Modification of Polyelectrolyte Layered Assembly Using an Active Ester of Azobenzene Carboxylate

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Introduction

A layer-by-layer deposition technique for constructing polyelectrolyte layered assemblies has recently attracted much attention because of its simplicity in procedure and wide choice of materials.[1−5] From the viewpoint of practical applications, it is interesting to modify the polyelectrolyte assemblies with functional molecules. In this context, positively or negatively charged dyes,[6] host−guest compounds,[7] and proteins[8] have been used to build up multilayer assemblies by being combined with the oppositely charged polyelectrolyte, in which the functional molecules were immobilized in the polymer networks through an electrostatic force of attraction. On the other hand, polyelectrolytes that contain functional groups in the main chain or in the side chains have also been used to construct functional assemblies.[9−12]

We propose here another route to fabricate functional multilayer assemblies on the basis of a chemical modification using an active ester. In the present study, we use multilayer assemblies containing poly(allylamine) (PAH) and poly(ethylenimine) (PEI), whose amino groups may be modified with an active ester of azobenzene carboxylate (Az-NHS) (Figure 1). The coupling reaction between *N*-hydroxysuccinimide (NHS) esters of carboxylate and the amino moiety has been well established and widely used for modifying surfaces of monolayers,[13] Langmuir−Blodgett films,[14] and proteins.[15] Miyashita and co-workers prepared dye-modified monomolecular films by the coupling reaction of amino group-substituted dyes to a monomolecular film containing a NHS ester.[13] The surface of Langmuir−Blodgett films composed of amphiphilic NHS esters can be easily functionalized with proteins because surface amino moieties in the proteins are reactive to the NHS ester.[14] The present technique may allow us to readily incorporate functional moieties into polyelectrolyte multilayer films. However, the reaction efficiency may not be same as in the other systems such as monolayer and LB films because the majority of amino moieties in the multilayer films are involved in the ionic bonding with the polyanionic counterpart. Therefore, we have to evaluate the reactivity of NHS active esters to multilayer films. In addition, we evaluate the formation of aggregates of the azo dye in the multilayer film because H- or J-aggregate formation on the surface of thin films has been often observed.[16−18] To our knowledge, this is the first paper reporting chemical reaction of an active ester to polyelectrolyte multilayer assemblies.

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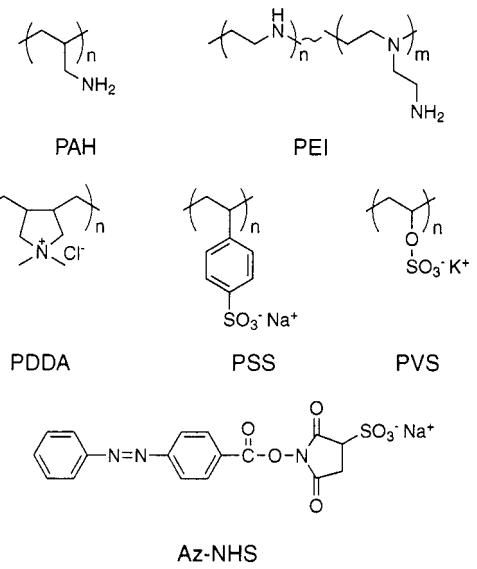

Figure 1. Chemical structure of polyelectrolytes used and Az-NHS.

Experimental Section

Materials. An aqueous solution (20%) of poly(allylamine) hydrochloride [PAH; average molecular weight (MW), ca. 10 000], 30% aqueous solution of poly(ethylenimine) (PEI; MW 60 000−80 000), and 20% aqueous solution of poly(diallyldimethylammonium chloride) (PDDA; MW 100 000−200 000) were purchased from Nittobo Co. (Tokyo, Japan), Nakalai Tesque Co. (Kyoto, Japan), and Aldrich Chemical Co. (Milwaukee, WI), respectively. Poly(potassium vinyl sulfate) (PVS; MW, 242 000) and poly(sodium 4-styrenesulfonate) (PSS; MW 35 000) were obtained from Nakalai Tesque Co. (Kyoto, Japan) and Pressure Chemical Co. (Pittsburgh, PA). Sulfosuccinimidyl *p*-phenylazobenzoate (Az-NHS) was prepared as follows: *N*-hydroxysulfosuccinimide (0.5 g) and *p*-phenylazobenzoic acid (0.52 g) were dissolved in 300 mL of dimethyformamide, and then dicyclohexylcarbodiimide (0.48 g) was added with stirring at 0−5 °C. After stirring the reaction mixture for 24 h at room temperature, the precipitate was filtered off. The filtrate was concentrated to ca. 10 mL, and ca. 200 mL of ethyl acetate was added to isolate Az-NHS. Yield: 0.54 g (55%). MS: *m*/*e*, 426 (M^+). IR (KBr): 1740 cm^{-1} (ester carbonyl) and 1778 cm^{-1} (succinimide carbonyl). ^1H NMR (300 MHz, DMSO-d_6): δ 8.33 (2H, d, J = 8.3 Hz), 8.08 (2H, d, J = 8.2 Hz), 7.98 (2H, m), 7.65 (3H, t, J = 3.0 Hz), 4.04 (1H, d, J = 8.3 Hz), 3.2−3.3 (1H, overlapped with water), 2.97 (1H, d, J = 18.0 Hz). The chemical structures of the polyelectrolytes and Az-NHS are illustrated in Figure 1. PAH and PEI were labeled with a small amount of azobenzene residue in order to determine the loading of the polymers in the layered assemblies by UV−vis absorption spectroscopy. The preparation of the labeled PAH and PEI was reported previously, and the content of azobenzene residues was 0.5 mol % for PAH and 0.9 mol % for PEI (vs total primary and secondary amino groups in the polymer chain).[12]

Preparation of Multilayer Films. The multilayer films were prepared on the surface of a quartz slide (50 × 10 × 1 mm) according to the reported procedure.[12] The quartz slide was first 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

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rinsed in water for 5 min, the polyanion-adsorbed quartz slide was immersed in an aqueous solution of polycation (1 mg mL^{-1}) for 10 min to deposit the polycations through electrostatic force of attraction. This treatment would provide a polyanion/polycation bilayer film on both surfaces of the quartz slide. All multilayer assemblies were prepared at ca. 20 °C.

Modification of the Multilayer Films. The quartz slide coated with the multilayer film was immersed in an Az-NHS solution (0.01 M phosphate buffer) at ca. 20 °C to introduce azobenzene residues into the multilayer film. The reaction was monitored by measuring the increase of the UV−vis absorption band of the quartz slide around 300−330 nm originating from the $\pi-\pi^*$ transition of the azobenzene chromophore, using a Shimadzu UV3100 spectrophotometer. The multilayer film-coated slide was rinsed carefully in the working buffer before measuring the UV−vis spectrum to remove unreacted Az-NHS or other reaction byproducts. FTIR spectra of the films prepared on gold were recorded with a Shimadzu FTIR 8200A spectrophotometer using an external reflectance sample mount, set to an incident angle of 80°.

Photoirradiation. A 500 W xenon lamp was used as light source for photoirradiation. The UV light was irradiated to the sample through a Corning 7-37 glass filter. The polyelectrolyte film-coated slide was irradiated in water immediately after the chemical modification. The content of *Z* isomer in the irradiated sample was calculated from the decrease in the $\pi-\pi^*$ absorption.[19]

Results and Discussion

Reaction of Az-NHS with the Multilayer Films. The NHS esters are currently widely used for modifying biological macromolecules because this reaction proceeds smoothly in an aqueous solution.[15] In the present study, we employed the NHS ester of *p*-phenylazobenzoic acid (AZ-NHS) to check the possibility of modification of polyelectrolyte assemblies containing poly(amine)s.

A series of preliminary experiments were carried out to check the reactivity of Az-NHS to the multilayer films. The multilayer film-coated quartz slide was immersed in an aqueous Az-NHS solution, and to check the modification reaction, the absorbance of the slide was recorded every 5 or 10 min after the slide had been rinsed thoroughly in the working buffer to remove any physically adsorbed Az-NHS. The absorbance of the PSS/PAH film- and PSS/PEI film-coated slides increased rapidly and reached a maximum absorbance in 30−40 min, while no increase in the absorbance was observed for the PSS/PDDA film-coated slide. A prolonged rinsing of the modified PSS/PAH and PSS/PEI films did not induce decrease in the absorbance. On the other hand, the absorbance did not increase even after prolonged treatment when the film-coated slides were immersed in a solution of *p*-phenylazobenzoic acid (0.1 mg mL^{-1}) in place of the Az-NHS solution. These results suggest that Az-NHS reacted with amino groups in the PAH and PEI to be immobilized covalently in the films. On the contrary, the PSS/PDDA film could not be modified with the active ester because PDDA contains no reactive amino group (i.e., a primary or secondary amino group). Thus, it is clear that *p*-phenylazobenzoic acid and Az-NHS are not electrostatically adsorbed to the films. This may be reasonable judging from the reported data that ionic dyes are not always adsorbed electrostatically to polyelectrolyte films.[20] To confirm the formation of covalent bonding of azobenzene residue in the film, FTIR spectra of the film were recorded before and after modification (Figure 2). Intense amide peaks are observed at 1540 and 1650−1670 cm^{-1} after modification, showing that the azobenzene moieties are introduced through amide linkage.[21] A possibility of electrostatic adsorption of Az-NHS to the film can be excluded because the spectrum exhibits no carbonyl peak of AZ-NHS. We confirmed separately that AZ-NHS itself has strong absorption peaks at 1740 and 1778 cm^{-1} due to its ester and succinimide carbonyl groups. Thus, both FTIR and UV−vis spectral data demonstrate unequivocally that the azobenzene residues are introduced in the multilayer assemblies through amide linkage.

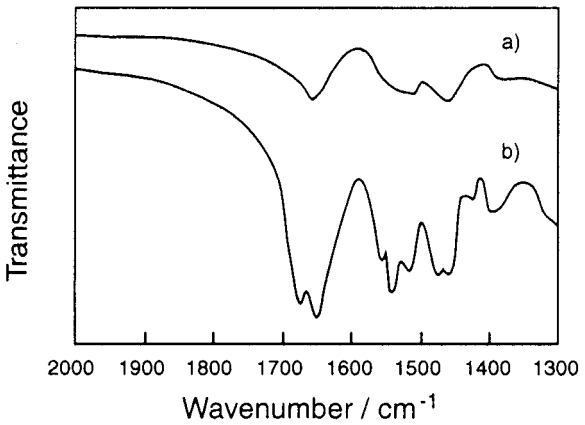

Figure 2. FTIR spectra of $(PVS/PEI)_5$ film before (a) and after modification (b).

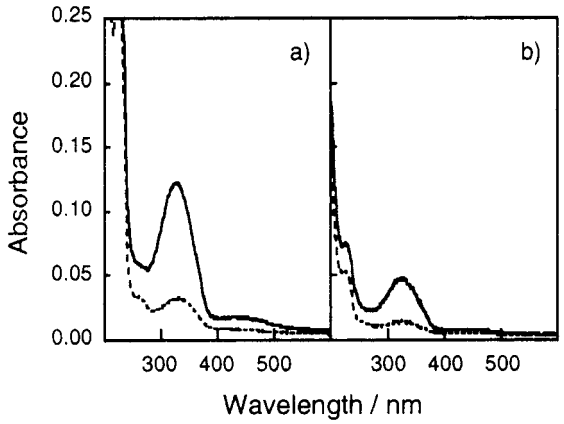

Figure 3. UV−vis absorption spectra of $(PSS/PAH)_{10}$ (a) and $(PSS/PEI)_{10}$ films (b) before (− − −) and after modification (—).

The effects of pH and the concentration of Az-NHS solution were studied. The modification of the PSS/PAH film was carried out in 0.01, 0.025, 0.05, and 0.1 mg mL^{-1} Az-NHS solutions in pH 7.0 buffer and found that the reaction rate depends significantly on the concentration of Az-NHS; the reaction rate increased with the increasing concentration, as expected. On the other hand, the effects of pH of the Az-NHS solution were not significant in the pH range of 6−8; the reaction was slightly slower in pH 6 buffer. Therefore, subsequent experiments were carried out using the 0.1 mg mL^{-1} Az-NHS solution in pH 7.0 buffer.

Loading of Azobenzene Residues in the Multilayer Films. Figure 3 shows absorption spectra of the $(PSS/PAH)_{10}$ and $(PSS/PEI)_{10}$ multilayer films (10 bilayers on both surfaces of the quartz slide) before and after modification with Az-NHS. Before modification, the $(PSS/PAH)_{10}$ multilayer film showed a weak absorption band around 330 nm arising from the azobenzene chromophore labeled intrinsically in PAH. The loading of PAH in the film was calculated to be 0.6×10^{-5} g

Table 1. Azobenzene Chromophores Introduced in the Multilayer Films by Modification with Az-NHS

multilayer film	azobenzene introduced[a] (10^{-9} mol cm^{-2})	modification[b] (%)
$(PSS/PAH)_5$	1.6	3.0
$(PSS/PAH)_{10}$	1.8	1.7
$(PSS/PAH)_{10}PSS$	0.8	0.7
$(PVS/PAH)_5$	2.7	6.8
$(PVS/PAH)_{10}$	3.6	4.5
$(PVS/PAH)_{10}PVS$	0.5	0.6
$(PSS/PEI)_{10}$	0.6	2.3
$(PSS/PEI)_{10}PSS$	0.1	0.4
$(PVS/PEI)_{10}$	2.9	4.5
$(PVS/PEI)_{10}PVS$	0.1	0.2

[a] The average values of three preparations are listed. These values contain ~±15% deviation.The values for PVS-based films may contain error to some extent because of H-aggregate formation. [b] Modification (%) was calculated on the basis of total primary and secondary amino groups in the film as follows; modification (%) = (mol of azobenzene residue introduced) × 100/(mol of total primary and secondary amino groups in the film). These values do not contain the azobenzene residues intrinsically labeled to PAH and PEI.

cm^{-2} (on each surface) from the absorption spectrum, using a molar extinction coefficient of 2.5×10^4 M^{-1} cm^{-1} for the azobenzene unit. Considering the fact that 99.5% of the amino groups in PAH are unsubstituted, the $(PSS/PAH)_{10}$ multilayer assembly contains 1.1×10^{-7} mol cm^{-2} of primary amino groups. After the $(PSS/PAH)_{10}$ film had been modified in the Az-NHS solution for 3 h, the absorbance of the film was enhanced significantly, showing azobenzene residues were immobilized covalently to the $(PSS/PAH)_{10}$ film. From the absorption spectra, the content of azobenzene residues immobilized by the chemical modification is calculated to be 1.8×10^{-9} mol cm^{-2}, which corresponds to ca. 1.7% of the total amino groups in the $(PSS/PAH)_{10}$ film. In a similar manner, the loading of azobenzene residues in the $(PSS/PEI)_{10}$ film was determined to be 0.6×10^{-9} mol cm^{-2} (2.3% vs total primary and secondary amino groups). Thus, the contents of azobenzene residues are rather low. In other words, the remaining 97−98% of amino groups in the multilayer films were not modified with Az-NHS under the present experimental conditions.

To clarify the reasons for low yield in the modification, we carried out modification reactions using three different types of PSS/PAH films: (1) $(PSS/PAH)_{10}$ film, which is constituted with 10 (PSS/PAH) bilayers and the outermost surface contains PAH layer, (2) $(PSS/PAH)_5$ film, which is constituted with 5 bilayers, and (3) $(PSS/PAH)_{10}PSS$ film, in which the outermost surface is covered with a PSS layer. In addition, PVS was also employed as an anionic counterpart in the multilayer films. Table 1 lists the contents of azobenzene residues introduced in the multilayer films by the chemical modification. The azobenzene contents depended clearly on the polyelectrolyte type in the outermost layer; the $(PSS/PAH)_{10}PSS$ and $(PVS/PAH)_{10}PVS$ films were modified significantly less effectively than the other films containing an outermost PAH layer. This suggests that Az-NHS reacted mainly with PAH in the outermost layer which is directly exposed to the Az-NHS solution, because the contents of amino groups in the $(PSS/PAH)_{10}PSS$ and $(PVS/PAH)_{10}PVS$ films are the same as those of $(PSS/PAH)_{10}$ and $(PVS/PAH)_{10}$ films. This view is further supported by comparing the data for the 5- and 10-bilayer films. The loadings of azobenzene residues in the 10-bilayer films are nearly comparable to those of the 5-bilayer films, although the contents of amino groups in the 10-bilayer films are basically double the 5-bilayer films. (A linear growth of the multilayer assemblies was confirmed separately by UV−vis absorption spectra.[12]) These observations support that Az-NHS reacted mainly with the amino groups located on the outermost surface of the films. In other words, Az-NHS reacted preferentially with the surface amino groups that are not involved in the ionic bonding with the sulfonate anion in the adjacent PSS layers. The formation of ion pairs of amino groups with sulfonate resulted in suppressed nucleophilicity to Az-NHS. Table 1 contains also the data for PEI-based layered assemblies. Similarly, the modification to the PSS- and PVS-terminated PEI films was extremely suppressed.

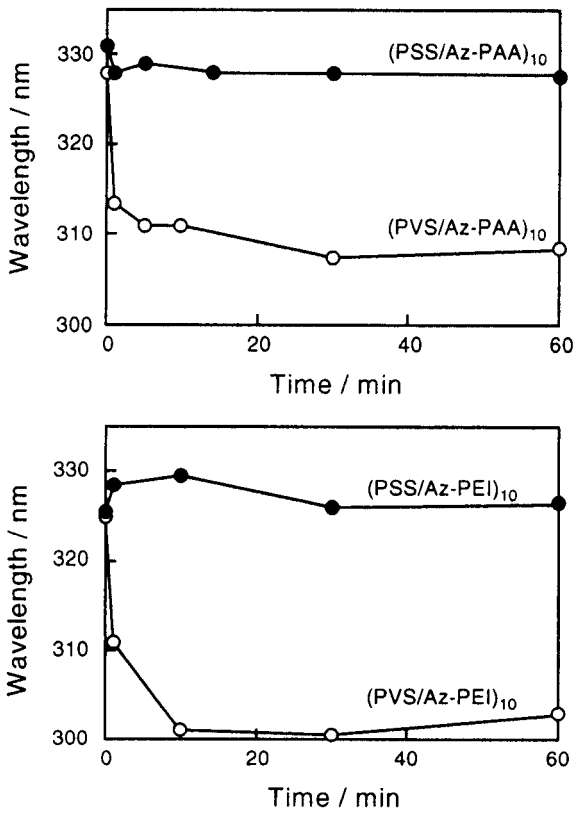

Figure 4. Shifts of absorption maxima (λ_{max}) of the polyelectrolytes multilayer films during the modification reaction with Az-NHS.

Formation of Azobenzene Aggregates in the Multilayer Films. Another interesting feature is the formation of aggregates of azobenzene residues in the modified films. We found that the absorption maximum (λ_{max}) in the UV−vis spectra of the films shifted gradually during the course of the modification reaction.

Figure 4 plots the shift in λ_{max} of the multilayer films during the chemical modification as a function of the reaction time. Before modification, the $(PVS/PAH)_{10}$ and $(PVS/PEI)_{10}$ films exhibited λ_{max} at 328 and 325 nm, respectively, which are originating from the azobenzene chromophores intrinsically bound to the PAH and PEI. The λ_{max} values of the films are nearly the same as those of the PAH and PEI aqueous solutions, suggesting that the azobenzene residues are isolated from each other in the multilayer films before chemical modification. This is reasonable because the contents of intrinsic azobenzene residues in the polymers are rather low (0.5 mol % for the PAH and 0.9 mol % for the PEI). The azobenzene residues are probably distributed homoge-

neously in the films, in view of the fact that the polyelectrolyte layers are interpenetrating each other to establish charge compensation.[22] During the modification in Az-NHS solution, the λ_{max} values of the (PVS/PAH)$_{10}$ and (PVS/PEI)$_{10}$ films shifted rapidly to a shorter wavelength to reach a constant value in ca. 30 min, the change in λ_{max} ($\Delta\lambda_{max}$) being 15−25 nm. This blue shift in λ_{max} may be ascribed to the formation of H-aggregates of azobenzene residues in the films.[23] It has been well documented that the λ_{max} value of azobenzene chromophores depends significantly on the mutual orientation, distance, and aggregation number of the chromophores.[24−27] A blue shift in λ_{max} is induced when the transition dipole moments of the molecules are aligned in parallel in the aggregates, which is called H-aggregates. When the dipole moments are aligned in line, rather than parallel, a red shift occurs, and the aggregates are termed J-aggregates. In practice, the mutual orientation of the dipole moments is between the two extreme orientations with an appropriate tilt angle, and the blue shift can be observed when the tilt angle is larger than ca. 55°. (The tilt angle is defined as the angle between the transition dipoles and the line connecting the centers of the dipoles.) The H-aggregates of azobenzene chromophores are often observed in well-organized monolayer[25] and Langmuir−Blodgett films.[26] Thus, the blue shifts observed for the (PVS/PAH)$_{10}$ and (PVS/PEI)$_{10}$ films suggest the formation of H-aggregates of the azobenzene residues.

In contrast, the $\Delta\lambda_{max}$ was small for the PSS-based films (less than 5 nm), indicating virtually no aggregate formation. It should be noted here that the loading of azobenzene residues in the (PSS/PAH)$_{10}$ and (PSS/PEI)$_{10}$ films after modification is rather low as compared to those in the corresponding PVS-based films (Table 1). Therefore, no aggregate formation in the PSS-based films may be ascribed in part to the low yield in the chemical modification. Additionally, a different surface composition between the PVS- and PSS-based films may also be responsible for the different behavior. In practice, the outermost poly(amine) layer of the films may contain an appropriate amount of PVS or PSS chains as a result of interpenetration of the polyelectrolyte chains.[22] Therefore, it is reasonable to assume that surface chemistry of the PSS-based films is not exactly the same as that of the PVS-based films even if the both films are terminated with the same poly(amine). In the (PSS/PAH)$_{10}$ and (PSS/PEI)$_{10}$ films, the aromatic moieties in PSS might disturb the aggregate formation of azobenzene residues probably due to the bulky and hydrophobic nature. It has recently been reported that azobenzene amphiphiles form aggregates in the polyelectrolyte-adsorbed monolayer films, depending on the type of the polyelectrolyte.[28]

It is interesting to discuss reasons for the aggregate formation. The aggregates of azobenzene chromophores are formed normally only in the condensed media such as monolayers[25] and Langmuir−Blodgett films,[26] where azobenzene chromophores are densely packed to contact with each other. In contrast, in the present system, the aggregates are induced by the chemical modification despite low contents of azobenzene chromophores in the films. This discrepancy may be rationalized by taking into account the localization of azobenzene chromophores on the surface of the film. As discussed previously, the majority of the azobenzene residues seem to be attached to the outermost poly(amine) layers. If the azobenzene residues are bound exclusively to the surface of the layered assemblies, the surface density of azobenzene residues can be calculated to be 3.6×10^{-9} mol cm^{-2} for (PVS/PAH)$_{10}$ film and 2.9×10^{-9} mol cm^{-2} for (PVS/PEI)$_{10}$ film (Table 1).[29] Assuming that the azobenzene molecules are aligned with arranging the longer molecular axis perpendicular to the surface and form a closely packed monomolecular layer, the surface density is calculated to be 6.5×10^{-10} mol cm^{-2}, based on the molecular dimensions of azobenzene residue ($13.6 \times 7.0 \times 3.6$ Å).[30] The observed values are ca. 5 times larger than the calculated value estimated by assuming a completely flat surface, although the true surface area may be much more larger because of the formation of loops and trains of the polymer chains on the surface. It is likely that the local concentration of the azobenzene residues on the surface is high enough to form aggregates.

Photoresponse of the Azobenzene-Modified Films. Azobenzene derivatives are known to isomerize from *E*-form to *Z*-form upon UV light irradiation.[20] Therefore, we studied photoisomerization of azobenzene residues in the modified multilayer films. The *E*−*Z* photoisomerization was suppressed moderately for all films, the contents of *Z*-form in the photostationary state being 30% or lower, whereas the contents of Z-isomers were 65−80% when the methanol solutions of the azobenzene-labeled PAH and PEI were irradiated. In particular, the *Z*% of the (PVS/PAH)$_{10}$ and (PVS/PEI)$_{10}$ films were 16% and 4%, respectively, and much lower than those of PSS-based films [30% for the (PSS/PAH)$_{10}$ film and 20% for the (PSS/PEI)$_{10}$ film]. These observations are consistent with the fact that the azobenzene chromophores form aggregates in the PVS-based films. It has been reported that photoresponse of azobenzene chromophores are severely suppressed or inhibited in the aggregates.[31,32]

Conclusions

Polyelectrolyte multilayer films containing PAH and PEI can be modified with an active ester of azobenzene carboxylate through amide linkage. The azobenzene residues were introduced mainly to the outermost poly(amine) layers, and the modification reaction was much less effective when the multilayer assembly was terminated with polyanion. The azobenzene residues introduced by the chemical modification formed H-aggregates in the multilayer films containing PVS as an anionic counterpart but did not in the PSS-based films. The azobenzene-modified layered assemblies showed *E*−*Z* photoisomerization to some extent, though the photoresponse was suppressed when the azobenzene chromophores formed aggregates. Thus, it became apparent that the modification reaction using NHS active ester is useful to functionalize polyelectrolyte multilayer films.

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