Synthesis, Photoresponsive Behavior, and Self-Assembly of Poly(acrylic acid)-Based Azo Polyelectrolytes

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ABSTRACT: A series of novel azo polyelectrolytes have been synthesized based on an extremely reactive precursor polymer, poly(acryloyl chloride) (PAC), prepared from acryloyl chloride by radical polymerization. The precursor polymer was post-functionalized by the Schotten-Baumann reaction of PAC and several aromatic azo reactants containing hydroxyl end groups. The degrees of functionalization were controlled by selecting suitable feed ratios between the azo reactants and poly(acryloyl chloride) and the unreacted acyl chloride groups were hydrolyzed to obtain ionizable carboxyl groups. The products were characterized by elemental analysis, FT-IR, ^{1}H NMR and UV−vis spectroscopy. Irradiated by 365 nm UV light, azo polyelectrolytes PPAPE, PEAPE and PCAPE showed a significant photochromic effect. The contact angles of water on the surfaces of spin-coated films of PPAPE and PEAPE decreased evidently upon UV irradiation. The extent of the photoinduced contact angle changes depends on the type of the azo chromophores and the degree of functionalization. Self-assembled multilayers of the azo polyelectrolytes were fabricated by a layer-by-layer adsorption method. A significant photochromic effect from cis−trans isomerization of the azo chromophores was observed for the multilayers. The photoinduced contact angle changes of water on the self-assembled multilayers were also observed.

Introduction

Recently, azo polymers have attracted considerable attention due to their potential uses in various optical applications.[1−3] One of the most important and well-known properties of aromatic azo compounds is the photochemical trans−cis isomerization induced by UV or visible light.[4,5] The trans−cis isomerization of the azo chromophores tethered covalently to polymeric chains can trigger drastic surface and inner structure changes such as photochemically inducing phase transition of liquid crystalline polymers,[6,7] changing liquid crystal alignment on the surfaces of side chain azo polymers,[8,9] inducing birefringence and dichroism,[10,11] and producing surface relief gratings.[12,13] Many studies have shown that the photoresponsive properties depend on the molecular architecture such as chemical structure of backbone, types of azo chromophores, and positions to which azo chromophores are attached.[1−3] To fully understand the structure−property relationship, various types of azo polymers have been synthesized, and their photoresponsive behavior has been studied.[13−19]

In contrast to the extensive studies mentioned above, the synthesis and properties of azo polyelectrolytes have rarely been reported so far. Polyelectrolytes (PEL) have exhibited scientific interest and practical importance in many areas.[20,21] Properties of a PEL solution such as viscosity strongly depend on the ionic strength or pH of the aqueous medium. The incorporation of ionizable segments in polymers is a very attractive molecular design option to prepare stimuli-responsive materials, which can exhibit drastic property changes in response to infinitesimal environmental variations such as temperature or pH.[22,23] Polyelectrolytes are able to form PEL complexes with oppositely charged macroions, surfactants, or colloid particles.[20] The latest development by exploring this property is to produce self-assembled multilayers through an electrostatic layer-by-layer assembly from two or more oppositely charged polyion solutions.[24,25]

Lovrien et al., in pioneering work, reported a polyelectrolyte bearing covalently bound azo side chains prepared by copolymerization of acrylic acid with 4-acrylamidoazobenzene.[26] Viscosity increases were found for the polymer solutions upon light irradiation, due to the changed polarity of the azo chromophores after photoisomerization. Pieroni et al. modified several types of polypeptides such as poly(L-glutamic acid) and poly(L-lysine) by introducing various percentages of azo chromophores into the polyelectrolytes.[27−29] It was found that the isomerization of azo groups could induce reversible conformational changes of the polypeptides in aqueous solutions. For poly(L-glutamic acid), the conformation depends on the molar content of azobenzene as well as on the degree of ionization of the unmodified carboxyl groups.[27] Wang et al. synthesized a series of epoxy-based azo polyelectrolytes containing ionizable groups on the azo chromophores by post azo coupling reaction and studied the photoresponsive properties.[30]

Recently, the preparation of organic thin films and monolayers, controlling the microscopic architecture on the level of both the molecular structure and the organization of the molecules, has become a focus of scientific research. Several groups reported that the multilayers, prepared from azo polyelectrolytes by alternating polyelectrolyte deposition (ADP), exhibited large and stable second-order optical nonlinearity.[31−34] Self-assembled multilayers of an azobenzene bolaamphiphile and polycations have been prepared, and the photoisomerization of the multilayers has been studied.[35] The photochemical reactivity of the multilayers significantly depends on the type of polycations used in the systems. Alternate multilayer films of a cationic bipolar azo amphiphile and an anionic polyelectrolyte

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have been prepared by a layer-by-layer deposition method.[36] Optical dichroism was induced in the films upon linearly polarized UV irradiation. This dichroism can be reversibly erased and rewritten. In another study, a commercially available azo polyanion and two different polycations have been used to build up multilayers.[37] A significant influence of the polycations on the molecular orientation of the azobenzene groups in the films and on the photoisomerization kinetics has been reported. Azobenzene monolayers on silicon or quartz slides have been prepared by chemisorption or transferring a Langmuir–Blodgett monolayer film.[38–40] The irradiation of the films with light effected a decrease in the water contact angle. The macroscopic motion of liquids on a flat solid surface has been realized by photoirradiation of an azo monolayer covering the surface, which suggests applicability to microscale chemical process systems.[40] These results have demonstrated that the cis–trans isomerization rate and extent can be controlled by the self-assembled multilayer or monolayer structure; on the other hand, the isomerization itself will significantly influence the properties of the multilayers or monolayers. Many new functional materials will be expected from this knowledge base.

Despite the demonstrated interesting properties and possible applications, versatile methods to prepare azo polyelectrolytes and a general understanding of the structure–property relationship in solutions, spin-coated films, and self-assembled multilayers are still lacking. In this work, a feasible method has been developed to prepare azo polyelectrolytes. A series of azo polyelectrolytes were synthesized by the chemical modification of poly(acryloyl chloride) (PAC). The precursor polymer PAC was prepared by the radical polymerization of acryloyl chloride[41,42] and then functionalized by the Schotten–Baumann reaction with azo chromophores bearing hydroxyl groups. The degrees of functionalization of azo chromophores were controlled to be lower than ca. 60%, and then unreacted acyl chloride groups were hydrolyzed to obtain COOH groups. One of the azo polyelectrolytes (PCAPE) was designed to contain azo chromophores bearing hydrophilic COOH end groups to promote the water solubility of the polyelectrolyte. The carboxyl groups tethered to both main chain and azo chromophores can be ionized in a suitable pH range, making the polymer have good aqueous solubility. For the other polyelectrolytes, the azo chromophores introduced are hydrophobic. It is possible to realize different types of self-assemblies by smartly exploring the hydrophobic and hydrophilic balance in these systems.[43,44] Not only associating the photoresponsive properties of azo chromophores with specialties of polyelectrolytes but also possessing the photocontrollable hydrophobic and hydrophilic balance, these kinds of azo polyelectrolytes may have attractive potential applications. The synthesized azo polyelectrolytes, except PNAPE, were found to exhibit a significant photochromic effect and photoresponsive properties. Photoresponsive multilayers of the azo polyelectrolytes were fabricated through the layer-by-layer adsorption technique. In this article, the synthesis, characterization, photoresponsive behavior, and self-assembly of the azo polyelectrolytes are reported in detail.

Experimental Section

Characterization. Elemental analyses (EA) of C, H, and N were measured by the Heratus CHN-Rapid method. The IR spectra were determined using a Nicolet 560-IR FT-IR spectrometer by incorporating samples in KBr disks. The ^{1}H NMR spectra were obtained on a Varian Unity-200 (200 MHz) FT-NMR spectrometer. The UV–vis spectra of the samples were recorded by a HP-8452A UV–vis spectrometer or a Perkin-Elmer Lambda Bio-40 spectrometer. The molecular weights and their distributions of the polymers were determined by gel permeation chromatography (GPC) utilizing a Waters model 515 pump and a model 2410 differential refractometer with three styragel columns HT2, HT3, and HT4 connected in a serial fashion. THF was used as the eluent at a flow rate of 1.0 mL/min. Polystyrene standards with dispersity of 1.08–1.12 obtained from Waters were employed to calibrate the instrument.

Materials. 1,4-Dioxane was refluxed with sodium for 6 h and distilled. *N*,*N*-Dimethylformamide (DMF) was azeotropically distilled with benzene for dehydration and then distilled under vacuum. Dimethyl sulfoxide (DMSO) and petroleum ether (60–90 °C) were dehydrated by adding 5 Å molecular sieve. Poly(diallyldimethylammonium chloride) (PDAC) (MW 20 000–35 000, 20% solution) was purchased from Aldrich and used after dilution. Azo compounds 4-(4′-nitrophenylazo)phenol (NAP), 4-phenylazophenol (PAP), 4-(4′-ethoxyphenylazo)phenol (EAP), and 4-(4′-carboxyphenylazo)phenol (CAP) were synthesized by the azo coupling reaction.[5,45] Analytic results are given below.

NAP: Yield 70%; mp 219–221 °C. EA: C 58.45 (calcd 59.26), H 3.99 (calcd 3.70), N 16.80 (calcd 17.58). IR **(**KBr**)**: 3450 (OH, str), 1610, 1580, 1520 (Benz ring, str), 1510, 1340 (NO_2, str), 1280 (C–O, str) cm^{-1}. ^{1}H NMR **(**$CDCl_3$**)**: δ 8.37 (d, 2H), 7.95 (t, 4H), 6.98 (d, 2H).

PAP: Yield 90%; mp 154–157 °C. EA: C 72.92 (calcd 72.71), H 4.97 (calcd 5.08), N 14.44 (calcd 14.13). IR **(**KBr**)**: 3180 (OH, str), 1605, 1585, 1505 (Benz ring, str), 1240 (C–O, str) cm^{-1}. ^{1}H NMR **(**$CDCl_3$**)**: δ 7.88 (d, 4H), 7.48 (m, 3H), 6.95 (d, 2H).

EAP: Yield 81%; mp 122–128 °C. EA: C 68.84 (calcd 69.40), H 6.04 (calcd 5.82), N 11.46 (calcd 11.56). IR **(**KBr**)**: 3320 (OH, str), 2900–2970 (C–H, str), 1600, 1585, 1500 (Benz ring, str), 1260 (C–O, str) cm^{-1}. ^{1}H NMR **(**$CDCl_3$**)**: δ 7.84 (t, 4H), 6.92 (q, 4H), 4.10 (q, 2H), 1.44 (t, 3H).

CAP: Yield 91%. IR **(**KBr**)**: 3120 (broad), 1590, 1500, 1470 (Benz ring, str), 1680 (C=O, str), 1286, 1245 (C–O, str) cm^{-1}. ^{1}H NMR **(**DMSO**)**: δ 8.12 (d, 2H), 7.90 (t, 4H), 6.98 (d, 2H).

The azo compounds 2-[4-(4′-nitrophenylazo)phenoxy]ethanol (NAPE), 2-(4-phenylazophenoxy)ethanol (PAPE), 2-[4-(4′-ethoxyphenylazo)phenoxy]ethanol (EAPE), and 2-[4-(4′-carboxyphenylazo)phenoxy]ethanol (CAPE) were synthesized by using a procedure similar to that reported in the literature.[46–48] Analytic results are given below.

NAPE: Yield 56%; mp 177–183 °C. EA: C 58.53 (calcd 58.54), H 4.88 (calcd 4.56), N 14.58 (calcd 14.63). IR **(**KBr**)**: 3260 (OH, str), 2950 2900 (C–H, str), 1595, 1575, 1495 (Benz ring, str), 1510 1340 (NO_2, str), 1250 (C–O, str) cm^{-1}. ^{1}H NMR **(**$CDCl_3$**)**: δ 8.38 (d, 2H), 7.98 (m, 4H), 7.08 (d, 2H), 4.22 (t, 2H), 4.03 (t, 2H). UV–vis **(**1,4-dioxane**)**: λ_{max} 372 nm.

PAPE: Yield 65%; mp 100–103 °C. EA: C 69.50 (calcd 69.40), H 5.85 (calcd 5.82), N 11.86 (calcd 11.56). IR **(**KBr**)**: 3270 (OH, str), 2950 2900 (C–H, str), 1600, 1580, 1500 (Benz ring, str), 1250 (C–O, str) cm^{-1}. ^{1}H NMR **(**$CDCl_3$**)**: δ 7.91 (t, 3H), 7.50 (m, 4H), 7.04 (d, 2H), 4.18 (t, 2H), 4.03 (t, 2H). UV–vis **(**1,4-dioxane**)**: λ_{max} 346 nm.

EAPE: Yield 67%; mp 176–178 °C. EA: C 66.59 (calcd 67.12), H 6.15 (calcd 6.34), N 9.82 (calcd 9.78). IR **(**KBr**)**: 3480 (OH, str), 2800–3000 (C–H, str), 1600, 1580, 1500 (Benz ring, str), 1250 (C–O, str) cm^{-1}. ^{1}H NMR **(**$CDCl_3$**)**: δ 7.88 (d, 4H), 7.00 (m, 4H), 4.16 (t, 2H), 4.08 (m, 2H), 4.00 (t, 2H), 1.46 (t, 3H). UV–vis **(**1,4-dioxane**)**: λ_{max} 358 nm.

CAPE: Yield 52%; mp 255 °C. EA: C 62.94 (calcd 62.94), H 4.93 (calcd 4.94), N 9.88 (calcd 9.79). IR **(**KBr**)**: 3280 (broad), 1600, 1581, 1500 (Benz ring, str), 1683 (C=O, str), 1250, 1296 (C–O, str) cm^{-1}. ^{1}H NMR **(**DMSO**)**: δ 8.12 (d, 2H), 7.93 (t, 4H), 7.17 (d, 2H), 4.12 (t, 2H), 3.75 (t, 2H). UV–vis **(**water**)**: λ_{max} 350 nm.

All other reagents and solvents were used as received without further purification.

Poly(acryloyl chloride) (PAC). Acryloyl chloride (10 mL), dry 1,4-dioxane (10 mL), and AIBN (0.334 g) were added into a flask under N_2 protection. The flask was sealed and then heated in an oil bath (50 °C) for 14 h. The polymer was precipitated by adding petroleum ether (40 mL), collected by filtration, and washed twice with petroleum ether. The product was dried at 60 °C under vacuum for 48 h. GPC (using poly(methyl acrylate) prepared from the same batch of PAC and methanol):[49] M_n 28 000, M_w 52 000, MWD 1.9. IR **(**KBr**)**: 2950 (C−H, str), 1785 (C=O, str), 1445 (CH_2, def) cm^{-1}.

Poly{2-[4-(4′-nitrophenylazo)phenoxy]ethyl acrylate-*co*-acrylic acid} (PNAPE). PAC (0.3 g, 0.0033 mol), triethylamine (0.56 mL, 0.0040 mol), and NAPE (whose amount was determined by the required degree of functionalization) were dissolved in anhydrous DMF (33 mL). The mixture was stirred at room temperature for 12 h under N_2 protection. Then suitable amount of water was added into the mixture and stirred for 10 min. The product was precipitated from HCl water solution (0.01 mol/L), collected by filtration, washed several times with water, and dried under vacuum. The polymer was further purified by dissolving in THF and precipitated from petroleum ether, collected by filtration, and washed twice with petroleum ether. The final product was dried at 70 °C under vacuum for 24 h. IR **(**KBr**)**: 3480 (OH, str), 2870−2980 (C−H, str), 1740 (C=O, str), 1600 1520 1500 (Benz ring, str), 1250 (C−O, str) cm^{-1}. ^{1}H NMR **(**DMSO**)**: δ 8.28, 7.86, 7.08, 4.33, 2.26, 1.90, 1.56, 1.26. UV−vis **(**1,4-dioxane**)**: λ_{max} 368 nm.

Poly{2-[4-phenylazophenoxy]ethyl acrylate-*co*-acrylic acid} (PPAPE). Via a procedure similar to that described above for the synthesis of PNAPE, PPAPE was obtained from the reaction between PAC and PAPE. IR **(**KBr**)**: 3450 (OH, str), 2870−2980 (C−H, str), 1730 (C=O, str), 1600 1580 1500 (Benz ring, str), 1250 (C−O, str) cm^{-1}. ^{1}H NMR **(**DMSO**)**: δ 7.80, 7.47, 7.07, 4.34, 4.26, 2.26, 1.86, 1.60, 1.26. UV−vis **(**1,4-dioxane**)**: λ_{max} 344 nm.

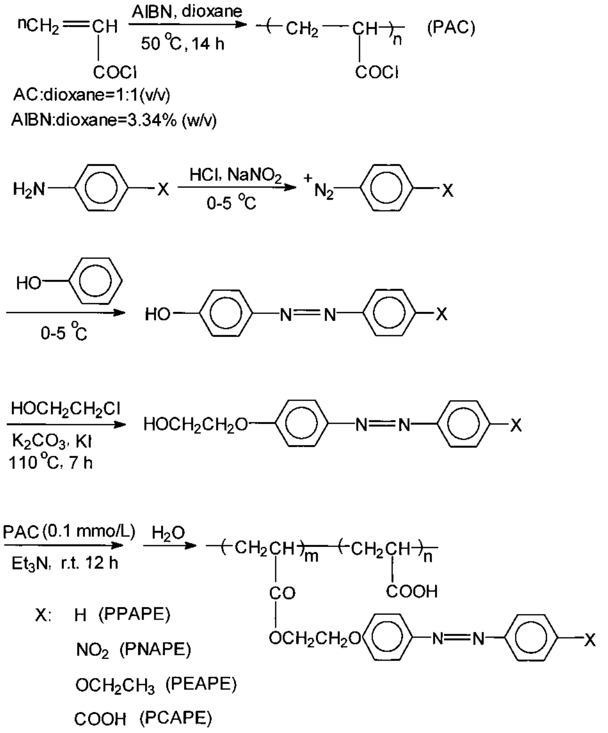
Poly{2-[4-(4′-ethoxyphenylazo)phenoxy]ethyl acrylate-*co*-acrylic acid} (PEAPE). Via a procedure similar to that described above for the synthesis of PNAPE, PEAPE was obtained from the reaction between PAC and EAPE. IR **(**KBr**)**: 3450 (OH, str), 2870−3000 (C−H, str), 1725 (C=O, str), 1600, 1580, 1500 (Benz ring, str), 1250 (C−O, str) cm^{-1}. ^{1}H NMR **(**DMSO**)**: δ 7.76, 7.02, 4.56, 4.33, 4.10, 2.28, 1.88, 1.60, 1.33. UV−vis **(**1,4-dioxane**)**: λ_{max} 358 nm.

Poly{2-[4-(4′-carboxyphenylazo)phenoxy]ethyl acrylate-*co*-acrylic acid} (PCAPE). Via a procedure similar to that described above for the synthesis of PNAPE, PCAPE was obtained from the reaction between PAC and CAPE. IR **(**KBr**)**: 1733 1697 cm^{-1} (C=O, str), 1600, 1500 cm^{-1} (Benz ring, str), 1250 cm^{-1} (C−O, str). ^{1}H NMR **(**DMSO**)**: δ 8.05, 7.83, 7.08, 4.32, 2.20, 1.80, 1.50, 1.30. UV−vis **(**water**)**: λ_{max} 350 nm.

Measurement of Photochromic Effect. The solutions of azo polyelectrolytes were prepared by dissolving the polyelectrolytes into aqueous solutions of NaOH (0.001 mol/L). The spin-coated polyelectrolyte films were prepared from solutions of the azo polyelectrolytes in DMF (40 g/L). The self-assembled multilayers were prepared through a layer-by-layer deposition process. The irradiating light was from a high-intensity 365 nm UV lamp equipped with 5 in. diameter filter (Cole-Parmer L-97600-05 long wave UV lamp, L-09819-23 filter). The intensity of the lamp was 7000 μW/cm^2 at a distance of 15 in. and 21 000 μW/cm^2 at a distance of 2 in. The samples were placed 10−15 cm away from the lamp. The surrounding temperature of the samples was controlled using a cold plate set to ca. 30 °C. The UV−vis spectra of the samples over different irradiation time intervals were measured by a HP-8452A spectrometer or a Perkin-Elmer Lambda Bio-40 spectrometer. For measuring the thermal cis-to-trans isomerization, the samples were kept in an oven in the dark with constant temperature 30 ± 1 °C, and the UV spectra were recorded over different time intervals.

Photoresponse of Contact Angle. Polyelectrolyte films were prepared by spin-coating or an electrostatic layer-by-layer self-assembly method. Before and immediately after irradiation by the UV light, the contact angles of water on the film surfaces were measured with the standard sessile drop technique by using a Dataphysics contact angle meter OCA-20. A water drop (2 μL) was made on the tip of a syringe and placed on a surface by moving the sample stage vertically until contact was made between the water drop and the surface. An image of the droplet was taken through a CCD camera and enlarged on computer screen. Contact angles were obtained by using the equipped software based on Young−Laplace fitting method. The contact angles reported in this paper are advancing contact angles. Experimental errors were estimated from the measurements on 10−14 droplets placed at different sample locations.

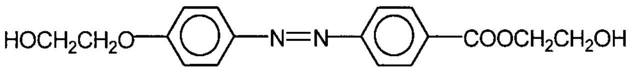
Scheme 1. Synthetic Route of the Azo Polyelectrolytes



Multilayer Fabrication. Poly(diallyldimethylammonium chloride) (PDAC) was used as polycation and was diluted to a 0.1 mmol/L concentration (repeat unit) with Milli-Q water (resistivity > 18 MΩ). The azo polyelectrolytes with various degrees of functionalization of the azo chromophores were used as polyanions and dissolved in the Milli-Q water with concentrations of 0.1 mmol/L (structural unit). A suitable amount of sodium hydrogen carbonate was added into the solutions to promote the solubility of the polymers. After completely dissolving, the pH values of the solutions were adjusted to be 6−7 by adding a few drops of HCl solution. Quartz slides (50 mm × 14 mm × 0.8 mm) were used as adsorption substrates and were treated as follows. The slides were sonicated in a 98% H_2SO_4/30% H_2O_2 solution (piranha solution) for 1 h and washed with excess Milli-Q water for several times and then sonicated in a $H_2O/H_2O_2/NH_4OH$ (5:1:1) solution for 1 h followed with a thorough rinse and dried with an air stream. A freshly treated quartz slide was alternately dipped in the PDAC solution and one of the azo polyanion aqueous solutions each for 10 min. After each dipping, the slide was washed with excess Milli-Q water for 2 min. The growth of azo polyanion/PDAC bilayers was monitored by an UV−vis spectrometer. The whole process was performed under room temperature.

Results and Discussion

Synthesis and Characterization of Azo Polyelectrolytes. The synthetic route of the azo polyelectrolytes is shown in Scheme 1. 4-(4′-Nitrophenylazo)phenol (NAP), 4-phenylazophenol (PAP), 4-(4′-ethoxyphenylazo)phenol (EAP), and 4-(4′-carboxyphenylazo)phenol (CAP) were prepared by the azo coupling reaction. The chemical structure of NAP, PAP, EAP, and CAP was verified by the characterization of elemental analyses, IR, and ^{1}H NMR spectroscopy. 2-[4-(4′-Nitrophenylazo)phenoxy]ethanol (NAPE), 2-[4-phenylazophenoxy]ethanol (PAPE), 2-[4-(4′-ethoxyphenylazo)phenoxy]ethanol (EAPE), and 2-[4-(4′-carboxyphenylazo)phenoxy]ethanol (CAPE) were prepared by the Williamson ether synthesis of NAP, PAP, EAP, and CAP with 2-chloroethanol in anhydrous DMSO. K_2CO_3 and KI were used as HCl absorbent and catalyst, respectively. From the reactions, NAPE, PAPE, and EAPE were obtained directly after purification, which was confirmed by the elemental analyses, IR, and ^{1}H NMR spectroscopy. However, under the same reaction conditions, the nucleophilic substitution reaction of CAP with 2-chloroethanol produced a compound with chemical structure as follows:



The structure was proved by elemental analysis, IR, and ^{1}H NMR spectroscopy. The stretching band of C=O in the IR spectrum appeared at 1712 cm^{-1} (ester) in contrast with 1680 cm^{-1} (carboxylic acid) for CAP. The resonances appearing at chemical shifts 3.8, 4.1, and 4.2 ppm showed two CH_2CH_2OH units in the molecule. Pure CAPE product was obtained by the hydrolysis in an aqueous solution catalyzed with sodium hydroxide and a small amount of ethanol.

Poly(acryloyl chloride) (PAC) was prepared by the radical polymerization of acryloyl chloride.[41,42] Solvent and precipitant used in the preparation were dehydrated carefully. The precipitation, washing, and drying were carried out under an anhydrous condition to protect poly(acyl chloride) from hydrolysis. Compared to the IR spectrum of acryloyl chloride, the disappearance of the 1610 cm^{-1} band (C=C stretching) in that of PAC confirmed the polymerization of acryloyl chloride and nonexistence of the monomer in the product. Since PAC is very reactive, it is difficult to directly measure molecular weight and its distribution. The measurement was carried out on a poly(methyl acrylate) sample that was prepared by the reaction between the synthesized PAC and excessive methanol.[49] The number-average molecular weight of the poly(methyl acrylate) sample determined by gel permeation chromatography (GPC) was 28 000 with a polydispersity index of 1.9.

The precursor PAC was postfunctionalized with NAPE, PAPE, EAPE, and CAPE to give polymeric intermediates, from which the azo polyelectrolytes were prepared by the hydrolysis of the unmodified acyl chloride groups. When pyridine was used as the HCl absorbent in the Schotten–Baumann reaction, the degrees of functionalization (DFs) of the azo chromophores of the obtained polyelectrolytes were very low (lower than 5%). In contrast, triethylamine as the acid absorbent was found to result in satisfied DFs. Pyridine is a weaker base compared with triethylamine and was proved to be less efficient as acid absorbent in the reactions. Unlike a small molecule reaction, the conversion of reactive groups attached to a polymeric chain is affected heavily by the conformation of the polymer. Therefore, the reaction mediums play an important role in a polymeric reaction. Dimethylformamide was found to be a good solvent which resulted in high degrees of functionalization due to its good solubility to PAC, the azo chromophores, and the polyelectrolytes. The chemical structure and purity of the final products were confirmed by ^{1}H NMR spectroscopy. The sharp and clearly separated proton resonances corresponding to low molecular weight azo reactants disappeared after the reactions, while those broad and overlapped resonances of azo chromophores bound to polymeric chains appeared at nearly the same positions. The ^{1}H NMR spectra of the azo polyelectrolytes verified that the azo chromophores were incorporated in the polymeric chains. The broad and overlapped peaks (in the δ 1–2.5 ppm range) corresponding to main-chain protons demonstrated random copolymerization sequence and atactic configuration. Comparing UV–vis spectra of the azo polyelectrolytes with the low molecular weight azobenzene reactants (Figure 1), the λ_{max} of the azo chromophores tethered to polymeric chains differs slightly from those of the corresponding azo compounds.

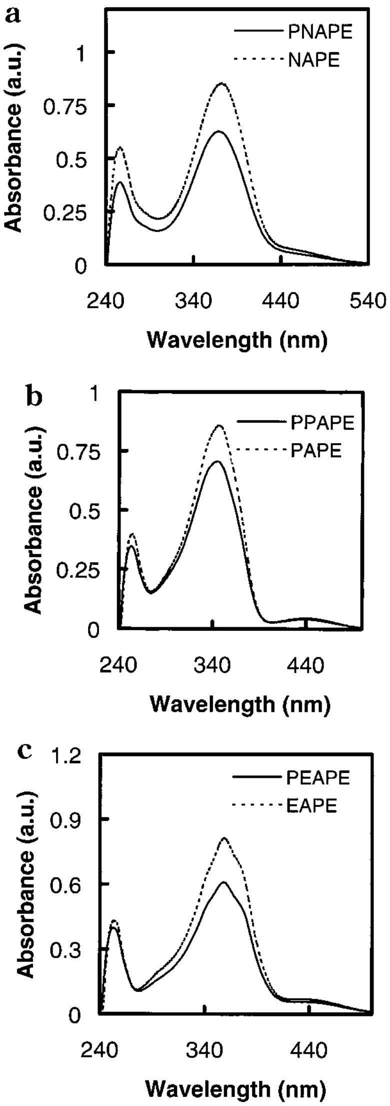


Figure 1. UV–vis spectra of the azo polyelectrolytes and the corresponding azo compounds in 1,4-dioxane solutions: (a) NAPE (0.0259 mmol/L) and PNAPE (0.228 mmol/L, DF = 10.3%), (b) PAPE (0.0258 mmol/L) and PPAPE (0.18 mmol/L, DF = 15.0%), (c) EAPE (0.0243 mmol/L) and PEAPE (0.207 mmol/L, DF = 11.8%). The concentrations for the polymers are the mole concentrations of the structural units.

Degree of Functionalization (DF). The determination and control of the DFs of the azo polyelectrolytes

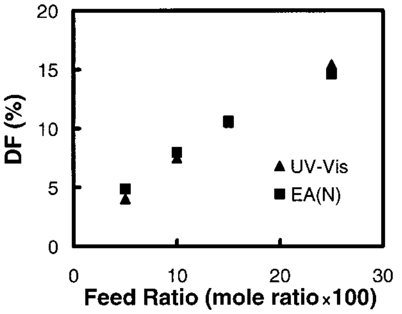


Figure 2. Relationship between the degree of functionalization of PEAPE and the feed ratio of EAPE to PAC. The reactions were carried out at room temperature for 12 h.

are crucial in this system, which is closely related to the water solubility and photoresponsive properties of the azo polyelectrolytes. An increase of DF was found to enhance the photoresponsive properties and to deteriorate the solubility of the azo polyelectrolytes in aqueous solution. Therefore, the control of DF was studied under the condition that the polymers could show significant photoresponsive properties and sufficient solubility in an aqueous solution.

In this study, the DFs of the azo polyelectrolytes were determined by UV−vis spectroscopy and elemental analysis. As the molar absorptivity ϵ ($\lambda_{\max}$) of the azo chromophores in the polyelectrolytes was assumed to be almost the same as that of the corresponding low-molecular-weight azo compounds, the DFs were calculated from absorption intensity at $\lambda_{\max}$, calibrated by working curves obtained from the low-molecular-weight azo compounds. The DFs were also estimated from the elemental contents (nitrogen/carbon) of the polyelectrolytes. The DFs calculated from UV−vis spectroscopy agreed with those from elemental analysis, which showed that both methods are effective to characterize the DFs of the azo polyelectrolytes.

The relationship between the DF of PEAPE and the feed ratio of EAPE to PAC is shown in Figure 2. The DF is linearly dependent on and slightly lower than the feed ratio of EAPE to PAC. Similar linear correlations were also observed in the reactions of PAC with other azo reactants. As a result, the DFs of azo chromophores of the polyelectrolytes can be easily adjusted by selecting suitable feed ratios. Although the acyl chloride groups of PAC are very reactive, the reaction with the azo reactants could not undergo a complete conversion. One possible reason is due to the steric hindrance between the polymeric chains and bulky azo reactants. Retaining certain percentages of acyl chloride groups on the main chain unreacted, which were hydrolyzed to produce carboxylic acid groups after the reactions, is necessary for PNAPE, PPAPE, and PEAPE to function as polyelectrolytes. The azo polyelectrolytes containing up to ca. 50% (DF) of the azo chromophores can maintain sufficient solubility in alkali water solutions.

Photoisomerization of Azo Polyelectrolytes. The photoisomerization of the azo polyelectrolytes in aqueous solutions 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 PPAPE aqueous solution varying with irradiation time are given in Figure 3a. Upon UV irradiation, the intensity of the $\pi-\pi^*$ transition band at 339 nm decreased and the intensity of the $n-\pi^*$ transition band at 430 nm increased gradually. The spectrum variations evidence the trans-to-cis isomerization of the azo chromophores.[4,5] Kept in the dark, the cis form slowly relaxed to the trans form, and the spectra gradually recovered to the original curve (Figure 3b). Similar spectrum variations upon UV irradiation and followed the recovery were also observed for PEAPE and PCAPE. Although the only difference among the four types of the azo polyelectrolytes is the substituents at 4′-positions of the azobenzene units, PPAPE, PEAPE, and PCAPE showed a significant photochromic effect in aqueous solutions while no obvious photochromic effect could be observed for PNAPE under the same conditions. The maximum intensities of $\pi-\pi^*$ transition bands for PPAPE and PEAPE aqueous solutions varying with the different irradiation time intervals are given in Figure 4a. The maximum absorbance A can be best fitted by the following first-order exponential decay function.

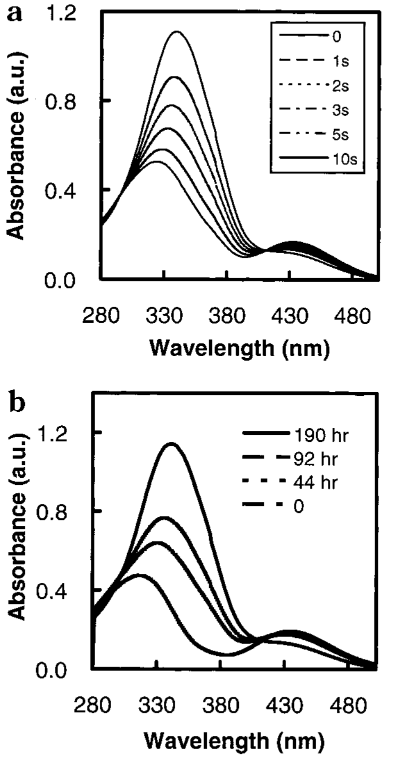


Figure 3. Variation of the UV−vis spectra of PPAPE aqueous solution (0.257 mmol/L, DF = 15.0%): (a) induced by UV light irradiation, (b) relaxed in the dark. The concentration for PPAPE is the mole concentration of the structural units.

$$A(t) = A_0 + A_1 \exp(-t/T_1) \tag{1}$$

The curve fits to the data are shown in the same figure (Figure 4a). The parameters obtained from the best fit are given in Table 1. It can be seen that the rates of photoisomerization obviously depend on the substituents at 4′-positions of the azo chromophores.

To study the thermal cis-to-trans isomerization more quantitatively, the samples were left in the dark with constant temperature, and the UV spectra were recorded over different time intervals. Under this condition, the rate of cis-to-trans isomerization was also observed to be dependent on the chemical structure of the azo chromophores. The absorption intensity of the azo polyelectrolytes in aqueous solutions at $\lambda_{\max}$ changing with recovery time is given in Figure 5. The

Table 1. Parameters of the Photoisomerization Kinetics Obtained from the Curve Fitting

	A_0	A_1	T_1 (s)	χ^2
aqueous solution				
PPAPE	$0.518 \pm 3 \times 10^{-3}$	$0.594 \pm 5 \times 10^{-3}$	2.3 ± 0.1	3.0×10^{-5}
PEAPE	$0.602 \pm 8 \times 10^{-3}$	0.64 ± 0.02	1.1 ± 0.1	2.5×10^{-4}
spin-coated films				
PPAPE	$0.343 \pm 2 \times 10^{-3}$	$0.319 \pm 3 \times 10^{-3}$	13.7 ± 0.3	1.0×10^{-5}
PEAPE	$0.402 \pm 5 \times 10^{-3}$	$0.475 \pm 7 \times 10^{-3}$	11.8 ± 0.5	8.0×10^{-5}

Table 2. Parameters of the Thermal Cis-To-trans Isomerization Kinetics Obtained Form the Curve Fitting

	A_0	A_1	T_1 (h)	χ^2
PEAPE	$0.133 \pm 1 \times 10^{-3}$	$-0.078 \pm 2 \times 10^{-3}$	6.06 ± 0.24	2.5×10^{-6}
PCAPE	$0.057 \pm 1 \times 10^{-3}$	$-0.036 \pm 1 \times 10^{-3}$	12.15 ± 0.83	8.1×10^{-7}
PPAPE	$0.170 \pm 2 \times 10^{-3}$	$-0.100 \pm 2 \times 10^{-3}$	19.53 ± 0.84	1.2×10^{-6}

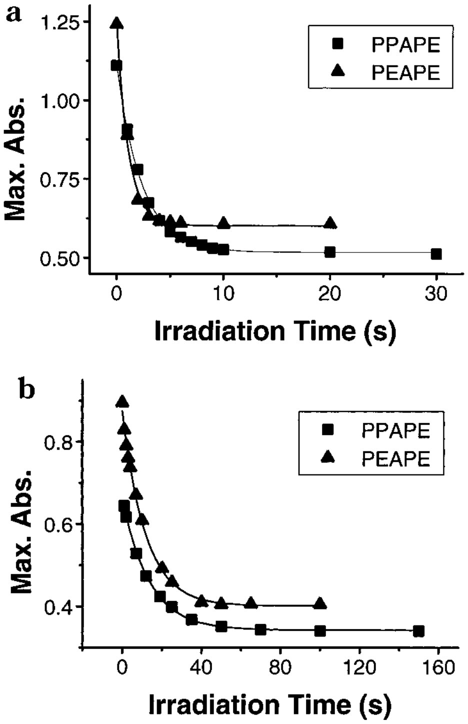


Figure 4. Maximum absorbance of the $\pi-\pi^*$ transition band of PEAPE and PPAPE recorded over different irradiation time intervals. The solid lines show the fitted curves. (a) Aqueous solutions, PPAPE (0.3 mmol/L, DF = 15.0%), PEAPE (0.4 mmol/L, DF = 10.1%); (b) spin-coated films. The concentrations for the polymers are the mole concentrations of the structural units.

maximum absorbance A for each polyelectrolyte can also be best fitted by the first-order exponential decay function (1) with a minus A_1. The fits to the data are shown in the same figure (Figure 5). The parameters obtained from the best fit are given in Table 2. The cis-to-trans isomerization of PEAPE, with ethoxy group at the 4′-position, reached equilibrium much faster than that for PPAPE. The time constant T_1 for PEAPE is 6.1 h in comparison with 19.5 h for PPAPE. The rate of the cis-to-trans isomerization for PCAPE is between PEAPE and PPAPE. From the results, it can be seen that the substitutents on 4′-positions have a significantly influence on the rates of both the photoisomerization and the thermal back-isomerization for the polyelectrolytes.

The rates of photoisomerization also depend on the local environments of the chromophores that change at different phases. The $\pi-\pi^*$ band maximum absorbance for PPAPE and PEAPE spin-coated films changing with the different irradiation time intervals is given in Figure 4b. The fits to the data are shown in the same figure,

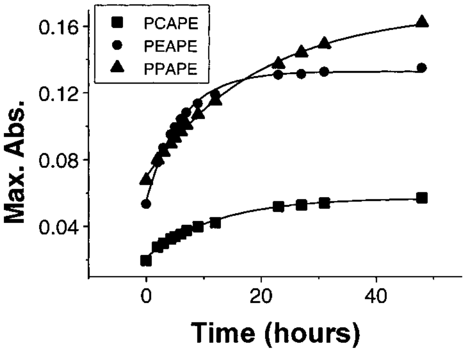


Figure 5. Cis-to-trans isomerization kinetics for PPAPE (0.07 mmol/L, DF = 15.0%), PCAPE (0.036 mmol/L, DF = 10.0%), and PEAPE (0.06 mmol/L, DF = 10.1%) aqueous solutions. The solid lines show the fitted curves. The concentrations for the polymers are the mole concentrations of the structural units.

and the parameters obtained form the best fit are given in Table 1. By comparing Figure 4a with Figure 4b, it can be concluded that the photoisomerization occurs much more slowly in spin-coated films than that in aqueous solutions. The cis-to-trans isomerization of the azo polyelectrolytes also occurs much more slowly in spin-coated films than in aqueous solutions. The time needed for complete recovery for PEAPE at the same temperature in a solid state and an aqueous solution is significantly different, 50 h for the spin-coated film and 24 h for the aqueous solution. A similar phenomenon was also observed for PPAPE, 310 h for the spin-coated film, and 180 h for the aqueous solution.

Surface Property of Azo Polyelectrolyte Films. In this work, the photoresponses of contact angles of water on the spin-coated film surfaces of the azo polyelectrolytes were studied. The photochromic study showed that the photoisomerization of the azo polyelectrolytes took less than 100 s to reach the photostationary states. The contact angles of water on the spin-coated films (θ_w) were measured after irradiation with exposure time of 3 min and compared with those of the unirradiated films at the same temperature and humidity. The hydrophobicity of the polyelectrolytes is related to the configuration and dipole moment of the azo chromophores that can be modified by the cis–trans isomerization. For azobenzene, the dipole moment was reported to change from 0 (trans) to 3 D (cis) after trans–cis isomerization.[1] The contact angles of three polyelectrolytes before and after UV irradiation are given in Table 3. PPAPE (DF = 50%) and PEAPE (DF = 48%) showed obvious photoinduced decreases in the contact angles, decreasing 5° and 8°, respectively, upon UV irradiation. In contrast, no contact angle

Table 3. Contact Angles of Water on the Spin-Coated Films of Three Polyelectrolytes before and after UV Light Irradiation within Experimental Error of ±2°

	PNAPE	PPAPE	PEAPE
DF (%)	51	50	48
θ_w before irradiation (deg)	75	78	85
θ_w after irradiation (deg)	75	73	77
$\Delta\theta_w$ (deg)	0	5	8

Table 4. θ_w of PEAPE Spin-Coated Films with Different DFs and the Photoinduced Changes of the Contact Angles within Experimental Error of ±2°

	PEAPE		
DF (%)	21	36	48
θ_w before irradiation (deg)	79	80	85
θ_w after irradiation (deg)	75	75	77
$\Delta\theta_w$ (deg)	4	5	8

change was observed for PNAPE (DF = 51%) in the same experimental condition, which is consistent with the result of the photochromic study mentioned above. The result for PNAPE also indicates that artifacts caused by the heating effects can be ruled out. To further confirm this point, as another control experiment we used spin-coated poly(methyl methacrylate) films and tested in exactly the same procedure, in this case no contact angle change was observed after UV irradiation. The changed contact angles of PPAPE and PEAPE could recover to original values (within experimental error of ±2°) under ambient laboratory conditions for less than 24 h. The azo chromophore of PEAPE has a rather symmetric structure, and its dipole moment can undergo a more significant change after the cis–trans isomerization; therefore, PEAPE exhibits a larger θ_w change than PPAPE after UV light irradiation.

The contact angle changes of the azo polyelectrolytes with different degrees of functionalization (DFs) were also studied. The θ_w of the PEAPE samples with different DFs and the photoinduced θ_w decreases are given in Table 4. The θ_w increases when DF increases due to the hydrophobic nature of the azo chromophores. After UV irradiation, all three azo polyelectrolytes with different DFs showed the contact angle decreases. The photoinduced decrease of θ_w is less significant at a low DF and more significant at a high DF. The θ_w decreases 4° for DF = 21% and 8° for DF = 48% after UV irradiation. It was reported that 2°–5° decreases in the water contact angles were observed for the 354 nm irradiation of the azobenzene-containing monolayers prepared by the chemisorption.[38] Ichimura and coworkers reported an 8° decrease in advancing water contact angle for a surface monolayer after the cis–trans isomerization.[40] The photoinduced contact angle changes obtained in this work are agreeable to these results. By the method developed in the work, it is easy to control the contact angles and the photoinduced changes through adjusting the DFs of the polyelectrolytes.

Self-Assembled Multilayers. The azo polyelectrolytes can be fabricated into uniform photoresponsive multilayer films through a layer-by-layer adsorption process in a wide range of pH values. The UV–vis spectra of PCAPE/PDAC multilayer films with increasing number of bilayers are shown in Figure 6a. A linear increase of the absorbance was observed as the number of the bilayer increased (Figure 6b), which maintained up to at least 40 bilayers. Similar linear relationships were also observed for PNAPE/PDAC, PPAPE/PDAC, and PEAPE/PDAC self-assembled multilayers. The linear increase of absorbance with the increasing number of the bilayers indicated that the multilayers on the substrates were growing in a layer-by-layer manner.[24,25] Due to the large molar absorptivity ϵ of the azo chromophores, the method is extremely sensitive to monitor the quality of the self-assembly process in this work. The atomic force microscopy (AFM) study indicated that the rough surfaces of the substrates became smooth after the multilayers formed on the surfaces. The significant differences between the surface morphologies verified that the multilayer films were uniformly formed on the surfaces, and the surface appearances of the substrates were modified due to this process.

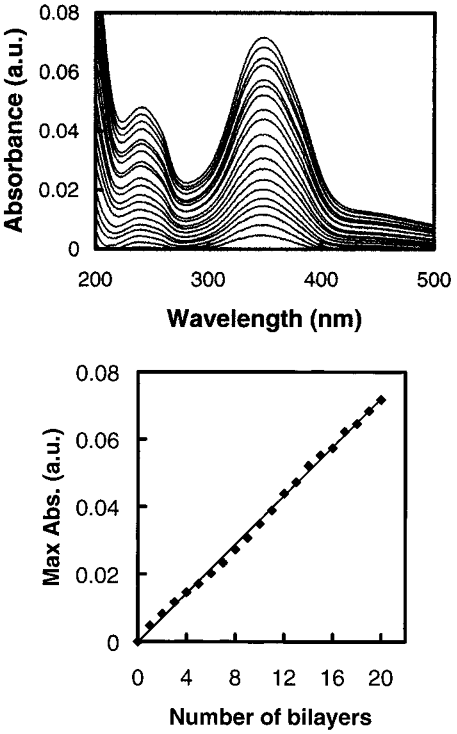


Figure 6. (a) UV–vis spectra of PCAPE(DF=33.6%)/PDAC multilayers changing with the number of bilayers. (b) The relationship between the maximum absorbance of the PCAPE/PDAC multilayers and the number of bilayers.

The multilayers of PCAPE/PDAC, PEAPE/PDAC, and PPAPE/PDAC were observed to be very sensitive to the UV light. The photoisomerization of a multilayer of PPAPE/PDAC with 15 bilayers is shown in Figure 7a. Upon irradiation of UV light, the azo chromophores in the multilayer can reach a trans–cis photobalance in about 120 s. The cis-to-trans isomerization monitored by UV–vis spectroscopy appeared to be slow (Figure 7b). The similar fast response and slow recovery phenomena were also observed for the multilayers of PEAPE/PDAC and PCAPE/PDAC. No significant photochromic effect was observed for PNAPE/PDAC multilayers, which is similar to the situations in aqueous solution and spin-coated films. The reason for lacking an obvious photochromic effect in PNAPE systems is still unclear to us at present stage. The absorption intensity of the PCAPE/PDAC multiplayer at λ_{max} over the different irradiation and recovery time intervals is given in Figure 8. The maximum absorbance A changing with the different irradiation or recovery time intervals can be best fitted by the first-order exponential decay function (1) with a plus or minus A_1. The fits to the data are shown in the same figures (Figure 8a,b). The parameters obtained from the best fit are given in Table 5. Because of the

Table 5. Parameters of the Isomerization Kinetics for PPAPE/PDAC Multilayer (DF = 15.0%, 15 Bilayers) Obtained from the Curve Fitting

	A_0	A_1	T_1	χ^2
trans-to-cis	$0.092 \pm 1 \times 10^{-3}$	$0.075 \pm 1 \times 10^{-3}$	4.3 ± 0.2 (s)	1.6×10^{-6}
cis-to-trans	$0.171 \pm 3 \times 10^{-3}$	$-0.102 \pm 2 \times 10^{-3}$	81 ± 5 (h)	1.8×10^{-6}

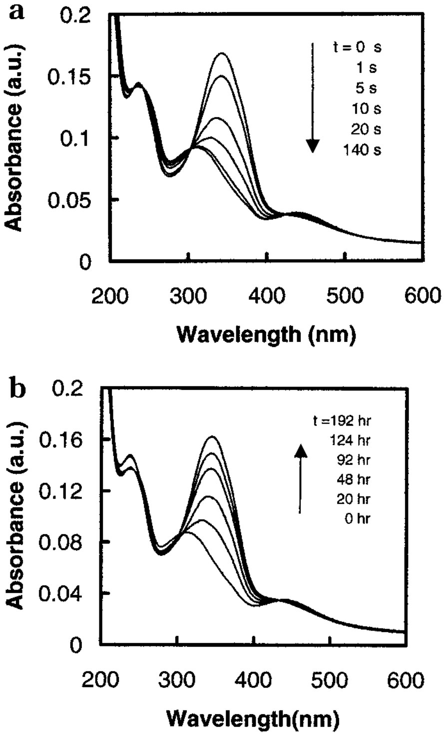


Figure 7. UV–vis spectra of PPAPE/PDAC multilayer (DF = 15.0%, 15 bilayers) recorded over different time intervals: (a) 365 nm UV light irradiation, (b) relaxed at 30 °C and the dark condition.

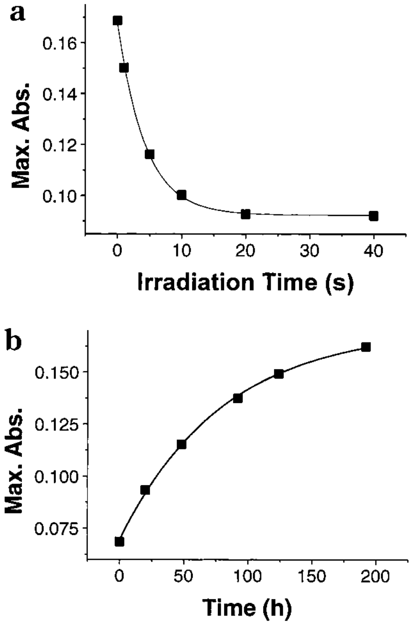


Figure 8. Maximum absorbance of the $\pi-\pi^*$ transition band of PPAPE/PDAC multilayer (DF = 15.0%, 15 bilayers) recorded over different irradiation time intervals. The solid lines show the fitted curves. (a) 365 nm UV light irradiation, (b) relaxed at 30 °C and the dark condition.

chromophore structure, the photoisomerization occurred much faster than that reported for polyion multilayers.[37] The photoisomerization rate is comparable with the self-assembled multilayers prepared from 4,4′-di(6-sulfatohexyloxy)azobenzene and PDAC.[35]

To further study the photoinduced changes, the water contact angles on the PEAPE/PDAC multilayer films before and after UV irradiation were measured. For a 10-bilayer PEAPE/PDAC multilayer prepared with the PEAPE (DF = 48) layer as the outmost layer, the contact angles before and after UV irradiation for 3 min were 67° and 58° with experimental error ±2°. The contact angles for the multilayer are less than the spin-coated films of the same polymers due to the reported layer interpenetration in multilayer films.[43,44] For self-assembled multilayers and spin-coated films of PEAPE, the photoinduced decreases of θ_w are within the same range. It has been reported that the thickness and wettability of multilayers prepared from poly(acrylic acid) and poly(allylamine) can be controlled by adjusting conformation and layer architecture manner induced by the charge density change in the dipping solutions.[43,44] Therefore, the multilayers reported in this paper, possessing sensitive photoresponsive properties and controllable surface and inner structure, will be promising in optical applications as a new type of optical-switchable materials.

Summary

A series of poly(acrylic acid)-based azo polyelectrolytes with different types of azo chromophores and degrees of functionalization (DFs) have been synthesized and characterized in this work. The azo polyelectrolytes were synthesized through postfunctionalization of an extremely reactive precursor poly(acryloyl chloride). The degrees of functionalization were controlled by adjusting the feed ratios between azo reactants and poly(acryloyl chloride) in the postfunctionalization reactions. Uniform self-assembled multilayers were prepared through an electrostatic layer-by-layer dipping process. The azo polyelectrolytes PPAPE, PEAPE, and PCAPE in aqueous solutions, spin-coated films, and self-assembled multilayers showed an obvious photochromic effect upon 365 nm UV light irradiation. The isomerization rates depend on the azo chromophore structure and the local environments of the condensation states. Evident photoinduced decreases of the contact angles were observed on the surfaces of spin-coated films and self-assembled multilayers of PPAPE and PEAPE. The extent of the contact angle changes was observed to be dependent on the type and the DF of the azo chromophores. Possessing both the good self-assembling ability and photoresponsive properties will enable the azo polyelectrolytes to exhibit unique optical functionalities through the way of ultrathin multilayers.

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Supporting Information Available: ^{1}H NMR spectra of azo polyelectrolytes and corresponding azo compounds: (a) NAP, NAPE, and PNAPE; (b) PAP, PAPE, and PPAPE; (c) EAP, EAPE, and PEAPE; atomic force microscopy (AFM) images of the substrate and multilayer film: (a) quartz slide surface and (b) PEAPE/PDAC multilayer (DF = 11.8%, 30 bilayers). This material is available free of charge via the Internet at http://pubs.acs.org.

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