Photosensitive Azopolymer Brushes via Atom Transfer Radical Polymerization for Protein Sensing

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Novel photosensitive azopolymer brushes were synthesized via surface initiated atom transfer radical polymerization using initiator self-assembled on Au surface. The chemical structures of azobenzene derivatives were confirmed by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). The surface morphology of azopolymers via atom transfer radical polymerization (ATRP) for different time was investigated by atomic force microscopy (AFM). Additionally, the photoisomerization of azopolymer was measured by ultraviolet-visible spectroscopy (UV-Vis). The results indicate that such azopolymers can undergo *trans-cis-trans* photoisomerization efficiently by photo-irradiation with UV light. Furthermore, this photoisomerization property could also induce the reversible adsorption of bovine serum albumin (BSA) adsorption on azopolymer brush surfaces. This adsorption kinetics of the reversible process can be measured by surface plasmon resonance (SPR) spectroscopy *in situ*. It suggests that the protein biochips could be regenerated safely by UV irradiation rather than by being rinsed with chemical reagents.

Keywords azopolymer, photoisomerization, atom transfer radical polymerization (ATRP), adsorption, biosensor

Introduction

Polymer brushes, defined as dense layers of end-grafted polymer chains on a solid surface, provide fascinating classes of flexible surfaces with various functionalities. Therefore, it is employed in bio-related areas, such as three-dimensional micro- and nanomemory chips, DNA- and protein-based biochips and biosensors.[1-3] In addition, it is very important to control the surface properties in the production of bio-related materials that can be used in biomedical and diagnostic applications. The introduction of light responsive properties of azobenzene into the surface-graft chains seems to be of great interest in the fabrication of "smart" surfaces. As known, azobenzene derivatives are well-known for their reversible *trans-cis* isomerization upon light irradiation.[4-6]

On the basis of the photoisomerization, polymeric thin films containing azobenzene chromophores exhibit diverse photoresponsive properties, such as dipole moment, wetting, molecule size and surface energy.[7,8] There are many methods to obtain the responsive azobenzene layer, such as self-assembly,[9,10] Langmuir-Blodgett (LB),[11] Layer-by-Layer (LBL),[12] and so on. Atom Transfer Radical Polymerization (ATRP) is a recently developed "living" or "controlled" radical polymerization method.[13,14] It is possible to prepare well defined polymer brushes on various substrates via surface-initiated ATRP.[15,16] Consequently, the obvious advantage of surface-initiated ATRP over other techniques is that the surface density of the polymer chains is so high that the polymer chains are forced to stretch along the direction normal to the graft surface.[17,18]

There is an important agreement that small chemical or physical changes in the sensing environment trigger macroscopically observable changes in material properties. Thereby the polymer brush containing responsive azobenzene moieties on surface that undergo molecular level changes, in turn, must translate into macroscopic responses.[19] Therefore, this signal amplification effect of azobenzene derivate can be employed for biomolecules detection. In the present work, the photoresponsive azopolymer brush on Au surface was designed via surface-initiated ATRP for the reversible bovine serum albumin (BSA) adsorption. The potential of this technique lies in its versatility and simplicity, with expected applications in the protein chips or biomolecules immobilization and macromolecular-scale fabrications.

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Received August 10, 2010; revised and accepted November 9, 2010.
Project supported by Program for New Century Excellent Talents in University of Henan Province (No. 2006HNC019) and International Cooperation Project of Henan Province (No. 104300510070).

Experimental

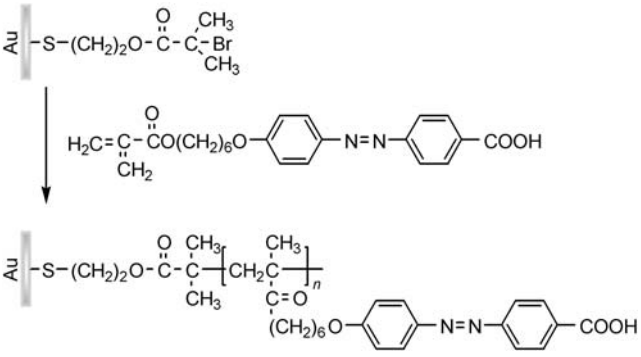
Regents and materials

Au substrates (2 nm chrome followed by 50 nm gold on float glass) were purchased from the Institute of Electronics, Chinese Academy of Sciences. Tetrahydrofuran (THF) was refluxed over sodium and distilled. Dimethylformamide was purified by vacuum distillation before used. Methacryloyl chloride, 6-chloro-1-hexanol, 2,2'-dipyridyl, phenol, and anisole were purchased from Aladdin-reagent, Shanghai, China. Potassium hydroxide (KOH), sodium nitrite ($NaNO_2$), sodium hydroxide (NaOH), anhydrous ethanol, cuprous chloride (CuCl), chloroform ($CHCl_3$), methol, and other chemicals were used as received from Sinopharm Chemical Reagent Co., Ltd., China. The other chemicals were used without further purification.

Synthesis of monomers and polymer

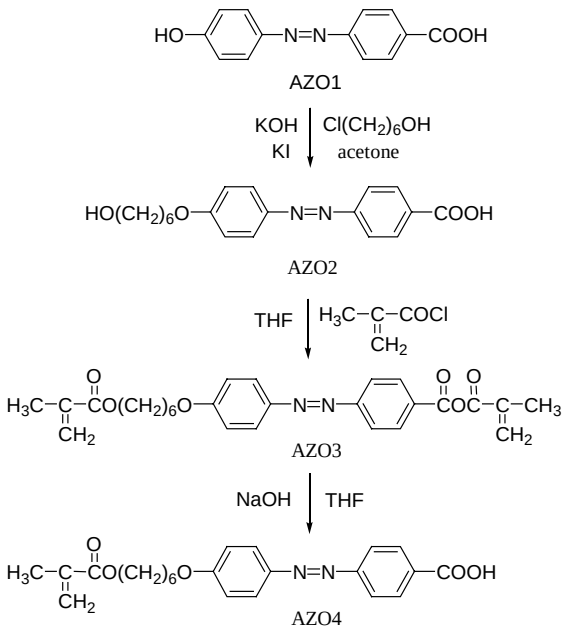
Schematic of experiment routes The initiator of $HS\text{-}(CH_2)_2OOCC(CH_3)_2Br$ was self-assembled onto Au surfaces by immersing the slides into the initiator solution (20 mL ethanol of initiator, 2 mmol•L^{-1}) at room temperature for 24 h. The modified substrates were rinsed thoroughly with THF and ethanol, followed by being dried in dry nitrogen stream and used for polymerization immediately. The whole routes were expressed in Scheme 1. And the synthesis route was summarized in Scheme 2.[21-23]

Scheme 1 Schematic of the whole experiment routes



Synthesis of the initiator, mercaptomethyl 2-bromo-2-methylpropanoate[20] BSA was purchased from Shanghai Biolife Science & Technology Co., Ltd., with a molecular weight of 67000. Bromoisobutyryl bromide (3.34 mmol, 0.41 mL) diluted by THF (5 mL) was added dropwise to a stirred solution of 2-mercaptoethanol (3.67 mmol, 0.48 mL) and pyridine (3.34 mmol, 0.27 mL) in dry dichloromethane (30 mL) at 0 ℃. The reaction was stirred at 0 ℃ for 1 h and then at room temperature for 16 h. Then the mixed solutions were poured into 100 mL of water. And the product was extracted with toluene, which was removed under reduced pressure. The extract was dissolved again in ether, washed with saturated sodium chloride and dried over Na_2SO_4. Volatiles were evaporated under reduced pressure. Finally, the product was purified by column chromatography (Al_2O_3, hexane) and distilled to give the product as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.5 (SH), 1.57—1.68 (m, 4H, CH_2), 2.02 (s, 6H, CH_3), 2.84 (2H, SCH_2), 3.96, 4.14 (2H, CH_2OCH_2).

Scheme 2 Synthesis routes of the azopolymer



4-[(4'-Hydroxyphenyl)diazenyl] benzoic acid (AZO1) 4-Aminobenzoic acid (2.74 g, 0.02 mol) was dissolved in 10 mL of aqueous HCl and kept in the ice bath at ice/salt. $NaNO_2$ (1.5 g, 0.22 mol) in water (5 mL) was added dropwise and stirred for 30 min. NaOH (1.2 g, 0.03mol) and phenol (1.88 g, 0.02 mol) were dissolved in water (40 mL) at 0 ℃. The former solution was added and stirred for 2 h. The crude product was filtered and recrystallized twice by ethanol.

4-((4-((6-Hydroxyhexyl)oxy)phenyl)diazenyl)benzoic acid (AZO2) AZO1 (2.42 g, 0.01 mol) and KOH (1.2 g, 0.22 mol) were dissolved in ethanol (100 mL), 0.02 mol 6-chloro-1-hexanol and a trace of KI were then added, and the solution was heated at reflux for 24 h. The mixture was poured into water and extracted with $CHCl_3$. The crude product was filtered and recrystallized twice by ethanol.

4-((4-((6-Hydroxyhexyl)oxy)phenyl)diazenyl)benzoate (AZO3) AZO2 (0.342 g, 0.01 mol), TEA (0.03 mol), were dissolved in dry THF (20 mL) at 0 ℃ and then methacryloyl chloride (0.02 mol) dissolved in THF (5 mL) was added dropwise under vigorous stirring. The mixture was stirred for 14 h at room temperature. The crude product was washed several time with water and recrystallized twice from $CHCl_3$.

4-((4-((6-(Methacryloyloxy)hexyl)oxy)phenyl)diazenyl)benzoic acid (AZO4) The compound AZO4 was obtained by the hydrolysis of AZO3 in an aqueous solution catalyzed with sodium hydroxide and a small amount of ethanol. The yield was 92%, melting point

was 125 ℃. ^{1}H NMR ($CDCl_3$) δ: 11.0 (s, 1H, OH), 8.12 (d, J=8.9 Hz, 2H), 7.93 (d, J=7.5 Hz, 2H), 7.85 (d, J=9.6 Hz, 2H), 6.93 (d, J=7.5 Hz, 2H), 6.32 (s, 1H, HC=C), 5.73 (s, 1H, HC=C), 4.36 (t, 2H, CH_2OCO), 4.04 (t, 2H, CH_2O), 2.01 (s, 3H, CH_3), 1.33—1.38 (m, 4H); ^{13}C NMR (d_6-DMSO) δ: 167.5 (C=O), 131.6 (C=C), 126.3, 124.9, 123, 117 (benzene ring), 40.5 (O=CCH_2), 18.5 (CH_2).

ATRP of the AZO4 In a typical surface initiated ATRP reaction, a solution of AZO4 and SAMs Au substrate in anisole was degassed for 30 min to reduce the amount of O_2 present in the reaction system, followed by another 10 min degassing upon the addition of the catalyst mixture of CuCl, $CuCl_2$, and 2,2'-bipyridyl at 1∶0.3∶2.9 in weight ratio.

Preparation of PBS solutions and BSA solution

Solution A: 9.465 g of Na_2HPO_4•$12H_2O$ dissolved in 1000 mL of DI water; solution B: 9.07 g of KH_2PO_4 dissolved in 1000 mL of DI water. 2.0 mL of solutions A and 8.0 mL of B were mixed to produce PBS with pH 7.4. The protein solutions were prepared immediately before used by dispersing commercially available BSA in PBS at a concentration of 1 wt%.

Property characterization of azobenzene monomers and polymer

Fourier transform infrared spectroscopy (FTIR) spectra of pure PPy films were recorded with a Nicolet 5700 FTIR spectrometer (Thermmo Electron Corporation) using the KBr pellet method. The spectra were recorded from 4000 to 400 cm^{-1}, with a 4 cm^{-1} resolution for 32 scans. Ultraviolet-visible absorption spectra (UV-Vis) were taken with a UV-1800 spectrophotometer. The photoisomerization of azopolymer film is tested by UV absorption spectra. A series of UV absorption spectra is obtain via irradiation with 365 nm UV light for 5, 10, 15 , 20 and 30 s. Similarly, the different irradiation time of visible light is 10, 30, 60, 120 and 180 min. The wavelength domain in this UV measurement is 200—600 nm. Changes in the azopolymer surface morphology were probed by atomic force microscopy (AFM). The surface was observed by contact-mode AFM (Digital Instruments Nanoscope E) and a silicon nitrite cantilever (the typical tip radius of curvature is 15 nm, Nanoworld). In this experiment the experimental error in the contact angle (CA) measurements is ±2°. The deionized (DI) water was used as the test liquid for all measurements.

BSA adsorption onto azopolymer surfaces measured by surface plasmon resonance spectroscopy (SPR) *in situ*

A glass slide covered with gold film suitable for the SPR apparatus (SPR 2005, Electronic Institute of the Chinese Academy of Sciences) was pressed onto the base of a half-cylindrical lens (n=1.61) using an index-matching oil. Linearly p-polarized light of wavelength 670 nm from a diode laser was directed through a prism onto the gold film in the Kretshmann configuration. The intensity of the reflected light was measured as a function of the angle of incidence, θ, using a photodiode with a chopper/lock-in amplifier technique. The baseline of the SPR binding curve was obtained after injecting buffer, *i.e.*, 0.01 mol•L^{-1} PBS (pH=7.4) into the cuvette. Afterwards, the protein was injected into the flow cell and time resolved kinetic measurements of protein adsorption were performed. Once the optical properties of the interface were stable (*i.e.*, no more protein was adsorbed), the cell was rinsed with large amounts of PBS buffer to remove any loosely adhered protein. The last reflectivity scan was recorded. As for the experiment of the effect of the azopolymer photoisomerization on protein adsorption, each protein adsorption kinetic scan was conducted immediately after the azopolymer was irradiated by UV light in the black box of SPR equipment. All experiments were carried out at room temperature.

Results and discussion

FTIR spectra of azobenzene derivatives

FTIR spectra of AZO1, AZO2, AZO3 and AZO4 were summerized in Figure 1. Complete conversion of all reaction had been detected by IR-spectrum. As an example, the IR spectra of AZO1 polymer and AZO2 show that full conversion of this reaction could be observed due to the appearance of the methylene (-CH_2-) band at 2926 cm^{-1}. The profile of AZO3 shows the complete vanishing of the activated —COOH bands at 2664 and 2540 cm^{-1}, which means that the —COOH of AZO2 has changed into ester completely. While the profile of AZO4 shows an intense peak at 3400 cm^{-1} compared with the curve of AZO3, which tells us that the ester of AZO3 is in a hydrolysis progress. All of above discussed in the FTIR spectra could confirm the structure of azobenzene derivatives basically.

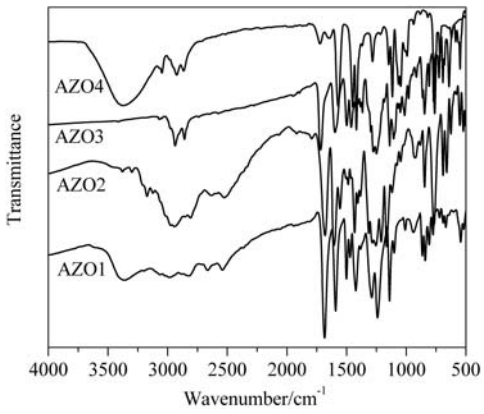


Figure 1 FT-IR spectra of AZO1, AZO2, AZO3 and AZO4.

UV-Vis absorption spectra of AZO4 (in THF solution)

The light-induced isomerization of azobenzene group of the AZO4 was investigated in 10^{-5} mol/L THF

solution. The *trans*-*cis* photoisomerization was achieved by irradiation with UV light of 365 nm and the backward isomerization of *cis*-from to *trans*-form was achieved by visible light of 450 nm. Figure 2a shows the UV absorbance changes of the AZO4 irradiated by UV at different time, 0 s, 15 s, 30 s, 1 min, 2 min, 5 min, and 10 min. It is clear that an intense absorption peak locates at 355 nm and a weak peak at about 445 nm. As one knows well, the peak at 355 nm corresponds to the π-π* electronic transition of the *trans* azobenzene side chain and the peak at about 445 nm originates from the weak n-π* electronic transition of the *cis* isomers. The absorption at 250 nm is due to the π-π* and the n-π* transition of the phenylbenzoate fragments and the aromatic Φ-Φ* transition of azobenzenes.[24] As the UV irradiation time going on, the intense absorption of π-π* electronic transition of the *trans* azobenzene side chain at 355 nm decreases. As while the peak of the weak n-π* electronic transition of the *cis* isomers at 445 nm becomes more pronounced, indicating that azobenzene chromophores undergo a *trans*-*cis* photoisomerization process in the AZO4. Figure 2b shows the changes in the absorption spectra of AZO4 upon the visible light irradiation for 0, 1, 2, 6, 15, 40, and 220 min at 450 nm. The subsequent visible light irradiation leads to recover of the shape of the absorbance spectra with the visible light irradiation time. The isomerization of *cis*-form achieved to *trans*-form gradually, and even recovered to the state before UV irradiation.

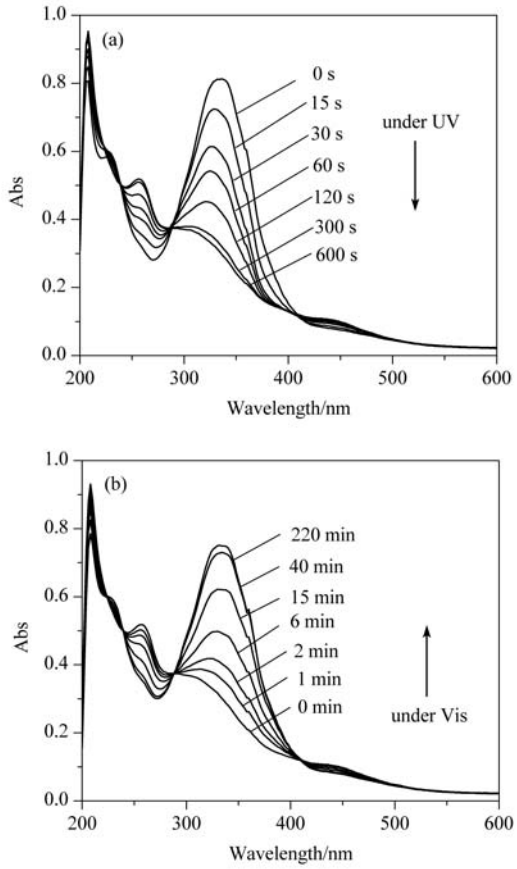


Figure 2 Changes in the absorption spectra of polymer in THF upon irradiation by UV at (a) 365 nm and (b) visible light above 450 nm.

The kinetic constants of the photoisomerization of AZO4 were calculated with the intense of UV absorption at different irradiated time by formula (1).

$$\ln\frac{A_\infty - A_t}{A_\infty - A_0} = -K_t \quad (1)$$

The slope of the curve formed by $\ln[(A_\infty - A_t)/(A_\infty - A_0)]$ to time was denoted as the kinetic constants of AZO4 photoisomerization. The results of the calculation shows that the constants of *trans*-*cis* photoisomerization $K_{t\text{-}c}$ was 4.00 min^{-1}, and the constants of *cis*-*trans* photoisomerization $K_{c\text{-}t}$ was 0.02 min^{-1}. This means the AZO4 also has the distinctive properties that was responded quickly and recovered slowly as previously reported.

Surface wettability of azopolymer thin film

In this work, the photoresponses of CA of water on the azopolymer were studied under UV-Vis irradiation. CA changes at various stages of irradiation are given in Figure 3 by the sessile drop technique. Before UV light irradiation, the average CA of azopolymer thin films is approximately 77°. After irradiation by 365 nm UV light, the average CA increased to 83°. Under the visible light irradiation again, the average CA recovered to 77°. The difference of the two CAs is up to 7°.[24,41] It is related to the existence of carboxyl group on surface and the photoisomerization of azo chromophores. The two factors would cause the change from 0 (*trans*) to 3 D (*cis*) of dipole moment of azopolymer and surface energy during the process of photoisomerization from *trans* to *cis*.[45] This contact angle change is almost completely reversible after visible light irradiation. On the other hand, the results of CA determination indicated the change of surface free energy of spin-coating films. It is obvious that the azopolymer film has higher surface free energy before UV irradiation, and then its surface energy decreased after UV irradiation. Moreover, this contact angle change is almost completely reversible

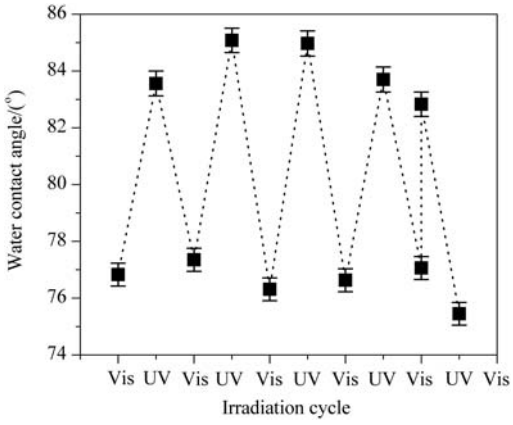


Figure 3 The contact angle of azopolymer film under UV and visible light irradiation.

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after several cycles. This implies photoisomerization of this unit in surface of azopolymer film under UV-Vis light irradiation.

Surface morphology of azopolymers via ATRP

The morphologies of the AZO4 polymer brush surfaces on silicon substrates were examined under AFM by means of a tapping mode. Figure 4 (b, c, d) shows AFM images of AZO4 polymers with the polymerization time of 16, 24 and 24 h. Before the preparation of azopolymer by ATRP, the surface of silicon wafers were extremely smoothed with the average roughness (Ra) of 0.9 nm. However, it became rougher during the formation of azopolymer. When the polymerization degree reached to a certain constant, the polymer brushes could turn to balls, forming AZO4 polymer nanoparticles. It demonstrates that the surface become rougher and rougher. When polymerization time was 24 h, the vertical height, *i.e.*, the thickness, approximately is 30 nm.

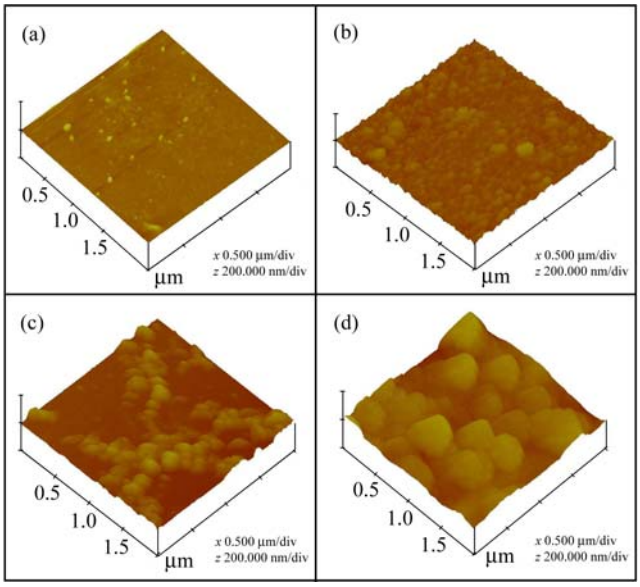

Figure 4 The 3 D AFM images of (a) bare silicon wafer and AZO4 brush films at the polymerization time of (b) 16, (c) 24 and (d) 48 h. The surface Ra is 0.9, 7, 13 and 23 nm, respectively.

BSA adsorption before and after UV irradiation

Once the reflectivity units of SPR kinetics behavior of AZO4 films in PBS reaches a stable state, BSA solution was introduced into the flow cell. The SPR kinetics of BSA adsorption on AZO4 polymer films was shown in Figure 5 (a). The systems were allowed to stabilize approximately over a period of 15 min but showed no further significant changes. After this stabilization period, the samples were rinsed with PBS which, in all cases, always caused a loss of some unbound protein from the surface. Figure 5 (b) shows the adsorbed amounts of BSA on polymer surfaces before and after being rinsed by PBS. Before UV irradiation on polymer surface, the amount of BSA adsorbed on the AZO4 polymer films was 130 RU. However, the adsorption

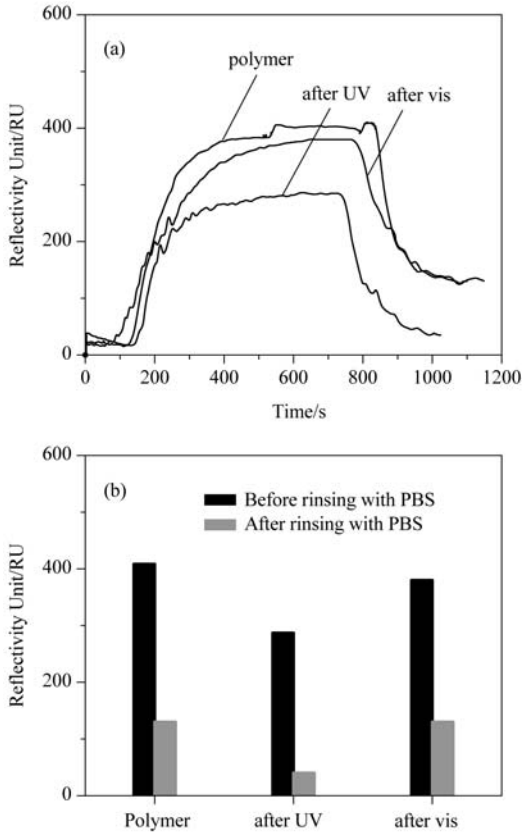

Figure 5 (a) The adsorption kinetic caves and (b) BSA adsorption amount on AZO4 polymer films.

amount decreased to 40 RU after being irradiated by UV light for 1 h. Additionally, the adsorption amount recovered to 130 RU again, when irradiating by Vis light for 24 h on the polymer film. It demonstrates that the *trans-cis* isomerization exchange induced by UV irradiation led to the remarkable decrease of BSA.

Actually, with the photoisomerization of azobenzene moieties from *trans* to *cis* state, the carboxyl groups on the film surface would transfer into the inner of film, so that the density of carboxyl groups on the surface of azopolymer thin films will be changed correspondingly. Before UV irradiation, azobenzene moieties appear in the planar *trans* state and stand vertically onto the film before UV light irradiation. The density of carboxyl groups (—COOH) on the surface of azopolymer thin films will be relatively large. Therefore, the surface tension will be relatively large. By absorbing UV light, the planar azobenzene moieties switch into *cis* state and assemble parallel to the film. Hence the density of carboxyl groups decreases on the surface, which means that surface tension binding sites for BSA adsorption will decrease. BSA is a protein with high surface energy. When the azobenzene moieties present *trans* state before UV irradiation, the carboxyl groups with high surface tension should have stronger interaction between carboxyl groups and amino in BSA molecules. In contrary, when the azobenzene moieties present *cis* state after UV irradiation, low surface tension of the film

surface will reduce the interaction between BSA and azopolymer films surface, which leads to less BSA adsorption on the film. The film above was irradiated again with visible light, azobenzene molecules were isomerized from *cis* to *trans* state. The surface energy of azopolymer film increases correspondingly.[11] After UV irradiation, the above films are exposed with visible light. It is obviously the binding curve of BSA almost recovered to the initial curve.

Conclusions

The polymeric brushes containing azobenzene moieties were prepared via ATRP as the adhesion layers for the reversible adsorption of BSA. With the polymerization going on, the surface roughness of azopolymer brushes increased due to the formation of the polymer particles. The surface wettability of azopolymer was photo responsive since there was a substantial cycle of CAs of the azobenzene polymer under UV-Vis irradiation. Furthermore, the reversible photoisomerization of azobenzene with a first-order isomerization rate was detected. Since the —COOH groups in AZO4 polymer chains point in or out from the films irradiated by UV and visible light, the *trans-cis-trans* photoisomerization properties can affect the BSA adsorption. The photodeformable surface on the azopolymer warrants further investigation for protein chip application since the azopolymer can hold protein molecules without denaturation caused by one-step photoirradiation.

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(E1008109 Pan, B.)

