thin polymeric, non-centrosymmetrical coatings of polyion containing azobenzene moiety based on layer-by-layer electrostatic SA methods, but studies on the photoisomerization of azobenzene in SA polymeric multilayer films are still lacking.

In order to study the photochromic process, we prepared a water-soluble bolaamphiphile, 4,4'-azobenzene-bis(12-trimethylammonium-N-yl dodecyloxy) dibromide (BA-12, **1**) and an ionene oligomer, poly(4,4'-azobenzene-bis(12-dimethyl-ammonium-N-yl dodecyloxy) bromide) (PAZ-12, **2**) bearing a photochromic chromophore, as shown in Scheme I. Additional interest arises from the question as to whether and to what extent the photoisomerization will take place in the multilayer assemblies, in which the molecular mobility in the photochromic layers is restricted by the oppositely-charged polyelectrolyte layers.

The aim of this article is to study the influence of the supramolecular order on the photoisomerization characteristics of azobenzene in the multilayer assemblies by varying the component of the photoactive layers sandwiched between oppositely-charged polyelectrolytes layers from the small molecule, bolaamphiphile BA-12 to the ionene oligomer PAZ-12.

Materials and Methods

Materials. 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 synthesis and characterization of the bolaamphiphile BA-12 were described in the literature[23]. The ionene PAZ-12 was prepared by an addition polymerization of the corresponding diamine and dibromide, which were synthesized according to the literature process[25]. The detailed description of the synthesis and characterization of PAZ-12 will be published in a forth-coming paper.

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 MΩ · cm. The substrates for all adsorption experiments were fused silica slides of size 25x50 mm^2. They were cleaned by ultrasonication in the mixture of H_2SO_4/H_2O_2 (7/3) and then heated in the mixture of $H_2O/H_2O_2/NH_3$ (5:1:1) at 80°C for 1 hr. The substrates were thoroughly washed with ultrapure water after both steps.

The bolaamphiphile, ionene oligomer and polyelectrolytes were deposited onto the negatively-charged substrate as described previously[1-2)]. After each adsorption step, the surface of the film was thoroughly rinsed and then blown dry with a stream of nitrogen. In order to adsorb BA-12 or PAZ-12, the substrate was precoated with five bilayers of PAH and PVS for providing a more homogeneous charge distribution on the substrate.

Multilayer film was achieved by dipping the substrate alternately into the aqueous solution of BA-12 (0.2 mM), and the aqueous solution of PVS (6 mM). Thus, the substrate was coated with ten bilayers of BA-12 and PVS.

Multilayer film of PAZ-12 and PVS was deposited by dipping the substrate alternately into the DMSO/H_2O (10/3) solution of PAZ-12 (0.5 mM) and the aqueous solution of PVS (6 mM). The quantity of material deposited at each step was determined from its absorption spectrum, which was generated on a UV/Visible spectrophotometer (Perkin-Elmer Lambda 40).

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/cm^2 for UV light and to 100 mW/cm^2 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.

Film Morphology. The film thickness of multilayer 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 and PAZ-12/PVS multilayer was estimated from the polarized UV spectra obtained at 45° incidence angle.

Results and Discussion

1. Alternating Multilayer Assemblies of Bolaamphiphile and Polyelectrolytes

1.1. Preparation of Multilayer Assemblies

In order to study the photoisomerization characteristics of the multilayer assemblies in which the photoactive layers are sandwiched between two polyelectrolyte layers, we have constructed a SA multilayer film composed of a cationic bolaamphiphile BA-12 and an anionic polyelectrolyte PVS on a fused silica precoated with five bilayers of PAH and PVS, as shown schematically in Fig. 1. Photoactive BA-12 layer exists between two polyelectrolyte layers in order to allow for a photoisomerization to take place.

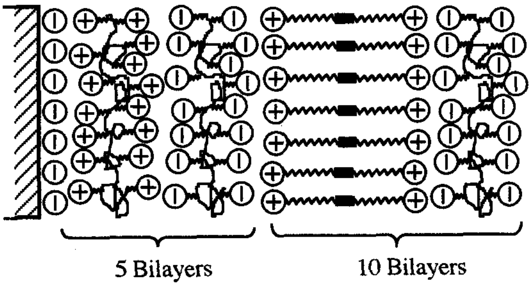


Fig. 1: Idealized schematic structure of the multilayer assemblies composed of the BA-12 dication and anionic polyelectrolytes PVS.

Fig. 2 shows the UV absorbance of azobenzene chromophore at 341 nm as a function of the number of bilayers deposited. The absorption occurs essentially uniformly, the same amount being deposited on each cycle. A linear fit of data yields an average increase of the optical density of 0.018 per layer of BA-12. Additionally, the absorbance of BA-12 in the multilayer assemblies differs essentially not from that in the aqueous solution. This suggests that the aggregates formed in solution were directly transferred on the substrate without big change of the aggregate state.

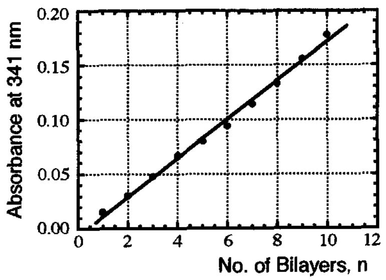


Fig. 2: UV absorbance at 341 nm vs. number of bilayers, BA-12/PVS.

1.2. Morphology of Multilayer Assemblies

The structure of the multilayer assemblies deposited on silicon wafer was probed by ellipsometry. We obtained the thickness of 136±4 Å for the precoated 5 bilayers of PAH/PVS and that of 358±12 Å for 10 bilayers of BA-12/PVS. 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±0.4 Å that is in the same order of magnitude as once reported for a polyelectrolyte monolayer adsorbed on silicon substrate$^{26)}$. According to the measurement, we can calculate the thickness of a BA-12 layer to be 22.2±1.6 Å, assuming the thickness of a PVS layer to be 13.6±0.4 Å which was estimated from the determined total thickness of the 5 bilayers of PAH/PVS.

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.$^{27)}$. The infinite dilution hypothesis was applied, and the $\pi\pi^*$ transition dipole of trans-azobenzene 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$^{27)}$. The average tilt angle of the azobenzene was computed to be 63.7° with respect to the surface normal.

From a molecular modeling calculation (Hyperchem), the molecular length of BA-12, in fully-stretched form, is estimated to be 46.2 Å. 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. This is approximately consistent with the value obtained from the measurement. The fact indicates that the BA-12 seems therefore to adopt a slightly parallel stance, when the bolaamphiphiles are adsorbed on the oppositely-charged polymer surface.

1.3. Photoinduced Cis-Trans Isomerization of Azobenzene

Fig. 3(a) shows the absorption spectra of the multilayer assembly composed of BA-12/PVS bilayers, before and after various UV irradiation times. The spectra are recorded with the linearly polarized probe light oriented parallel to the irradiating UV light polarization. The maximum absorbance of molecularly dispersed azobenzene at 358 nm is blue-shifted to 341 nm in the dilute aqueous solution and the SA film, indicating the interaction of the chromophores in BA-12 forming H-aggregates. The trans-azobenzene chromophores should be arranged "face-to-face" in dimers or higher aggregates. The process can be described qualitatively by the exciton model introduced by Kasha$^{28)}$. 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 π-π^* band of trans isomer (341 nm) and an increase of the n-π^* band of cis isomer (450 nm). The absorption band at 320 nm observed upon UV irradiation can be assigned to the π-π* transition of the cis isomer.

When the photostationary state is attained after 20 min. of UV irradiation, the cis-trans reverse isomerization that is induced by irradiation with unpolarized blue light (450 nm), can bring the azobenzene back to the initial state. In Fig. 3(b), the recovery of the trans state and the existence of the isosbestic points clearly demonstrate that the blue light induced cis-trans back isomerization. The trans state prior to UV irradiation was restored after only $2^1/_3$ min. of blue light irradiation. However, it should be also noted that after first trans-cis-trans cycle, the absorbance maximum at 341 nm was drastically shifted to that of the molecularly isolated chromophore at 358 nm. This reveals that the H-aggregate of the azobenzene in the multilayer assemblies was destroyed to the molecularly dispersed state by the isomerization cycle.

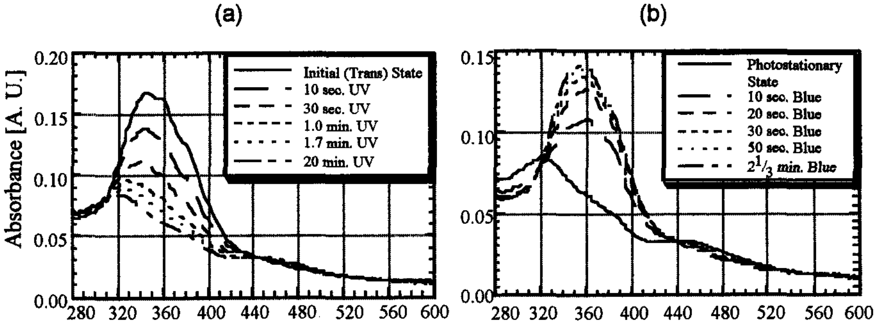


Fig. 3: UV/Vis-absorption spectra of a multilayer assembly composed of BA-12 and PVS on a fused silica precoated with 5 bilayers of PAH and PVS: (a) before and after various timed doses of linearly polarized UV (360 nm) irradiation, (b) before and after various amounts of unpolarized blue (450 nm) irradiation.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

In order to study reversible photochemical switching between the two isomers, the multilayer assemblies containing 10 bilayers of BA-12 and PVS were irradiated with UV (360 nm) and blue light (450 nm) for trans-cis and cis-trans isomerization, respectively. In the first trans-cis-trans isomerization cycle, the photostationary state reached by irradiating the sample with the UV light for 20 min. However, after first one cycle, the irradiation time for the photostationary state in the following isomerization cycles decreased markedly from 20 min. to 30 sec. The difference in switching times required for trans-cis isomerization can be ascribed to the increased free volume in the multilayer that is created by the first trans-cis-trans cycle. Since the cross-sectional area of the cis isomer is larger than that of the trans isomer, free volume is considered to be necessary for the molecule to photoisomerize. Hence, the photochemical behavior directly allows conclusions to be drawn about the free volume available in the multilayer assemblies. The trans-cis and cis-trans photoisomerization were repeated in 10 cycles without appearance of any fatigue in the multilayer film, as shown in Fig. 4.

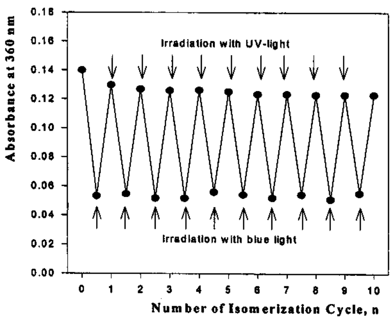


Fig. 4: The change of the maximum absorbance at 360 nm after 30 sec of UV and blue light irradiation for trans-cis and cis-trans isomerization, respectively.

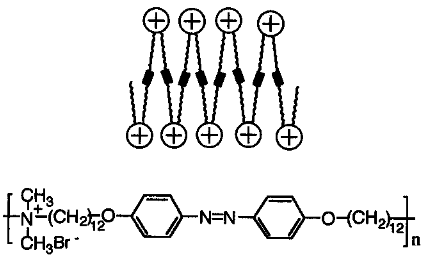
2. Alternating Multilayer Assemblies of Polyelectrolytes and Ionene-type Polyion

2.1. Preparation and Structure of Multilayer Assemblies

The electrostatic SA technique is now shown to allow the multilayer assemblies with excellent control over thickness and molecular architecture. However, especially in the case of the polyelectrolyte multilayer, we rarely encounter the assembly that consists of internal orderings in each polymer monolayer. Laschewskey et. al. reported about layered nanostructures with an internal ordering of the assembly using liquid crystalline ionomers[29]. In this article, we will show that an internal ordering of the multilayer assemblies can be achieved by using an ionene oligomer PAZ-12 bearing azobenzene unit on main-chain. The molecular weight of the ionene was about 13 estimated by using the characteristic signals of its nmr spectrum.

Kunitake et. al.[25] reported that stable molecular membranes are formed in an aqueous solution spontaneously from ionene-type amphiphiles (see Scheme II). The ionene amphiphile is an oligomer composed of a repeating unit with a bolaamphiphile. Taking the work into account, we designed an ionene polymer containing an azobenzene chromophore connected with C_{12} alkyl chains, assuming that stable molecular membranes form from ionene oligomers in a dilute solution, as shown in the Scheme II.

Scheme II



PAZ-12, 2

We have constructed a SA multilayer film composed of a cationic ionene PAZ-12 and an anionic polyelectrolyte PVS on a fused silica precoated with five bilayers of PAH and PVS, as shown schematically in Fig. 5. Photoactive PAZ-12 layer exists between two polyelectrolyte layers in order to allow for a photoisomerization to take place.

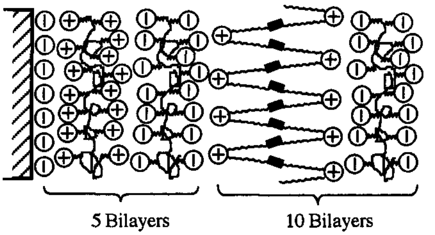


Fig. 5: Idealized schematic structure of the multilayer assemblies composed of the cationic ionene PAZ-12 and the anionic polyelectrolytes PVS.

By UV/Vis-spectroscopy we have also demonstrated that the consecutive adsorption of layers is a stepwise and regular process. The regular formation of each PAZ-12 layer is illustrated by a linear correspondence between the number of bilayers deposited and the absorbance of the multilayer film up to at least 10 bilayers, as shown in the insets of Fig. 6. The points can be fitted with a linear fit, yielding an average optical density of 0.011 per layer.

The orientation of azobenzene moiety in the PAZ-12/PVS film was estimated by referring to the optoelectric equations reported by Vandevyver et. al. 27) based on the polarized UV spectra obtained at 45° incidence angle. The infinite dilution hypothesis was applied, and the π–π^* transition dipole was assumed to be directed along molecular axis of azobenzene. The refractive indices of fused silica and PAZ-12 layer were taken to be 1.47 and 1.43 27). On this basis, the average tilt angle of the azobenzene moiety with respect to the substrate normal was calculated to be 49.1°.

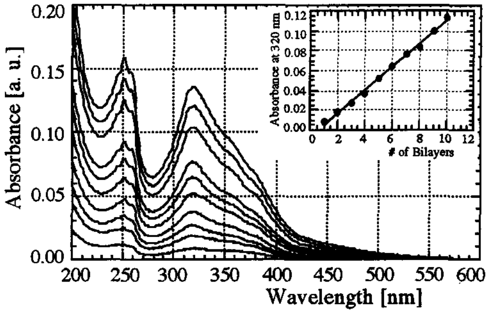


Fig. 6: Optical absorption spectra of self-assembled multilayer built up by alternate adsorption of PAZ-12 and PVS. Samples differ in the number of dipping cycles applied. In the Insets, the maximum absorbance of PAZ-12 in the respective multilayer is plotted versus number of bilayers of PAZ-12 and PVS.

The thickness of a PAZ-12 layer sandwiched between the poly-electrolyte layers was estimated by using an optical ellipsometry. According to the measurement, we have obtained 24.8±2.1 Å for the thickness of a PAZ-12 layer based on 13.6 Å for that of a PVS monolayer, assuming a film refractive index to be 1.54 in analyzing the ellipsometric data. Anticipated from the ellipsometry data, the azobenzene moiety should adopt a rather parallel orientation. The thickness of a PAZ-12 layer (24.8 Å) deviates slightly from the theoretical value (28.2 Å) that is obtained from the simple geometrical calculation with the molecular length of the repeat unit (46.2 Å) and the measured tilt angle of the chromophore (49.1°). However, more work has to be done to obtain a more complete picture of PAZ-12/PVS multilayers.

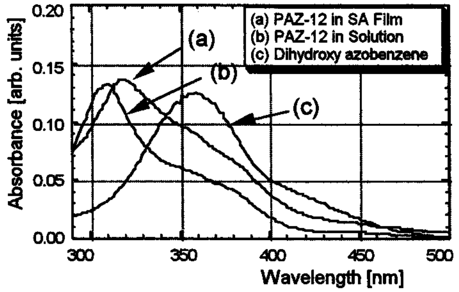


Fig. 7: Comparison of the UV/Visible absorption spectra of PAZ-12 in solution (a), and SA film (b), and the normalized spectra for 4,4'-dihydroxy azobenzene in solution (c).

2.2. Photoisomerzation of Multilayer Assemblies

Fig. 7 compares UV/Visible spectra of the SA 10 bilayers of PAZ-12 and PVS on a fused silica (a), PAZ-12 in DMSO/H_2O (10/3) (b), and molecularly dispersed 4,4'-dihydroxy azobenzene (c). The maximum absorbance of the molecularly dispersed chromophore at 358 nm is drastically blue-shifted to 310 nm in the solution of PAZ-12. The symmetric shape of the π-π^* absorption band becomes asymmetic and narrow. Both facts indicate a strong excitonic interaction of the aromatic chromophores forming H-aggregates. The UV absorbance depending temperature indicates that the formed H-aggregate of PAZ-12 in solution are destroyed to the molecularly dispersed state around 90°C and reformed after cooling to r.t. The multilayer assembly had a strong band with maximum at 320 nm, indicating highly crystalline layers of H-aggregated chromophores in parallel alignment. We found that the absorbance of the PAZ-12 in SA film differs essentially not from that in solution. The fact supports our assumption that the polymeric multilayer assembly with the internal orderings can be realized by transferring the monolayer membrane formed in solution on substrate. Upon irradiation the azobenzene undergoes trans-cis photoisomerization and a wavelength-dependent steady state is established between rod-like trans isomers and bent cis isomers. Fig. 9 shows the change of the absorption spectrum of the SA film bearing 10 bilayers of PAZ-12 and PVS on irradiation with blue light (450 nm). The photoisomerization occurs relatively large within 12 min. (ca. 95% with regard to the photostationary state) and the stationary state was established by irradiating the film for ca. 48 min. The trans-cis isomerization was revealed by the decrease and the increase of the absorption at 320 nm and at 447 nm that can be ascribed to the π-π^* band

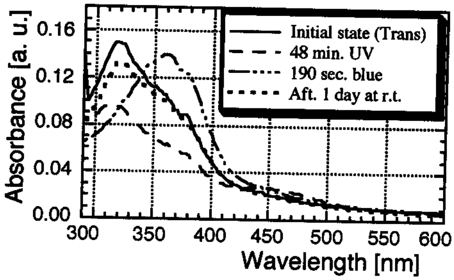


Fig. 8: UV/Visible absorption spectra of the multilayer assemblies composed of 10 bilayers of PAZ-12 and PVS; (a) initial (trans) state, (b) cis state after UV irradiation, (c) trans state after blue irradiation, (d) trans state after storage at r.t. for one day.

of the trans isomers and the n-π* band of the cis isomers, respectively. The subsequent irradiating with unpolarized blue light induces cis-trans back isomerization with the rapid increase of the maximum absorbance at 357 nm. Once again, a clear isosbestic point at 422 nm was observed during the reverse cis-trans isomerization. The photostationary state was attained by irradiating the sample with the blue light for ca. 190 sec. An important observation in this trans-cis-trans cycle, however, was that the maximum absorbance in SA film at 320 nm is shifted to 357 nm with the formation of the symmetric shape of π-π* band. The red-shifted absorption spectrum returned slowly to the original state and to the almost same state after one day. From the spectral data presented above, it is clear that the aggregates are destroyed to the molecularly dispersed state with the disordering of main-chain by bent cis isomers resulted from trans-cis photoisomerization process, and slowly reformed again with realignment of the chains in the solid film by keeping it at r.t. for one day.

In order to study reversible photochemical switching between the two isomers, the multilayer assemblies containing 10 bilayers of PAZ-12 and PVS were irradiated with UV (360 nm) and blue light (450 nm) for trans-cis and cis-trans isomerization, respectively. In the first trans-cis-trans isomerization cycle, the photostationary state reached by irradiating the sample with the UV light for ca 48 min. However, after first one cycle, the irradiation time for the photostationary state in the following isomerization cycles decreased markedly from 48 min. to 30 sec. The difference in switching times required for trans-cis isomerization can be ascribed to the increased free volume in the multilayer that is created by the first trans-cis-trans cycle, as observed in the sample of

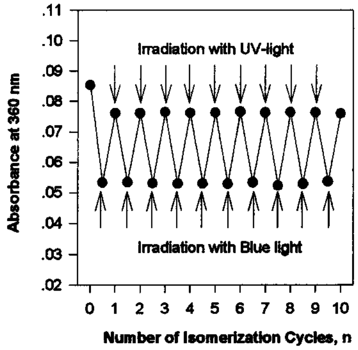


Fig. 9: The change of the maximum absorbance at 360 nm after 30 sec of UV and blue light irradiation for trans-cis and cis-trans isomerization, respectively.

BA-12 and PVS. The trans-cis and cis-trans photoisomerization were repeated in 10 cycles without appearance of any fatigue in the multilayer film, as shown in Fig. 9.

Conclusions

We have shown that multilayer assemblies of a new ionene oligomer bearing azobenzene unit on main chain and an anionic polyelectrolyte can be prepared by electrostatic layer-by-layer adsorption method. The influence of the supramolecular order in the multilayer assemblies on the photoisomerization was discussed with varying the component of the photoactive layers sandwiched between oppositely-charged polyelectrolytes layers from a small molecule, bolaamphiphile BA-12 to an ionene oligomer PAZ-12. We have observed that the chromophore interaction in PAZ-12 is stronger than that in BA-12 in solution and SA film (λ_{max} = 310 nm or 320 nm compared to 341 nm), although the aggregate formation should be considered to be hindered by the strains of the polymer chains.

By the photoisomerization, it has been found that after first one cycle, the irradiation time for the photostationary state in the following isomerization cycles decreased markedly from 20 min. and 48 min. to 30 sec. for BA-12/PVS and PAZ-12/PVS multilayers, respectively. Also, we could demonstrate that the trans-cis and cis-trans photoisomerization were repeated in 10 cycles without appearance of any fatigue in the multilayer film. The differences in switching times required for trans-cis isomerization can be ascribed to the increased free volume in the multilayer that is created by the first trans-cis-trans cycle. Finally, we believe that the molecular assemblies are useful as a medium for reversible photochemical switching and optical storage of information

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