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RESEARCH ARTICLE

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Effect of dipping solution pH values on electrostatic layer-by-layer self-assembly of side-chain azo polyelectrolyte

Abstract The effect of pH value on the electrostatic layer-by-layer self-assembly and the photo-responsive behavior of Poly{2-[4-(4-ethoxyphenylazo)phenoxy]ethyl acrylate-*co*-acrylic acid} (PEAPE) was studied. Results show that in the studied pH value range, the lower the pH value is, the higher is the UV-vis absorbance and the larger is the thickness of the multilayer films. FTIR studies indicate that the azo polyelectrolyte exhibits a different ionization degree in solutions with different pH values. The higher absorbance and the larger thickness of the layer-by-layer films can be attributed to the low ionization degree and the shrinkage conformation of PEAPE in the solution with low pH values. FTIR analysis also confirms that the driving force for layer-by-layer self-assembly of PEAPE and PDAC is the electrostatic interaction.

Keywords layer-by-layer self-assembly, azo polyelectrolyte, pH value

Recently, photoresponsive azo polymers have gained much attention due to their potential applications in light-driven devices [1–3]. Self-assembly is the self-directed association of components into patterns or structures which can control the microscopic architecture at the molecular level. The electrostatic layer-by-layer deposition method, first introduced by Decher in 1992, is an innovatory way to prepare polymeric multilayer thin films. Using a layer-by-layer adsorption scheme, a uniform and controllable thin film can be deposited on a solid substrate from two oppositely charged polyelectrolyte solutions [4]. This method became a hot research topic because of its simple and controllable feature. Incorporation of aromatic azo polyelectrolytes in self-assembled structures is a promising way to prepare novel azo polymer thin films with interesting functionalities such as optical storage and photo-recording [5–15]. Recently, various azo polyelectrolytes have been synthesized in our laboratory [13,16–20]. By using these polyelectrolytes as polyanions, a series of self-assembled multilayers were prepared and the influence of solution conditions on the self-assembly was investigated through the "probe" effect of azo chromophores. These self-assembly multilayers show various interesting photo-responsive behaviors. However, up to now, the question of how to exactly control the microscopic architecture of layer-by-layer self-assembled multilayers of azo polyelectrolytes is still unsolved.

There are many factors influencing the microstructure of the layer-by-layer self-assembly multilayers, such as the molecular configuration of polyelectrolytes, stretching extent of polymer chains, average charge density, adsorption speed, etc. These factors can be adjusted by changing temperature, substrates, solubility of polyelectrolytes, charge density of molecular chains, concentration, pH values, solvent composition, etc [21–23]. For fully charged polyelectrolytes, the thickness of the adsorbed layers can be fine-tuned at the molecular level by adjusting the ionic strength of the dipping solution. However, for weak polyelectrolytes, including azo polyelectrolytes, the existing states of molecules are extremely sensitive to dipping solution pH values and solvent polarity. Here the solution pH is the key factor and the charge density of the weak polyelectrolytes can be controlled by adjusting the pH values [22]. The influence of the solution pH on the weak polyelectrolytes has been widely investigated. The results show that the surface charge density, the thickness and the level of interlayer interpenetration of sequentially adsorbed layers can be significantly changed through adjusting pH. Even with a pH value difference of 0.5, the thickness and surface morphology of self-assembly multilayers may have obvious changes. Therefore, adjusting the pH is a practical way to control the microstructure of the self-assembled multilayers of weak polyelectrolytes. The above mentioned factors determine the degree of ionization, the degree of charge shielding and the molecular configuration

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of the polyelectrolytes, which show a direct influence on the existing status of the micromolecules in dipping solutions used for layer-by-layer adsorption processes.

In the present work, the influence of the solution pH on the self-assembly multilayers of azo polyelectrolytes and their photoresponsive behaviors were investigated in detail and the conditions for controlling the multilayer structure have also been explored. Through analysis of FTIR spectra of the multilayers, the fact that the ionization degree of azo polyelectrolytes changed with pH was confirmed. The lower the pH value is, the less is the charge density of the polymer chains for self-assembly and the more shrunken the configuration of the molecules are. These studies explain the absorbance difference of azo polyelectrolyte multilayers prepared under different pH conditions and provide a way to control the self-assembly structure and photoresponsive properties of azo polyelectrolytes.

1 Experimental

1.1 Materials

Azo polyelectrolyte PEAPE (Poly{2-[4-(4-ethoxyphenylazo)phenoxy]ethyl acrylate-co-acrylic acid}) was synthesized in our laboratory. As shown in Fig. 1, PEAPE can be considered as a random copolymer composed of acrylic-acid units and azobenzene-containing acrylate units. PEAPE was prepared by the Schotten-Baumann reaction between poly(acryloylchloride) and 2-[4-(4-ethoxyphenylazo)-phenoxy]ethanol, and the unreacted acyl-chloride groups were then hydrolyzed to obtain the carboxyl groups. The preparation and characterization details can be seen in our previous paper [13]. The average molecular weight (M_n) of poly(acryloyl chloride) was estimated to be 28500 and the polydispersity index was 1.9. The PEAPE sample used in this study had the degree of functionalization (DF) of 18.1%, defined as the percentage of the structure units bearing azo chromophores among the total units. All the other reagents and solvents were used as received without further purification.

1.2 Multilayer preparation

Deionized water (resistivity > 18 MΩ) was obtained from a Millipore water purification system and used for the experiments. Quartz and CaF_2 slides were used as adsorption substrates and were treated as follows: The quartz slides were sonicated in a 98% H_2SO_4/30%H_2O_2 (1:1) solution for 1 h, rinsed with deionized water for 3–4 times and then sonicated in a $NH_4OH/H_2O/H_2O_2$ (1:4:5) solution for 2–3 h followed by a thorough rinse with water for 3–4 times. The CaF_2 slides (20 mm × 10 mm × 1 mm) were cleaned with acetone and dried with an air stream. After being treated, these quartz slides and CaF_2 were stored in deionized water.

Poly(diallyldimethylammonium chloride) (PDAC, M_W 2.0×10^6–3.5×10^6, 20% solution, Aldrich), used as polycation, was diluted to a concentration of 0.1 mmol/L (repeated unit) with Milli-Q water (resistivity > 18 MΩ). The azo polyelectrolyte PEAPE with a content of 0.1 g/L was used as polyanion and the solution pH was adjusted by hydrochloric acid (1 mol/L) and sodium hydroxide (1 mol/L) solutions.

In the deposition process, a freshly treated quartz slide was first dipped in the polycation solution for 10 min. After being immersed in Milli-Q water for 1 min, the slide was rinsed with Milli-Q water for 3–4 times and blown dry with a cold air stream. In the same way, this slide was then dipped in the polyanion solution for 10 min, immersed and rinsed with Milli-Q water and blown dry. This process was repeated until the multilayers with the required number of layers were obtained. The UV-vis absorption spectra of the multilayers were measured after each bilayer (one layer of polycation and one layer of polyanion) was formed.

1.3 Characterization

The UV-vis spectra of the azo polyelectrolytes in solution or as self-assembled multilayers were recorded on a Perking Elmer Lambda Bio-40 spectrometer. The scanned wavelength was in the range of 200–700 nm and the scanned space was 0.5 nm/1 nm.

The photoisomerization of the azo chromophores was induced by irradiating UV light, which was from a high-intensity 365 nm UV lamp equipped with 12.7 cm diameter filter (Cole-Parmer L-97600-05 long wave UV lamp, L-09819-23 filter). The intensity of the lamp was 21000 mW/cm^2 at a distance of 5.08 cm. The samples were placed at ca. 10 cm away from the lamp. The UV-Vis spectra of the samples were measured over different

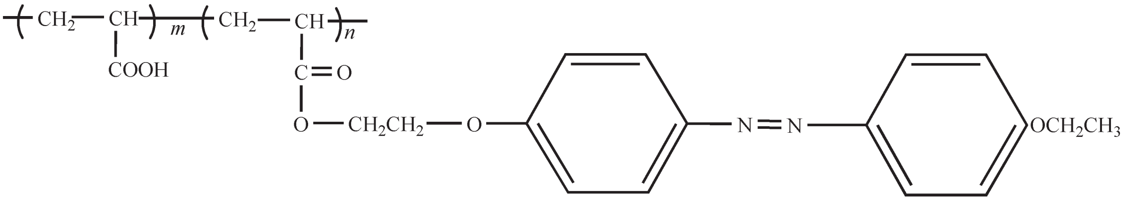

Fig. 1 Chemical structure of PEAPE

irradiation time intervals. Infrared spectra of the multilayers were measured using a Nicolet 560-IR spectrometer. For Infrared spectral measurements, CaF_2 slides were chosen as substrates, and the samples were prepared from azo polyelectrolytes with different pH values by using the layer-by-layer adsorption method.

2 Results and discussion

2.1 Effect of pH value on the electrostatic layer-by-layer self-assembly

Azo polyelectrolytes in both acidic and basic solutions could form uniform multilayer films on quartz slides through an electrostatic layer-by-layer adsorption process by using PDAC as an oppositely charged polyelectrolyte. The UV-vis spectroscopy was used to monitor the layer-by-layer process of PEAPE/PDAC multilayer films. Figure 2 shows the UV-vis spectra of PEAPE/PDAC multilayer films varying with the number of bilayers by using the dipping solutions with solution pH of 4.36. Here, the term "bilayer" means a pair of layers including one layer of polycation and one layer of polyanion formed after each deposition cycle. By increasing the number of bilayers, a linear increase of the maximum absorbance of PEAPE/PDAC multilayer was observed for these systems indicating that the multilayers on the substrates grew an equal amount after each dipping cycle.

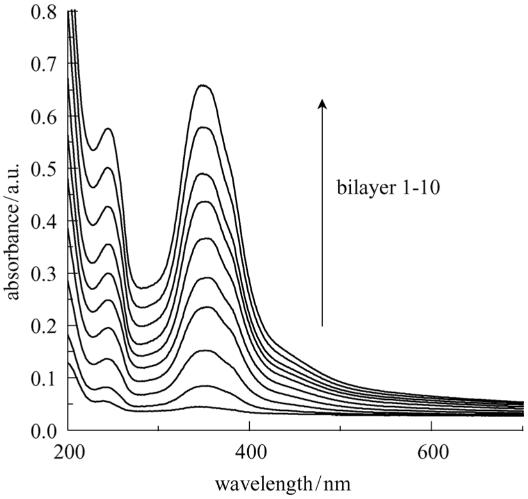

Fig. 2 UV-vis spectra of PEAPE/PDAC multilayers with different bilayer numbers (pH = 4.36)

The adsorption rate of azo polyelectrolytes on the substrates changed with the solution pH. As shown in Fig. 3, during the layer-by-layer self-assembly process, the lower the solution pH of the azo polyelectrolytes, the stronger the bilayer absorbance. It meant that the bilayer thickness increased with decreasing solution pH. This phenomenon can be explained as follows: When the solution pH was low, only a small amount of the carboxylic acid groups of the azo polyelectrolytes was ionized. In this case, azo polyelectrolytes carried little charge, so the intermolecular repulsion was weak. The shrunken molecular conformation caused a significant increase in bilayer thickness. However, when the solution pH was high, it was easy for azo polyelectrolytes to ionize. Azo polyelectrolytes carried a large amount of charges resulting in a strong intermolecular repulsion. The extended molecular configuration induced an obvious decrease in bilayer thickness. The relationship between the bilayer thickness and the solution pH of azo polyelectrolytes will be further discussed in the next section by using FTIR spectroscopy.

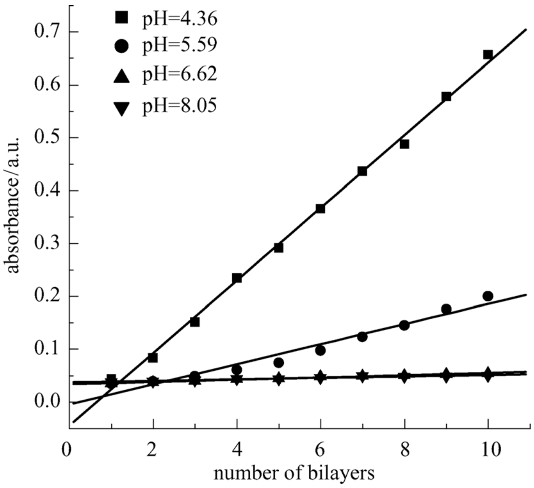

Fig. 3 Relationship of the maximum absorbance and number of bilayers, obtained from layer-by-layer self-assembly of PEAPE/PDAC with different pH values

For the multilayers obtained from azo polyelectrolyte with different pH values, the maximum absorbance wavelength (λ_{max}) appeared at about 348 nm and there were no obvious spectral shifts during the layer-by-layer adsorption process. For the azo polyelectrolyte dipping solution, the maximum absorbance peaks changed with the solution pH. The λ_{max} of the azo polyelectrolyte with pH of 8.05 was at 348 nm, while that of the azo polyelectrolyte with pH of 4.36 was at 343 nm. This phenomenon is related to the H-aggregation behavior of the azo chromophores of the azo polyelectrolytes. The water-soluble azo polyelectrolyte PEAPE includes hydrophobic azo side-chains, which tend to form H-aggregates induced by strong $\pi-\pi$ interaction of the conjugated planar structures. H-aggregation of azo chromophores can be detected with significant spectral blue shifts to the single molecular band. For PEAPE dipping solutions with low pH, the shrunken molecular conformation makes it easy to form H-aggregates of azo chromophores. The hypsochromic shifts indicate that the degree of H-aggregation is enhanced when pH decreases. On the other hand, there hardly exist H-aggregates of azo chromophores in the layer-by-layer multilayers fabricated under various pH conditions. These results indicate that H-aggregates of azo chromophores, formed in the azo polyelectrolyte solution with low pH, are disaggregated when the azo polyelectrolytes are transferred from solutions to solid films.

2.2 Effect of pH value on the Photoresponsive properties of the self-assembly multilayers

The photoisomerization of the azo polyelectrolytes in layer-by-layer multilayers was studied by UV-vis spectroscopy after irradiation with 365 nm UV light. The UV spectra were recorded over different time intervals until photostationary states were reached. The UV-vis spectra of PEAPE multilayers at pH of 4.36 varying with irradiation time are given in Fig. 4. Upon UV irradiation, the intensity of the π-π^* transition band at 345 nm decreased and the intensity of the n-π^* transition band at 410 nm increased gradually. The spectrum variations evidence the trans-to-cis isomerization of the azo chromophores. The maximum intensities of π-π^* transition bands for PEAPE under different pH conditions varying with the different irradiation time intervals are given in Fig. 5. The maximum absorbance A can be best fitted by a first-order exponential decay function. As shown in Fig. 5, the azo polyelectrolyte in the layer-by-layer multilayer fabricated under lower pH condition (*e.g.* pH = 4.36) has quicker photoresponsive rate.

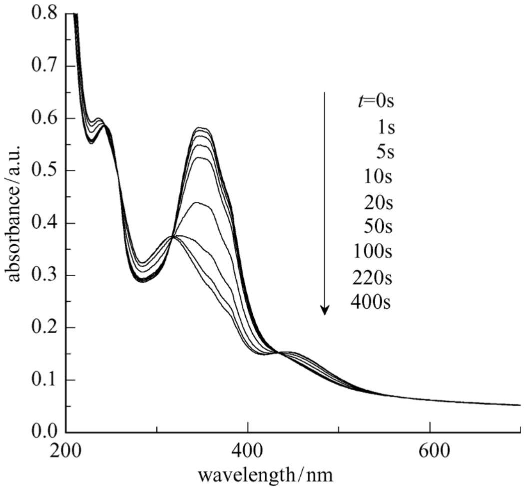

Fig. 4 UV-vis spectra of layer-by-layer PEAPE/PDAC multilayers recorded over different UV light irradiation time intervals (pH = 4.36)

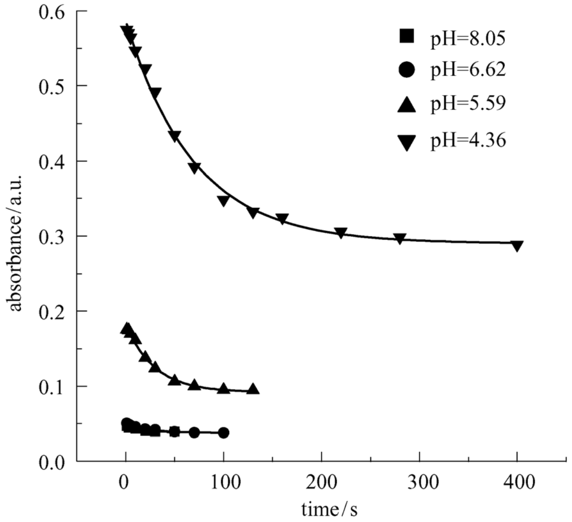

Fig. 5 Relationship of maximum absorbance (345 nm) of layer-by-layer PEAPE/PDAC multilayers and UV light irradiation time intervals for samples obtained with different pH values

2.3 Mechanism of the effect of pH value on the electrostatic layer-by-layer self-assembly

FTIR spectroscopy is a useful tool providing the ionization information of carboxyl acid groups of PEAPE in the layer-by-layer multilayers. CaF_2 is stable in water, and shows no spectral band in the FTIR measurement range. Therefore, CaF_2 was used as substrates for fabrication of the azo polyelectrolyte multilayers for FTIR spectroscopy. Figure 6 shows the FTIR spectra of layer-by-layer PEAPE/PDAC multilayers obtained from the solutions with different pH values.

As shown in Fig. 6, the band at around 1720 cm^{-1} is attributed to the carbonyl stretching vibrations of carboxylic acid groups in the PEAPE/PDAC multilayers, and the band at around 1580 cm^{-1} is attributed to the carbonyl stretching vibrations of carboxylate. With the pH increase, the carbonyl absorbance peak of carboxylate groups (–COO–) at 1580 cm^{-1} increases and the carbonyl stretching vibrations of carboxylic acid groups (–COOH) at 1720 cm^{-1} decreases for the multilayers fabricated from the azo polyelectrolyte solutions.

The degree of ionization (α), defined as the fraction of the ionized carboxylate groups among the total functional acid groups, is used to calculate the ionization capacity of PEAPE in the multilayers under various pH conditions. An integral area method is used to estimate the degree of ionization of the azo polyelectrolytes in multilayers. First, the integral area of A_{-COO-} and A_{-COOH} were calculated and recorded in Tables 1 and 2. Here, A_{-COO-} is the absorbance integral area of carbonyl stretching vibrations of carboxylate groups (–COO–) in the range of 1519.7–1589.1 cm^{-1} (baseline: 1519.7–1616.1) and A_{-COOH} is the absorbance integral area of the carbonyl stretching vibrations of carboxylic acid groups in the range of 1683.6–1758.8 cm^{-1} (baseline:1616.1–1758.8).

Secondly, the degree of ionization of PEAPE in the multilayer films fabricated from various pH conditions

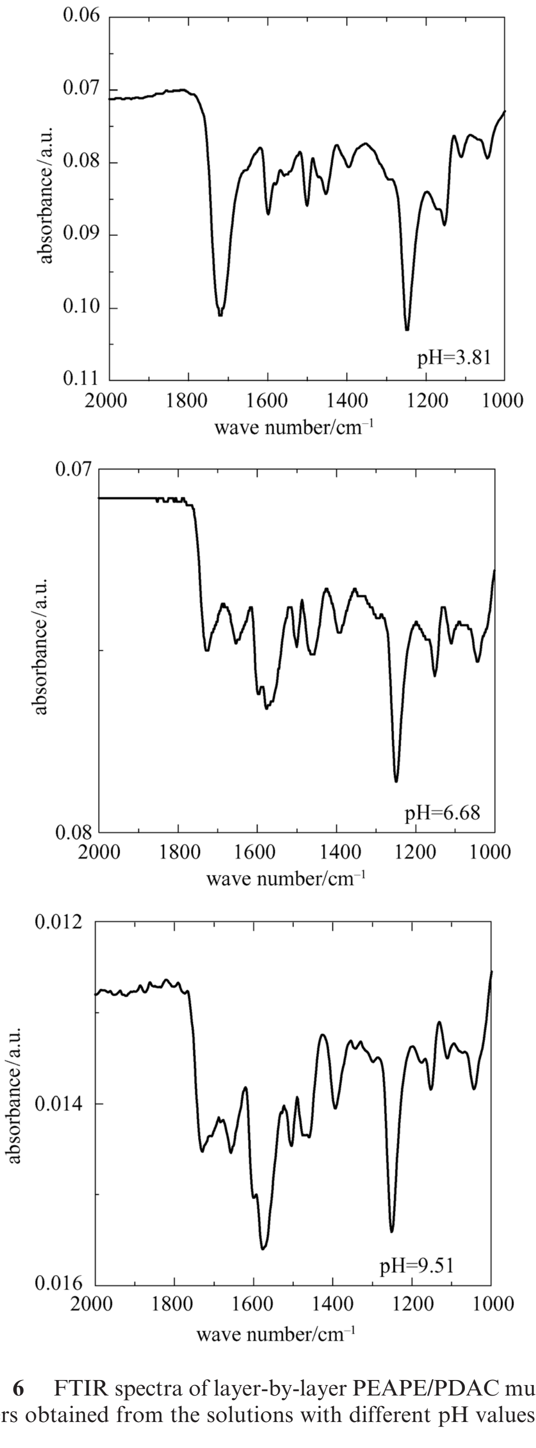

Fig. 6 FTIR spectra of layer-by-layer PEAPE/PDAC multilayers obtained from the solutions with different pH values

is estimated by using the equations described below:

$$\alpha_{3.81} = \frac{A_{-\mathrm{COO}-}}{A_{-\mathrm{COO}-} + A_{-\mathrm{COOH}}} = 0.139$$

$$\alpha_{6.68} = \frac{A_{-\mathrm{COO}-}}{A_{-\mathrm{COO}-} + A_{-\mathrm{COOH}}} = 0.460$$

$$\alpha_{9.51} = \frac{A_{-\mathrm{COO}-}}{A_{-\mathrm{COO}-} + A_{-\mathrm{COOH}}} = 0.481$$

Table 1 Integral area of FTIR absorbance peak at 1720 cm^{-1} of layer-by-layer PEAPE/PDAC multilayers obtained from solutions with different pH values

pH	3.81	6.68	9.51
$A_{-\mathrm{COOH}}$	1.2632	0.1467	0.0744

Table 2 Integral area of FTIR absorbance peak at 1580 cm^{-1} of layer-by-layer PEAPE/PDAC multilayers obtained from solutions with different pH values

pH	3.81	6.68	9.51
$A_{-\mathrm{COO}^-}$	0.2038	0.1252	0.0690

For the multilayer films fabricated from the three pH conditions such as 3.81, 6.68 and 9.51, the degree of ionization of the acid groups in PEAPE is 0.139, 0.460, and 0.481, respectively.

The FTIR spectra of PEAPE/PDAC multilayers obtained from the solutions with different pH values show that as the pH increases, the carbonyl absorbance peak of carboxylate groups (–COO–) at 1580 cm^{-1} increases and the carbonyl stretching vibrations of carboxylic acid groups (–COOH) at 1720 cm^{-1} decreases. Therefore, for the multilayer films fabricated from various pH conditions, the degree of ionization of the acid groups in PEAPE increases significantly with increasing pH, which acts in accord with the ionization principles of the PEAPE dipping solutions.

The FTIR spectra provide evidence to the fact that the degree of ionization of carboxylic acid groups changes with pH which induces the change of the absorbance intensity and bilayer thickness of the PEAPE/PDAC multilayers. On the one hand, during the PEAPE/PDAC self-assembly process, when the solution pH is lower, the degree of ionization of carboxylic acid groups becomes lower. The intermolecular repulsion is weaker because the charge density of azo polyelectrolytes is lower. On the other hand, when solution pH is higher, the degree of ionization of carboxylic acid groups becomes higher. Azo polyelectrolytes have a higher charge density resulting in stronger intermolecular repulsion. Therefore, the bilayer thickness increased with a decreasing solution pH due to the shrunken molecular conformation of the azo polyelectrolytes in dipping solutions. When the azo polyelectrolytes are transferred from the solutions to solid films by layer-by-layer methods, the carboxylate groups (–COO–) ionized from carboxylic acid groups (–COOH) can be fixed and the relationship between the degree of ionization of carboxylic acid groups and solution pH can be detected by FTIR spectroscopy. The photoresponsive property of the PEAPE/PDAC multilayers is related to the pH of the dipping solutions. When the pH is lower, the electrostatic interaction is weaker and the photoisomerization rate becomes quicker.

As discussed above, the azo polyelectrolyte exhibits a different ionization degree in the solutions with different pH values and the pH value has a great influence on the electrostatic layer-by-layer self-assembly. The lower the pH value is, the higher is the UV-vis absorbance and the larger is the thickness of the multilayer films, which is also responsible for the quicker photo-responsive rate. On this basis, the electrostatic multilayers with controllable thickness and photoresponsive properties can be achieved by adjusting the preparation conditions.

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