# Sequentially Adsorbed Electrostatic Multilayers of Branched Side-Chain Polyelectrolytes Bearing Donor-Acceptor Type Azo Chromophores

## Haopeng Wang, Yaning He, Xinlin Tuo, and Xiaogong Wang\*

Department of Chemical Engineering, Tsinghua University, Beijing, P. R. China 100084 Received August 15, 2003; Revised Manuscript Received October 31, 2003

ABSTRACT: Two newly synthesized polyelectrolytes (PBANT-AC and PBACT-AC) functionalized with branched side chains bearing electron donor–acceptor type azobenzene chromophores were used as polyanions to build up multilayer films through an electrostatic sequential adsorption process by using poly(diallyldimethylammonium chloride) (PDAC) as the polycation. When dissolved in anhydrous DMF and a series of DMF–H<sub>2</sub>O mixed solvents with different DMF to H<sub>2</sub>O ratios, both azo polyelectrolytes could form uniform multilayer films through the layer-by-layer adsorption process. Altering the water content of the dipping solutions of both azo polyelectrolytes was found to dramatically change the thickness of the sequentially adsorbed bilayers, chromophore orientation, and surface roughness of the multilayer films. On the other hand, the solvent effect on the H-aggregation in the multilayer films was determined by the structural details of the azo polyelectrolytes. After the irradiation with a linearly polarized Ar<sup>+</sup> laser beam at 488 nm, significant dichroism was induced in the PBANT-AC/PDAC multilayer films prepared from the DMF dipping solution. Upon exposure to an interference pattern of Ar<sup>+</sup> laser beam at modest intensities, optically induced surface modulation on the multilayer surfaces was observed.

## Introduction

Azobenzene derivatives are well-known for their character to undergo the trans-cis isomerization upon light irradiation. On the basis of the photoisomerization, polymeric thin films containing azobenzene chromophores can exhibit diverse photoresponsive properties, which promise potential applications in areas such as holographic information storage, photoswitching, sensors, and many others.<sup>1–3</sup> Interaction of linearly polarized light with the azobenzene moieties can induce the groups in polymeric films to align perpendicular to the direction of light polarization and generate birefringence and dichroism.<sup>4,5</sup> By exploring the nature, reversible optical storage has been demonstrated in different ways.<sup>6,7</sup> Photoinduced surface modulation is another interesting effect caused by the photoisomerization, which has attracted considerable attention and has been intensively investigated in recent years.<sup>8,9</sup> The photoinduced surface structures such as surface relief gratings (SRGs) can be formed on azo polymer surfaces in a reversible way upon exposure to an interference pattern of Ar<sup>+</sup> laser beams at modest intensities.<sup>8-10</sup> A number of azobenzene-containing polymers as spincoated films, Langmuir-Blodgett films, or monolayers have been studied over recent years for the photoin-duced properties.  $^{11-18} \,$ 

The electrostatic layer-by-layer deposition method, first introduced by Decher, is an innovatory way to prepare novel types of polymeric multilayer thin films.<sup>19,20</sup> For many applications, it is the most feasible method to create multilayer thin films incorporating a wide variety of functional groups.<sup>20–23</sup> The electrostatic self-assembled multilayer films containing azo chromophores have been considered to be promising for photonic and other applications.<sup>24–34</sup> Several groups have reported that noncentrosymmetric thin films, prepared from electrostatic layer-by-layer deposition of azo polyelectrolytes, can demonstrate significant nonlinear optical

properties without electric field poling.<sup>24-26</sup> Self-assembled multilayers of an azobenzene bolaamphiphile and polycations have been prepared, and the photoswitching function based on photoisomerization of the multilayers has been studied.<sup>27</sup> Alternate multilayer films of a cationic bipolar azo amphiphile and an anionic polyelectrolyte have been prepared by a layer-by-layer deposition method.<sup>28</sup> In the study, optical dichroism was induced in the films upon linearly polarized UV irradiation, which could be reversibly erased and rewritten. It has been reported that ionenes containing rigid azobenzene chromophores separated by flexible spacers can form internally ordered multilayers through the electrostatic layer-by-layer deposition method.<sup>29</sup> Photoinduced switching of self-assembled multilayers formed by an alternate adsorption of azobenzene-containing ionene polycations and anionic polyelectrolytes has been studied.<sup>30</sup> The ionenes used could be in the trans- or cis-rich state of the azobenzene units. Use of cis-rich ionene solutions was found to adsorb up to 3 times more material at each dipping cycle as compared with the solution of the trans polymer. A commercially available side-chain azo polyanion and two polycations have been used to build up multilayers.<sup>31</sup> UV light irradiation was found to be responsible for reversible changes in the optical thickness of the films. A significant photochromic effect of cis-trans isomerization of the azo chromophores, accompanied by the contact angle changes of water on the multilayer surface, has been observed for the multilayers of a series of poly(acrylic acid)-based azo polyelectrolytes.<sup>32</sup> Commercially available low-molarmass azo dyes also present promise in creating ordered layer-by-layer thin films.<sup>33</sup> Surface relief gratings were fabricated on the multilayer films of poly(diallyldimethylammonium chloride) and a commercial azo dve. Congo Red. Reported in a separate article by the same group, multilayer films formed by a poly(acrylic acid)based anilino-functional precursor polymer have been postfunctionalized through azo coupling reaction and studied for photoinduced surface modulation.<sup>34</sup>

\* Corresponding author.

It has been known for a quite long time that the local structure of polymeric matrix influences both photo- and thermochromism of azo chromophores.<sup>35,36</sup> It has been reported that the photochemical reactivity of the electrostatic multilayers is considerably dependent on the type of polycations used in the systems.<sup>30</sup> A significant influence of the polycations on the molecular orientation of the azobenzene groups in multilayer films and on the photoisomerization kinetics has also been observed.<sup>31</sup> It has been shown that in most cases the polyelectrolytes are not stratified into well-defined layers but are dispersed and interpenetrating in the multilayer films.<sup>20,23,37,38</sup> For fully charged polyelectrolytes such as poly(styrenesulfonate) and poly(allylamine), the thickness of the adsorbed layers can be fine-tuned at the molecular level by adjusting the ionic strength of the dipping solution.<sup>39</sup> The organization and thickness of the multilayers are also influenced by dielectric constant of the deposition solvent and identity of the salt.<sup>37</sup> The thickness and the level of interlayer interpenetration of sequentially adsorbed layers of weak polyelectrolytes are extremely sensitive to dipping solution pH.<sup>40,41</sup> For molecules or polymers containing azo dyes, H-aggregation has been observed in the dipping solutions or electrostatic self-assembled multilayer films.<sup>26–31</sup> The name H-aggregation originated in the observation of hypsochromic or H-bands in UV-vis spectra of ionic dyes, which mean those transitions that are blue-shifted and thus appear at shorter wavelengths than molecular absorption band (M-band).42 The appearance of Hbands is rationalized in terms of face-to-face dye aggregation through the formation of dimers, trimers, or even *n*-mers.<sup>43–46</sup> Azobenzene bolaamphiphile with branched structure has been reported to be able to form self-assembled order architecture through H-aggregation.47 Besides the direct effects on the spectral and photoresponsive properties, H-aggregation causing the intermolecular association and intramolecular aggregation could induce conformational change of polymer chains in solution and consequently influence organization and thickness of multilayers. This means that, in the process to controllably alter dipping solution conditions of azo polyelectrolytes, the variation of the H-aggregation degree in both the dipping solutions and multilayer films caused by the change should be understood. However, the study along this line is still lacking.

In the present work, two azo polyelectrolytes (PBANT-AC and PBACT-AC) with branched side chains containing donor-acceptor type azobenzene chromophores were synthesized. The polymers can be considered as random copolymers of acrylic acid units and acrylate units bearing branched side chains containing donor-acceptor type azobenzene chromophores. The molecular design is in order to ensure that the polyelectrolytes can contain an adequate amount of photoresponsive azo chromophores and also enough hydrophilic COOH groups to promote the water solubility of the polyelectrolytes. The polyelectrolytes dissolved in dimethylformamide (DMF) and a series of DMF-H<sub>2</sub>O mixed solvents with different DMF to H<sub>2</sub>O ratios were used as deposition solutions. The electrostatic layer-by-layer self-assembly behavior of the azo polyelectrolytes in the solutions was investigated. The effects of the DMF to H<sub>2</sub>O ratios on the H-aggregation, self-assembled multilayer thickness, surface roughness, and azo chromophore orientation in the multilayers were studied in detail. Photoinduced

dichroism and SRGs of the multilayer films were also explored in the study.

## **Experimental Section**

Characterization. Infrared spectra were measured using a Nicolet 560-IR spectrometer by incorporating the sample in a KBr disk. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Varian Inova 500NB NMR spectrometer. Elemental analysis of C, H, and N was completed through the Heratus CHN-Rapid method. The glass transition temperatures  $(T_{gs})$  of the polymers were determined with TA Instrument DSC 2910 at a heating rate of 10 °C/min. The molecular weights of the polymers were measured by gel permeation chromatography (GPC) (Viscotek TDA 302 GPC); THF was used as the eluting solvent at the rate of 1.0 mL/min with the temperature of 40°C. UV-vis spectra of the azo polyelectrolytes in solutions, as self-assembled multilayers and spin-coated films, were recorded on a Perking-Elmer Lambda Bio-40 spectrometer. The thickness of the multilayer films on silicon wafers was determined by using an optical ellipsometer (SE400, Sentech Instruments) with a He-Ne laser (632.8 nm) at an incident angle of 70°. The surface images of the multilayers were monitored using AFM (Nanoscope IIIa, tapping mode).

**Materials.** 1,4-Dioxane, tetrahydrofuran (THF), and petroleum ether (bp 30-60 °C) were refluxed with cuprous chloride for 1 h and distilled, then were refluxed with sodium for 6 h, and distilled before use. *N*,*N*-Dimethylformamide (DMF) was azeotropically distilled with benzene six times for dehydrating and then distilled under vacuum before use. All the other reagents and solvents were used as received without further purification.

N-Ethyl-N-(2-chloroethyl)aniline (ECA). Phosphorus oxychloride (2 mL, 0.021 mol) solution of THF (10 mL) was added dropwise at room temperature into a solution of N-ethyl-*N*-hydroxyethylaniline (5.00 g, 0.030 mol, from ACROS Co.) in 10 mL of anhydrous tetrahydrofuran (THF). The mixture was stirred at room temperature for 4 h, and then the solution was concentrated by removing the solvent THF. The residue was diluted with water (adjusted pH to 9) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. After dried with MgSO<sub>4</sub>, the extract was collected by distilling off the solvent at reduced pressure and further purified by vacuum distillation; yield 45%, bp 102-104 °C/ 399Pa. IR (KBr): 2970 (s; C–H), 1600 1500 (s; benz ring), 1340 (s; C–N), and 720 (s; C–Cl) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.16$ (t, -CH<sub>3</sub>, 3H), 3.40 (m, N-CH<sub>2</sub>CH<sub>3</sub>, 2H), 3.60 (s, N-CH<sub>2</sub>CH<sub>2</sub>-Cl, 4H), 6.68 (m, Ar-H, 3H, ortho and para to N), 7.22 (t, Ar-H, 2H, meso to N). Elemental analysis: C<sub>10</sub>H<sub>14</sub>NCl (183.68) Calcd: C, 65.40; H, 7.87; N, 7.63; Cl, 19.30. Found: C, 64.10; H, 7.70; N, 7.81; Cl, 18.74.

3,5-Bis[2-(*N*-ethylanilino)ethoxy]benzyl Alcohol (EEBA). A mixture of ECA (4.041 g 0.022 mol), 3,5-dihydroxybenzyl alcohol (1.401 g, 0.01 mol), anhydrous potassium carbonate (10 g, 0.072 mol), potassium iodide (0.5 g), and 30 mL of dimethyl sulfoxide (DMSO) was heated to 110 °C under nitrogen protection with vigorous stirring for 48 h. The reaction mixture was then poured into 500 mL of cold water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The extract was concentrated and precipitated with petroleum ether. The precipitate was dried at 70 °C under vacuum for 48 h. IR (KBr): 3400 (s; OH), 2970 (s; CH), 1600 1500 1460 (s; benz ring) and 1340 (s; C-N) cm<sup>-1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta = 1.16$  (t,  $-CH_3$ , 6H), 3.42 (m, N-CH<sub>2</sub>-CH<sub>3</sub>, 4H), 3.70 (t, N-CH<sub>2</sub>CH<sub>2</sub>-O, 4H), 4.00 (t, N-CH<sub>2</sub>CH<sub>2</sub>-O, 4H), 4.58 (s, Ar-CH2-OH, 2H), 6.34 (s, Ar-H, para to -CH<sub>2</sub>OH, 1H), 6.48 (s, Ar-*H*, ortho to -CH<sub>2</sub>OH, 2Ĥ), 6.68 (m, Ar-H, 6H, ortho and para to N), 7.22 (t, Ar-H, 4H, meso to N).

**Poly(acryloyl chloride) (PAC).**<sup>32</sup> Acryloyl chloride (10 mL), dry 1,4-dioxane (10 mL), and AIBN (0.332 g) were added into a flask. The mixture was reacted at 55 °C under the protection of nitrogen for 14 h. The polymer was precipitated by adding petroleum ether (60 mL) and then washed twice with petroleum ether. The product was dried at 60 °C under vacuum for 48 h. GPC:  $M_n$  53 200 (estimated by using poly-

(methyl acrylate) prepared from the same batch of PAC and an excess of methanol);<sup>48</sup> MWD: 1.3.

Poly{3,5-bis[2-(N-ethylanilino)ethoxy]benzyl acrylateco-acrylic acid } (PBA-AC). PAC (0.3 g, 0.0033 mol), triethylamine (0.56 mL, 0.0040 mol), and EEBA (whose amount was determined by the degree of functionalization required) were dissolved in anhydrous DMF (40 mL). The mixture was stirred at 70 °C for 16 h under the protection of N2. Then 3 mL of water was added into the mixture and stirred for 10 min. After precipitated in 300 mL of water solution (adjusting pH by HCl to 3.5-4), the precipitate collected by filtration was washed with water and dried. The crude product was further purified by extraction with CH<sub>2</sub>Cl<sub>2</sub> for 24 h and dried at 60 °C under vacuum for 48 h. IR (KBr): 3500-2500 (broad, O-H), 1700-1750 (s; C=O), 1600 1500 (s; benz ring) cm<sup>-1</sup>. <sup>1</sup>H NMR (DMSO $d_6$ , ppm):  $\delta = 1.04, 1.20 - 2.40, 3.62, 4.01, 4.90, 6.30, 6.47, 6.55, d_6$ 6.70, 7.14. <sup>13</sup>C NMR (DMSO- $d_6$ , ppm):  $\delta = 175.6$ , 174.0, 159.5, 147.1, 138.2, 129.2, 115.6, 111.6, 106.2, 100.5, 65.4, 49.0, 44.6, 40.0, 34.7, 32.0, 11.7.

**Poly**{**3,5-bis**[**2-(***N***-ethy**]**-4-(**4'**-nitropheny**]**azo**)**anilino**)**ethoxy**]**benzy**] **acry**]**ate**-*co*-**acry**]**ic acid**} (**PBANT-AC**). The azo polyeletrolyte was prepared by a postpolymerization azo coupling reaction.<sup>12</sup> *p*-Nitroaniline was diazotized by a similar method as the literature reported, and the diazonium salt solution was added dropwise into a solution of PBA-AC in dimethylformamide (DMF) at 0 °C. PBANT-AC was obtained by precipitation of the above solution in plenty of water and dried at 60 °C under vacuum for 48 h. <sup>1</sup>H NMR (DMSO*d*<sub>6</sub>, ppm):  $\delta$  = 1.08, 1.20–2.40, 4.10, 4.90, 6.30–6.47, 6.80, 7.78, 8.24. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm):  $\delta$  = 175.6, 174.0, 159.4, 156.1, 151.4, 146.7, 142.8, 138.2, 126.0, 124.7, 122.3, 111.5, 106.4, 100.6, 65.5, 49.0, 45.2, 40.8, 35.0, 32.2, 11.9. UV-vis (DMF): 488 nm ( $\epsilon$  = 3.71 × 10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup>).

**Poly**{**3,5-bis**[**2-(***N***-ethyl-4-(***4***'-carboxyphenylazo)anilino)ethoxy]benzyl acrylate-***co***-acrylic acid**} (**PBACT-AC**). Via a similar procedure as the synthesis of PBANT-AC. 4-Aminobenzoic acid was used instead of *p*-nitroaniline in the reaction. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, ppm):  $\delta = 1.05, 1.20-2.40, 4.10,$ 4.90, 6.30–6.47, 6.80, 7.78, 8.08. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, ppm):  $\delta = 175.4, 174.0, 166.6, 159.4, 155.1, 150.8, 142.6, 138.2, 130.8,$ 130.3, 125.4, 121.6, 111.4, 106.3, 100.6, 65.5, 49.0, 45.1, 40.6, 34.4, 32.2, 11.9. UV-vis (DMF): 438 nm ( $\epsilon = 2.40 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>).

Multilayer Preparation. Poly(diallyldimethylammonium chloride) (PDAC, MW 20 000-35 000, 20% solution, Aldrich) was used as polycation and diluted to a concentration of 0.1 mmol/L (repeated unit) with Milli-Q water (resistivity >18  $M\Omega$ ). The azo polyelectrolytes PBANT-AC and PBACT-AC were used as polyanion and dissolved in anhydrous DMF and a series of DMF-H<sub>2</sub>O mixed solvents with a concentration of 0.2 mg/mL, respectively. Quartz slides (50 mm  $\times$  14 mm  $\times$  8 mm) and silicon wafers were used as adsorption substrates and were treated as follows. The slides and wafers were sonicated in a 98% H<sub>2</sub>SO<sub>4</sub>/30% H<sub>2</sub>O<sub>2</sub> solution (piranha solution) for 1 h and then sonicated in a H<sub>2</sub>O/H<sub>2</sub>O<sub>2</sub>/NH<sub>4</sub>OH (5:1:1) solution for 1 h followed with a thorough rinse and then dried with an air stream. A freshly treated quartz slide was first dipped in the polycation solution for 10 min. The slide was rinsed with Milli-Q water and blown dry with an air stream, and then the slide was dipped in the polyanion solution for 10 min and thoroughly rinsed with the same solvent as the polyanion solution 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 monolayer (polycation or polyanion layer) was formed. To monitor the thickness of the multilayers formed, the silicon wafers were dipped and washed under the same condition. The thickness of the multilayer films formed on the silicon wafers was measured by ellipsometry.

DMF solutions of both azo polyelectrolytes were spin-coated onto glass slides to form good optical quality thin films used as a control. The thickness of the spin-coated films of PBANT-AC and PBACT-AC was about 100 nm.

Photoinduced Anisotropy and SRGs. Photoinduced anisotropy of the polyelectrolyte films (both as multilayers and spin-coated films) was investigated by using a polarized Ar<sup>+</sup> laser beam at 488 nm with an intensity of 150 mW/cm<sup>2</sup> as the writing beam. The optically induced dichroism was measured by using polarized UV–vis spectroscopy. The experimental setup for the surface relief grating formation was similar to that reported in the literature.<sup>8,9</sup> A linearly polarized laser beam at 488 nm from an Ar<sup>+</sup> laser was used as recording light source. The p-polarized laser beam was expanded and collimated. Half of the collimated beam was incident upon the film directly. The other half of the beam was reflected onto the film from a mirror. The intensity of the recording beam was about 150 mW/cm<sup>2</sup>. The diffraction efficiency of the first-order diffracted beam from the gratings in transmission mode was probed with an unpolarized low power He–Ne laser beam at 633 nm.

## **Results and Discussion**

Synthesis and Characterization of Azo Polyelectrolytes. The synthetic route of the azo polyelectrolytes is shown in Scheme 1. *N*-Ethyl-*N*-(2-chloroethyl)aniline (ECA) was prepared by chloridizing *N*-ethyl-*N*-hydroxyethylaniline with phosphorus oxychloride (POCl<sub>3</sub>). 3,5-Bis[2-(*N*-ethylanilino)ethoxy]benzyl alcohol (EEBA) was prepared by the Williamson ether synthesis of 3,5dihydroxybenzyl alcohol with ECA in anhydrous DMSO using K<sub>2</sub>CO<sub>3</sub> and KI as HCl absorbent and catalyst, respectively. The chemical structure of both compounds was verified by the characterization of elemental analyses, IR, and <sup>1</sup>H NMR spectroscopy.

Poly(acryloyl chloride) (PAC) was prepared by the radical polymerization of acryloyl chloride.<sup>32</sup> As it was difficult to measure the molecular weight and its distribution of PAC directly due to the high reactivity of acyl chloride groups, a GPC measurement was carried out on a poly(methyl acrylate) sample that was prepared by the reaction between the synthesized PAC and excessive methanol.<sup>48</sup> The number-average molecular weight of the PAC estimated by the result of the poly-(methyl acrylate) sample was 53 200 with a polydispersity index of 1.3.

PAC was reacted with EEBA to give the precursor polymer PBA-AC through the Schotten–Baumann reaction with triethylamine as the HCl absorbent.<sup>32</sup> The chemical structure and purity of the product were confirmed by spectroscopic analyses. The <sup>1</sup>H NMR spectrum of PBA-AC is given in Figure 1. The chemical shift of methylene protons next to the hydroxyl groups of EEBA shifts from 4.58 to 4.90 ppm, which indicates the formation of the ester linkages. The other proton resonances corresponding to the branched groups tethered to the polymeric chains appear at nearly the same positions except that the peaks become broad. The board and overlapped peaks (in the  $\delta$  1–2.5 ppm range) corresponding to main-chain protons demonstrate a random copolymerization sequence and atactic configuration. The degree of functionalization (DF) is defined as the percentage of the structure units bearing ester linkages among the total number of the structure units after postfunctionalization. In this study, the DF of PBA-AC was 17% estimated from the elemental analysis

The azo polyelectrolytes were prepared by postpolymerization azo coupling reactions between PBA-AC and the diazonium salts of *p*-nitroaniline and 4-aminobenzoic acid, respectively. In the reactions, the feed ratios of the diazonium salts to PBA-AC were determined according to the DF mentioned above to guarantee the anilino moieties to be reacted completely. The chemical structure and purity of the products were confirmed by





 Table 1. Glass Transition Temperature (Tg) of PBA-AC,

 PBANT-AC, and PBACT-AC

polymer	PBA-AC	PBANT-AC	PBACT-AC
<i>T</i> <sub>g</sub> (°C)	112	139	159

elemental analyses, IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopy. The <sup>1</sup>H NMR spectra of PBANT-AC and PBACT-AC with the assignments are compared with that of PBA-AC in Figure 1. For precursor polymer PBA-AC, the chemical shifts of unreacted anilino moieties appear at about 7.14, 6.70, and 6.55 ppm, attributed to the protons at meta, ortho, and para positions of the amino groups, respectively. After azo coupling reaction, the 6.55 ppm resonance corresponding to protons at the para positions of the amino groups in the anilino moieties almost disappear, which indicates that the substitutions have taken place at the para positions with a high yield. Further, the chemical shifts of protons ortho and meta to the amino groups shift to lower magnetic field as the result of the introduction of the electron-withdrawing groups and the increase of the conjugation length. Additional resonances corresponding to chemical shifts of the introduced benzene ring protons can also be observed. When a slight excess of diazonium salts (molar ratio to anilino moieties of the precursor polymers) was used in the reactions, the resonances corresponding to unreacted anilino moieties totally disappeared from the <sup>1</sup>H NMR spectra of the final products. As the DF of PBA-AC was 17%, the molar ratios of azobenzene chromophores to the repeated units were estimated to be 34% both for PBANT-AC and PBACT-AC.

The glass transition temperatures ( $T_{\rm g}$ s) of PBA-AC, PBANT-AC, and PBACT-AC were determined by differential scanning calorimetry (DSC) and are listed in Table 1. The  $T_{\rm g}$ s of the azo polyelectrolytes PBANT-AC and PBACT-AC are considerably higher than the precursor polymer PBA-AC, which is a result of the significant increase of the dipole moment of the side groups. PBACT-AC exhibits a significantly higher  $T_{\rm g}$  than that of PBANT-AC (with a 20 °C difference), which can be attributed to the hydrogen bonds of carboxyl groups on the azobenzene groups of PBACT-AC.

**H-Aggregation in Solutions.** Polyelectrolyte PBACT-AC bearing ionizable COOH groups on the azo chromophores exhibited high solubility in deionized water. On the contrary, PBANT-AC could hardly be dissolved in deionized water under similar conditions due to the hydrophobicity of the azo chromophores. Both polyelectrolytes could be well dissolved in a series of DMF $-H_2O$  mixed solvents with different DMF to  $H_2O$  ratios. However, it will be shown that the aggregate states of azo chromophores in the solutions were found to be different.

Figure 2a shows the UV-vis spectra of PBANT-AC dissolved in anhydrous DMF and a series of DMF-H<sub>2</sub>O solvents. The maximum absorbance of PBANT-AC in DMF appears at 488 nm, which is related to the  $\pi$ - $\pi$ \* transition of the trans isomers of the azobenzene units. By decreasing the ratio of DMF to  $H_2O$  (v:v), the maximum absorbance blue-shifts first gradually and then drastically. The maximum absorbance appears at 481 nm when the ratio is 4:1 and drastically blue-shifts about 70 to 415 nm when the ratio is 2:1. The hypsochromic shift is a typical spectral characteristic of the card-packed H-aggregates formed by the azobenzene chromophores in solutions.<sup>42–44</sup> According to the exciton model advanced by Kasha, the spectral changes is due to a splitting of the excited state, in which a transition to the higher excited-state level is allowed while to lower energy level is forbidden.<sup>45,46</sup> The above observation demonstrates that the azo chromophores of PBANT-AC exist predominately in the "isolated" state in the anhydrous DMF solution and transform into H-aggregates with the increase of water content in the solutions.

For PBACT-AC solutions, the H-aggregation of the azo chromophores in the  $DMF-H_2O$  solutions was also studied by the UV-vis spectroscopy. Figure 2b shows some representative results. Although the maximum



Figure 1. <sup>1</sup>H NMR spectra of (a) PBA-AC, (b) PBANT-AC, and (c) PBACT-AC.

absorbance in the absorption spectra of PBACT-AC in the solutions also shows blue shifts associated with the H-aggregation of the azo chromophores in the solutions, the degree of H-aggregation and the ratio of DMF to H<sub>2</sub>O at which the spectra vary significantly are obviously different. The spectrum of PBANT-AC in a solution of DMF:H<sub>2</sub>O = 2:1 (v:v) mixed solvent is predominated by the H-band; on the contrary, there is only a slight blue shift of the maximum absorbance for PBACT-AC spectrum under the same conditions. By comparing the structural difference between PBACT-AC and PBANT-AC, it is believed that the ionizable carboxylic acid groups at the 4'-positions of the azobenzene units play an important role to enhance hydrophilicity of the azo chromophores and inhibit the chromophores parallel packing under the condition.

Sequentially Adsorbed Electrostatic Multilayers. Both PBANT-AC and PBACT-AC could form uniform multilayer films through an electrostatic layer-bylayer adsorption process by using dipping solutions of the polyelectrolytes in anhydrous DMF and in DMF–  $H_2O$  mixed solvents. During the process, anhydrous DMF or DMF– $H_2O$  mixed solvents with the same DMF to  $H_2O$  ratio were used to rinse the multilayers formed after the deposition of azo polyelectrolytes on the substrates (both quartz slides and silicon wafers). A



**Figure 2.** UV–vis spectra of (a) PBANT-AC and (b) PBACT-AC in solutions of anhydrous DMF and a series of DMF– $H_2O$  mixed solvents. The concentration of azo chromophore is 0.012 mmol/L for PBANT-AC and 0.015 mmol/L for PBACT-AC.

linear increase of the maximum absorbance with the increasing number of the bilayers was observed for these systems, which indicated that the multilayers on the substrates grew an equal amount after each dipping cycle.<sup>19,20</sup> We use the term "bilayer" in accordance with previous publications on this type of films, which means a pair of layers including one layer of polycation and one layer of polyanion formed after each deposition cvcle.<sup>24–26,29,40</sup> Although it has been reported that polyelectrolytes can be adsorbed onto multilayer films through an electrostatic adsorption in mixed solvents,<sup>29,37</sup> the result obtained in current work shows that the azo polyelectrolytes can also be self-assembled in a layer-by-layer manner by using a solution of a nonaqueous polar organic solvent such as anhydrous DMF. This process is favorable for the applications to a variety of functional polyelectrolytes with poor solubility in water.

Parts a and b of Figure 3 show UV–vis spectra of PBANT-AC/PDAC multilayer films with the increasing number of deposition cycles, using anhydrous DMF and a DMF–H<sub>2</sub>O mixed solvent (DMF:H<sub>2</sub>O = 2:1, v:v) as solvents for the dipping solutions, respectively. A significant blue shift of the maximum absorbance band can be seen for the latter, which indicates a high degree of H-aggregation existing in the multilayer films. Although a linear increase of the maximum absorbance can be observed as the number of bilayers increases for both the anhydrous DMF dipping solution and the DMF–H<sub>2</sub>O dipping solutions (Figure 4), the incremental absorbance for each bilayer is considerably dependent on the solvents. The solvent effect on multilayer formation is complicated. Lesser solvation of solution polymer



**Figure 3.** UV-vis spectra of PBANT-AC/PDAC multilayers changing with the deposition cycles for two types of dipping solutions: (a) PBANT-AC in anhydrous DMF; (b) PBANT-AC in a DMF-H<sub>2</sub>O solution (DMF:H<sub>2</sub>O = 2:1, v:v). The concentrations are 0.2 mg/mL for both.



**Figure 4.** Relationship between the maximum absorbance of the PBANT-AC/PDAC multilayers and the number of bilayers. Concentrations of the azo polyelectrolytes in the dipping solutions are all 0.2 mg/mL. The solvents of the dipping solutions are anhydrous DMF ( $\blacksquare$ ), DMF:H<sub>2</sub>O = 4:1 (v:v) ( $\blacklozenge$ ), and DMF:H<sub>2</sub>O = 2:1 (v:v) ( $\blacklozenge$ ).

segments would decrease intrapolymer segment repulsion, allowing more to accumulate at the surface.<sup>37</sup> Decreasing the dielectric constant enhances the electrostatic interaction between charges, which causes charges on polymer chain to repel each other and leads to chain expansion<sup>50</sup> and at the same time makes the solvation energy for the charged polyelectrolyte become less favorable and drives polymer to the interface.<sup>37</sup> For polyelectrolytes bearing chromophores such as azo dyes, the effect caused by changing solvent is even more complicated. As discussed in above section, it may result



**Figure 5.** Relationship between the maximum absorbance of the PBACT-AC/PDAC multilayers and the number of bilayers. Concentrations of the azo polyelectrolytes in the dipping solutions are all 0.2 mg/mL. The solvents of the dipping solutions are anhydrous DMF ( $\blacksquare$ ) and DMF:H<sub>2</sub>O = 2:1 (v:v) ( $\blacklozenge$ ).



**Figure 6.** Ellipsometric thickness vs the number of bilayers on silicon wafers prepared from different dipping solutions: PBANT-AC dissolved in a DMF-H<sub>2</sub>O mixed solvent (DMF: H<sub>2</sub>O = 2:1, v:v) ( $\blacklozenge$ ), PBANT-AC dissolved in anhydrous DMF ( $\blacksquare$ ), PBACT-AC dissolved in a DMF-H<sub>2</sub>O mixed solvent (DMF: H<sub>2</sub>O = 1:1, v:v) ( $\blacklozenge$ ), PBACT-AC dissolved in anhydrous DMF ( $\blacktriangle$ ). The concentrations of the polyelectrolytes in the solutions are all 0.2 mg/mL.

in a significant amount of the H-aggregation in the solutions, which will influence the multilayer formation and organization through interpolymeric association and intrapolymeric aggregation. This point cannot be overlooked for polyelectrolytes such as PBANT-AC, for which the H-aggregation degree is significantly dependent on the solvents. For the PBACT-AC/PDAC system, the incremental absorbance for each bilayer is also increased when changing the solvent of dipping solution from anhydrous DMF to DMF $-H_2O$  mixed solvents (Figure 5). However, by comparing with the PBANT-AC/PDAC system (Figure 4), the dependence on the solvent variation is considerably less significant for the PBACT-AC/PDAC system.

The thickness of the multilayers assembled on silicon wafers, measured by ellipsometry, also exhibits a linear increase with the number of adsorbed bilayers (Figure 6). The incremental rates are dependent on the solvents of dipping solutions, which suggests that the thickness of the bilayers containing the same azo polyelectrolyte can be significantly adjusted by the ratio of DMF to H<sub>2</sub>O. For PBANT-AC/PDAC multilayer formed by deposition in the DMF solution of PBANT-AC, the average thickness of each bilayer was measured to be 0.8 nm, which is similar to that reported for the multilayers of strong polyelectrolytes.<sup>39</sup> On the contrary, the averaged bilayer

Table 2. $\lambda_{max}$ of (a) PBANT-AC and (b) PBACT-AC in	
Solutions, as Multilayer Films and Spin-Coated Film	s

	$\lambda_{\max}$ (nm) (solution)	$\lambda_{ m max}$ (nm) (multilayer film) <sup>a</sup>	$\lambda_{\max}$ (nm) (spin-coated film) <sup>b</sup>
	PBANT-A	2	
DMF	488	468	470
$DMF:H_2O = 4:1$ (v:v)	481	458	
$DMF:H_2O = 3:1$ (v:v)	472	443	
$DMF:H_2O = 2.75:1$ (v:v)	465		
$DMF:H_2O = 2:1$ (v:v)	415	429	
	PBACT-AC	2	
DMF	438	436	425
$DMF:H_2O = 2:1$ (v:v)	433	434	
$DMF:H_2O = 1:1$ (v:v)	429	435	
$DMF:H_2O = 1:2$ (v:v)	424		
H <sub>2</sub> O	423		

<sup>*a*</sup> PBANT-AC/PDAC and PBACT-AC/PDAC multilayer films were prepared by using the dipping solutions with the same DMF to  $H_2O$  ratios as listed in the first column. <sup>*b*</sup> Spin-coated film was prepared by using DMF solution.

thickness of the multilayer obtained by deposition in the solution of PBANT-AC in DMF-H<sub>2</sub>O (v:v = 2:1) mixed solvent was about 4.2 nm, which is comparable with those of weak polyelectrolyte multilayer films formed in a low-pH solution.<sup>40,41</sup> The averaged bilayer thickness of PBACT-AC/PDAC formed from the DMF-H<sub>2</sub>O solution was also observed to be thicker than that of the multilayer film formed from the DMF solution of the azo polyelectrolytes. However, the difference of the thickness caused by the solvent variation is not so remarkable as those found in the PBANT-AC/PDAC system. Even though this disparity cannot only be attributed to the H-aggregation degree difference between both polyelectrolytes, by comparing with the effect of DMF/H<sub>2</sub>O ratio on the H-aggregation degree, it has reason to believe that the H-aggregation plays an important role in the process. When PBANT-AC was dissolved in DMF, a good solvent for azo chromophores, the polymeric chains with a very low H-aggregation extent would be expanded and form thinner layers after adsorption. On the contrary, when PBANT-AC was dissolved in a DMF-H<sub>2</sub>O mixture (v:v = 2:1), as mentioned above, a predominate amount of azo chromophores formed H-aggregates. The resultant interpolymeric association and intrapolymeric aggregation would result in conformation change in solution and cause the averaged bilayer thickness of PBANT-AC/ PDAC to increase significantly. In some ways, the effect is similar to that which causes the thickness variation of weak polyelectrolyte multilayer films through adjusting solution pH.40,41 For PBACT-AC, the solvent effect on the layer thickness was observed to be much less significant, as the H-aggregation degree was lower in this system.

 $\lambda_{max}$ s of the multilayers obtained from different dipping solutions are summarized in Table 2 in comparison with those of the corresponding solutions. For PBANT-AC, the  $\lambda_{max}$  of the DMF solution is 488 nm while the  $\lambda_{max}$  of the multilayer film formed from the DMF solution is 468 nm, which is similar to that of the spin-coated film of PBANT-AC (470 nm).  $\lambda_{max}$ s of the multilayers prepared by using the PBANT-AC solutions of DMF-H<sub>2</sub>O mixed solvents may appear at a much shorter wavelength compared with the  $\lambda_{max}$ s of PBANT-AC in the same solutions. For the case of DMF:H<sub>2</sub>O = 3:1 (v:v), a blue shift about 30 nm can be observed when PBANT-AC chains transfer from the solution to the



**Figure 7.** UV-vis spectra of the multilayers before and after PDAC layer deposition: (a) the PBANT-AC layers were adsorbed from a DMF dipping solution; (b) the PBANT-AC layers were adsorbed from a DMF-H<sub>2</sub>O dipping solution (DMF:H<sub>2</sub>O = 2:1, v:v). The concentrations are 0.2 mg/mL for both. The numbers on the figures are the sequential number of the layers.

multilayer film through the adsorption process. The absorption band shift of the solvatochromic effect caused by changing surrounding medium of the chromophores is much smeller than that.<sup>12</sup> Such large shift of the  $\lambda_{max}$ is obviously related with the H-aggregation of the azo chromophores. Therefore, the significant  $\lambda_{max}$  blue shifts of PBANT-AC, after transferred from the dipping solutions to the multilayer films, indicate that some azobenzene chromophores not forming H-aggregates in solution further aggregate during the adsorption of the PBANT-AC. When DMF:H<sub>2</sub>O reaches 2:1 (v:v), a red shift of 14 nm can be seen after forming multilayer. As in the case the H-aggregation degree in the solution was already predominantly high, electrostatic adsorption caused deaggregation to some extent. For PBACT-AC, the maximum absorbance of the multilayer formed from the DMF solution appears at 436 nm, which is similar to that of the DMF solution (438 nm). When compared with the corresponding solutions, no obvious blue shift can be seen for the multilayer films formed by deposition in the solutions of the DMF-H<sub>2</sub>O mixed solvents. A red shift of 6 nm can be observed for PBACT-AC in the case of DMF: $H_2O = 1:1$  (v:v).

To further investigate the solvent effect on the Haggregation, the UV-vis spectra of the multilayers after deposition in the PDAC water solutions were also measured in each dipping cycle to compare with those measured before the deposition. Figure 7 shows the difference between the two groups of spectra. After the substrate covered by the multilayer had been dipped into the PDAC water solution, a reduction of the trans  $\pi - \pi^*$  band intensity at 468 nm and a hypsochromic shift of  $\lambda_{max}$  (from 468 to 458 nm) were noticed for the multilayers formed from the DMF dipping solution (Figure 7a). This can be ascribed to the formation of H-aggregates induced by the aqueous media, as it is know that hydrophobic azobenzene groups tend to form H-aggregates in aqueous media.<sup>42</sup> It can also be seen from the figure that the multilayers including more layers show more significant blue shifts. Meanwhile, the electrostatic interaction between the polycation (PDAC) and polyanion (PBANT-AC) was proved to be strong enough because no desorption was observed when the film was rinsed with DMF, and the thickness of the multilayer films kept increasing linearly after alternately dipped in the DMF solutions. When PBANT-AC multilayer films were formed by deposition in the solutions of the DMF-H<sub>2</sub>O mixed solvents with a relatively high degree of H-aggregation, no obvious spectral variation was observed after following deposition in the PDAC water solution. Figure 7b shows the UV-vis spectra of the PBANT-AC multilayer films formed from a solution of the DMF-H<sub>2</sub>O (v:v = 2:1) mixed solvent, which do not show an obvious difference before and after deposition in the PDAC water solution. As it can be seen from the spectra, in this case, the H-aggregation degree in the multilayer is predominately high. Therefore, no further H-aggregation can be induced by the aqueous medium.

The results demonstrate the different H-aggregation behavior of the two polyelectrolytes. For PBACT-AC, the H-aggregation degrees of azo chromophores in the dipping solutions are relatively low and do not show obvious variation when transferred from the dipping solutions to multilayer films and after dipped in the aqueous PDAC solutions. On the other hand, the Haggregation degrees of PBANT-AC in both solutions and multilayer films are sensitive to the solvents and can alter obviously during the adsorption process or even after dipped in the aqueous PDAC solutions.

The solvent effect can be further demonstrated by its influence on the surface morphology. It was observed that the surface roughness of the multilayer films also significantly depended on the composition of the dipping solutions in which azo polyelectrolytes were dissolved. The AFM images for the PBANT-AC/PDAC multilayers (20 bilayers) on quartz slides recorded in the tapping mode are given in a 3-D view (Figure 8a,b). As it can be seen from Figure 8a, the film surface of PBANT-AC/ PDAC obtained by deposition in the DMF solution of PBANT-AC is relatively smooth with a small-scale fluctuation on the surface. On the contrary, for the multilayer obtained by deposition in the DMF-H<sub>2</sub>O solution (DMF: $H_2O = 2:1$ , v:v) of PBANT-AC, the surface is rough and exhibits a "mount-and-valley" morphology.

Azo Chromophore Orientation in Multilayers. Orientation of the azobenzene chromophores in PBANT-AC/PDAC and PBACT-AC/PDAC multilayer films was estimated from the polarized UV–vis spectra obtained at a 45° incident angle. The ratio  $A_p/A_s$  was used to characterize the orientation, where  $A_p$  represents the maximum absorbance of the multilayer film for ppolarized light and  $A_s$  for s-polarized light.<sup>51,52</sup> p-Polarized light with the electric vector parallel to the plane of incidence is sensitive to the out-of-plane orientation, while s-polarized light with the electric



**Figure 8.** Tapping mode AFM images ( $2.0 \ \mu m \times 2.0 \ \mu m$ ) of the PBANT-AC/PDAC multilayer films on quartz slides ( $20 \ \text{bilayers}$ ), prepared by using dipping solutions with two different solvents: (a) anhydrous DMF, (b) DMF-H<sub>2</sub>O mixed solvent (DMF:H<sub>2</sub>O = 2:1, v:v).

Table 3.  $A_p/A_s$  Values of the Azobenzene Chromophores in PBANT-AC/PDAC and PBACT-AC/PDAC Multilayer Films<sup>a</sup>

multilayer films	solvents <sup>b</sup>	$A_{\rm p}/A_{\rm s}$
PBANT-AC/PDAC	DMF	0.77
	$DMF:H_2O = 4:1$ (v:v)	0.86
	$DMF:H_2O = 2:1$ (v:v)	0.95
PBACT-AC/PDAC	DMF	0.80
	$DMF:H_2O = 2:1$ (v:v)	0.89
	$DMF:H_2O = 1:1$ (v:v)	0.95

 $^{a}$   $A_{\rm p}$  is the maximum absorbance of the film for p-polarized light, and  $A_{\rm s}$  is the maximum absorbance of the film for s-polarized light.  $^{b}$  In which the azo polyelectrolytes were dissolved with concentrations of 0.2 mg/mL.

vector perpendicular to the plane of incidence is relatively inert to it.<sup>51</sup>  $A_p/A_s = 1$  represents an azimuthally isotropic orientational distribution of the azobenzene units, while  $A_p/A_s < 1$  or  $A_p/A_s > 1$  means that the azo chromophores tend to bear in-plane or out-of-plane orientation.<sup>52</sup> In Table 3, the ratios of  $A_p/A_s$  of some representative samples are listed. For PBANT-AC/ PDAC multilayer prepared by adsorbing in the DMF solution, the ratio  $A_p/A_s$  is 0.77 and indicates the tendency of chromophore in-plane orientation. While for the films formed by using DMF-H<sub>2</sub>O dipping solutions, the  $A_p/A_s$  ratio increases as the amount of H<sub>2</sub>O increases and reaches a value of 0.95 at DMF: $H_2O = 2:1$  (v:v), which shows isotropic chromophore orientation in the multilayer films. A similar tendency can be seen for the PBACT-AC/PDAC multilayers (Table 3).

**Comparison with Other Electrostatic Multilayer Films Containing Azo Chromophores.** To our knowledge, no directly comparable results have been published about the H-aggregate state in both solutions and multilayer films, chromophore orientation, and solvent effect for the polyelectrolytes with branched side chains bearing electron donor-acceptor type azobenzene chromophores. The most closely related results appeared in previous publications are the study on the azo amphiphile and ionenes.<sup>26,27,29,49</sup> It has been reported that the spacer length of the main-chain azobenezene ionenes and the chain length of the amphiphile influence the aggregate state of azobenzene in aqueous solutions.<sup>29,49</sup> The H-aggregate state of the azobenzene ionene in the electrostatic multilayer films is dependent on the charge densities of the counter-charged polyanions.<sup>26</sup> The Haggregation degree of the azobenzene bolaamphiphile in the electrostatic multilayer films is dramatically affected by the charge densities of the counter-charged polycations, in which poly(allylamine hydrochloride) (PAH) with a high concentration of charged groups causes a significantly higher degree of the H-aggregation than PDAC.<sup>27</sup> The azobenzenes adopt a more tilted alignment in the direction to the surface with increasing the spacer length of main-chain azobenzene ionene.<sup>29</sup> The current study demonstrates that the aggregate state of the branched side-chain azo polyelectolytes in solutions considerably depends on the terminal substitutes on the azobenzenes and the type of solvent. Even the same polycation (PDAC) is used in the process, the H-aggregation degree of the azo polyelectrolytes in the multilayer films is closely related with the substitutes on the azobenzenes and can be significantly altered by changing the solvents of the dipping solutions. The orientation of the azobenzene chromophores in the multilayer films can also be adjusted by the variation of solvent for the dipping solutions. This understanding can be used to controllably alter the H-aggregation



**Figure 9.** UV-vis spectra of PBANT-AC/PDAC multilayer films (20 bilayers): curve a, perpendicular to the polarization direction of laser beam; curve b, parallel to the polarization direction of laser beam. The samples were prepared by using an anhydrous DMF dipping solution of PBANT-AC and measured after irradiation with linearly polarized Ar<sup>+</sup> laser beam for 20 min.

Table 4. Orientation Order Parameter (*S*) of the Azobenzene Chromophores in PBANT-AC/PDAC and PBACT-AC/PDAC Multilayer Films after Irradiation with a Polarized Ar<sup>+</sup> Laser Beam for 20 min

samples	S
PBANT-AC/PDAC multilayer film <sup>a</sup>	0.09
PBANT spin-coated film <sup>b</sup>	0.11
PBACT-AC/PDAC multilayer film <sup>a</sup>	0.03
PBACT spin-coated film <sup>b</sup>	0.09

<sup>*a*</sup> The azo polyelectrolytes were dissolved in anhydrous DMF as the dipping solutions with concentrations of 0.2 mg/mL. <sup>*b*</sup> Spincoated films with thickness about 100 nm were prepared by using DMF solutions.

degree, chromophore orientation, and even surface morphology of the azo polyelectrolyte multilayer films through adjusting polymeric architecture and solution conditions.

**Photoinduced Anisotropy and Surface Relief** Gratings. As the multilayer films prepared from the DMF dipping solutions had relatively smooth surfaces and showed little H-aggregation, the films were used for the photoresponsive tests. To study the photoinduced anisotropy, the self-assembled multilayer films were irradiated with linearly polarized Ar<sup>+</sup> laser beam at 488 nm. In-plane dichroism was induced in the film as indicated by the polarized UV-vis spectroscopy (Figure 9). The film was exposed to the laser beam for 20 min to guarantee that the photoinduced chromophore orientation had been saturated. Figure 9 shows that the absorbance in the direction of the polarization of the laser beam is smaller than that in the direction perpendicular to the polarization of the laser beam. From the dichroic ratio, an orientation order parameter of ca. 0.09 can be estimated.<sup>53</sup> The orientation order parameters induced by the linearly polarized light for different multilayer films and spin-coated films (as the control samples) are listed in Table 4. For PBANT-AC/PDAC multilayer, the photoinduced orientation order of the film is comparable with that of the spin-coated film, while for PBACT-AC/PDAC film the photoinduced orientation order is much less than that of the spin-coated film. It is believed that the decreased capability for the photoinduced orientation of PBACT-AC/PDAC multilayer film is related with the electrostatic interaction between the ionized carboxyl group (COO<sup>-</sup>) at the end



**Figure 10.** AFM image of the surface modulation: (a) a PBACT-AC/PDAC multilayer film (20 bilayers) prepared by deposition in an anhydrous DMF dipping solution; (b) a spin-coated 1  $\mu$ m thick film of PBACT-AC.

of azo chromophores and the cationic group in PDAC, which can inhibit the azo chromophores from free rotation.

Figure 10a shows an AFM image of the 20-bilayer PBACT-AC/PDAC multilayer film surface after exposing the sample to an interference pattern of Ar<sup>+</sup> laser beams at modest intensities (150 mW/cm<sup>2</sup>). Under similar conditions, surface modifications were also observed for the PBANT-AC/PDAC multilayer films. Figure 10b shows a typical surface-relief-grating (SRG) image for a spin-coated film of PBACT-AC with a modulation depth of 85 nm. The sinusoidally modulated surface structure on the azo polyelectrolyte film was observed after Ar<sup>+</sup> laser beam irradiation with the same intensity and irradiation time as the multilayer film. Compared with the AFM image of SRG on the spin-coated film of PBACT-AC, the surface modulation on the multilayer surface is relatively small and overlapped with the random structures on the surface. Photofabrication of SRGs has been extensively investigated for spin-coated azo polymer films.<sup>8–18</sup> The earlier attempt to fabricate SRGs on electrostatic layer-by-layer multilayer films of polyelectrolytes containing azo chromophores was not very successful.<sup>12</sup> Since the electrostatic attraction between layers exists in the multilayer films, the lightdriven mass transport process is much more difficult to be achieved.<sup>33,34</sup> Improved results have been presented for electrostatic multilayer films containing lowmolecular-weight azo dye and electrostatic multilayers obtained through layer-by-layer post-azo-coupling reaction.<sup>33,34</sup> Current result shows another improved example for direct photofabrication of SRGs on sequentially adsorbed multilayer films of azo polyelectrolytes. Even the quality of SRGs is still not as good as spincoated films, the electrostatic layer-by-layer self-assembly method can offer an easy way to control the thickness of thin film and a possible new route to explore the mechanism of SRG formation.

#### Conclusions

Two polyelectrolytes (PBANT-AC and PBACT-AC), functionalized with branched side chains bearing electron donor-acceptor type azobenzene chromophores, were synthesized and characterized by using spectroscopic methods and thermal analysis. H-aggregation extent of the azo chromophores of PBANT-AC and PBACT-AC in solutions of anhydrous DMF and DMF-H<sub>2</sub>O mixed solvents was related with the solvent composition and chromophore structure. Adjusting the ratio of DMF to H<sub>2</sub>O could considerably alter the H-aggregation degree of PBANT-AC. When the ratio reached 2:1, the absorption band was predominated by the absorption of the H-aggregates. The ionizable carboxylic acid groups on the azo chromophores of PBACT-AC hindered the azo chromophores from forming cardpacked H-aggregates, which caused a significantly lower H-aggregation degree than those observed for PBANT-AC under the same conditions.

Both azo polyelectrolytes could form uniform multilayer films through a layer-by-layer adsorption process by deposition in solutions of anhydrous DMF or DMF-H<sub>2</sub>O mixed solvents together with an alternate deposition in a PDAC aqueous solution. Although the thickness of the multilayer films all increased linearly with the dipping cycles, the incremental rates were found to be considerably dependent on the water content in the dipping solutions. The multilayer films of PBANT-AC/ PDAC formed from the DMF-H<sub>2</sub>O solutions showed significant azo chromophore H-aggregation. The Haggregate state of PBANT-AC in the multilayer films was closely related with the H-aggregation extent in the dipping solutions, which could be adjusted by the change of water content in the solutions. Except for a dipping solution with a high water content such as DMF:H<sub>2</sub>O = 2:1 (v:v), the H-aggregation was enhanced when the polyelectrolyte molecules were transferred from the dipping solutions to the multilayer films through adsorption process. For PBANT-AC/PDAC multilayers formed from a DMF solution, the H-aggregation was also be enhanced when the multilayer was dipped in the aqueous PDAC solution. For PBACT-AC, the Haggregation degrees of azo chromophores in the multilayer films were relatively low. No obvious variation was observed after the adsorption of PBACT-AC from aqueous dipping solutions or sequentially dipped in the aqueous PDAC solutions. The orientations of azo chromophores in the multilayer films and the surface roughness of the multilayer films of both polyelectrolytes were also related with the ratio of DMF to H<sub>2</sub>O in the dipping solutions of the azo polyelectrolytes. Birefringence and dichroism, optically induced under the irradiation of a polarized Ar<sup>+</sup> laser beam at 488 nm, were observed for the multilayer films of both polyelectrolytes. The resulting dichroism detected from UVvis spectra indicated that a significant chromophore orientation was photoinduced in the PBANT-AC/PDAC multilayer films formed from the DMF dipping solution, which is comparable with that of the spin-coated film

of the same azo polyelectrolyte. Optically induced surface modulation on the multilayer surfaces of both polyelectrolytes was observed upon exposure to an interference pattern of  $\mathrm{Ar}^+$  laser beam at modest intensities.

Results in this work show that it is possible to prepare photoresponsive multilayers with controllable thickness, organization, and required properties through a proper molecular design and by selecting suitable solution conditions. It is believed that the incorporation of donor-acceptor type azo chromophores into electrostatic multilayers through the controllable manner can finally extend the sequentially adsorbed technology to some new optical applications.

Acknowledgment. The financial support from the NSFC under Project 59925309 is gratefully acknowledged.

Supporting Information Available: <sup>13</sup>C NMR spectra of the precursor polymer PBA-AC and the azo polyelectrolytes PBANT-AC and PBACT-AC. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA035208U