Stable sensor layers self-assembled onto surfaces using azobenzene-containing polyelectrolytes

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Polyelectrolytes functionalized with photoisomerizable azobenzene chromophores were multi-layered onto inorganic and metal surfaces, by the repeated adsorption from dilute aqueous solution, alternating between oppositely charged polymers. These layer-by-layer ionically self-assembled thin films were investigated for their suitability as sensor host materials with respect to the criteria of control over physical layer properties, versatility to different substrates and adsorption geometries, and stability of the formed layers to heat, solvent, and sonication. Layer thickness was found to be controllable between 5 Å and 500 nm by varying the total number of layers deposited, from a single monolayer to 1000 layers. Control over individual layer thickness was achieved by varying the pH of the adsorption solutions. This multi-layer self-assembly was demonstrated to be suitable for a wide range of metal and inorganic substrates, and achievable with surfaces of high curvature ($r = 50$ nm), and confined geometry. The deposited layers exhibited good stability to desorption in a range of organic solvents, aqueous temperatures to 100 °C, and cleaning protocols such as sonication. The laser-induced geometric isomerization of the azobenzene chromophores was shown to be strongly dependent on aqueous solution properties, demonstrating an application as a hydroxide ion sensor in highly alkaline media.

1. Introduction

Ionically self-assembled multi-layer (ISAM) films of poly-electrolytes have received much recent attention as a route to designing highly tailored surfaces,[1] for a wide range of applications. They have been employed in such areas as bio-compatiblilty,[2,3] photo-responsive materials,[4] microelectronic devices such as electroluminescent LEDs,[5–7] conducting polymer composites,[8,9] and sensitive gas sensors.[10] Sequential layer-by-layer (L-B-L) physisorption of alternately charged polyelectrolytes is achieved through a method of electrostatic self-assembly first described by Decher.[11,12] With this technique, multi-layer films are assembled by first immersing a negatively charged flat substrate in a positively charged polymer solution, followed by thorough rinsing of the surface in an aqueous bath to remove unadsorbed polymer. The resulting polycation coated surface is subsequently immersed in the oppositely charged polyion solution, and followed with another wash. The cycle is then repeated until a desired number of layers is achieved. This L-B-L coating technique is particularly attractive because of the ease and efficiency of fabrication in aqueous solution, and the versatility with respect to incorporation of secondary functionalities in the polyions assembled. The potential to create highly tailored film structures and to impose specific chemical functionalities provides an excellent opportunity for applying the ISAM technique to novel surface sensor applications. Various means exist for manipulating the material properties of ISAM films (such as layer thickness and surface chemistry) either through choice of substrate or polyion, adsorption bath conditions, or post self-assembly functionalization. The irreversible nature of the ISAM adsorption process results in films with good stability and high reproducibility. We report here our recent investigations of various strategies that can be employed for manipulating properties of organic multi-layered thin films, in weak polyelectrolyte systems containing an optically responsive azobenzene chromophore. This paper seeks to present the L-B-L ISAM technique as a promising host platform for sensors, which is facile and inexpensive to assemble, and stable to a range of solvent environments.

One distinct advantage that ISAM films possess over other tailorable surface modification techniques, such as self-assembled monolayers (SAMs), is the potential for the incorporation of a large number of sensor groups. In contrast to SAMs, where sensor coverage is limited to the surface area, ISAM films can be highly swollen in contact with analyte solution, and incorporate many nanometers of sensor-containing polymer layers, greatly increasing sensitivity. Furthermore, ISAM films may offer an advantage of stability to temperature, cleaning, and solvent and pH resistance. We examine in the following the applicability of the polyion layering technique to surface sensor modification through study of: (a) various methods for film thickness control with a focus on the effects of polymer charge density on film growth, (b) possible substrates amenable to L-B-L self-assembly, and (c) film stability/resistance to harsh solvent environments and consequences of high temperature exposure, sonication, and cleaning. As an example application of ISAM layers as sensor host materials, we will also demonstrate the applicability of these multi-layers for use as hydroxide ion sensors in extreme alkaline media.

2. Experimental

2.1 2.1 Materials

The polyions used were commercially available poly(allyl)amine hydrochloride (PAH; Polysciences; M 60K), poly{1-4[4-(3-carboxy-4-hydroxyphenyl-azo) benzenesulfonamido]-1,2-ethanediyl sodium salt} (P-Azo; Aldrich; M 90K) and poly(diallyldimethylammonium chloride) (P-DAC; Aldrich, M 200–350K), the structures of which are presented in Fig. 1. Azobenzene chromophore [2-[4-(diethylamino)phenylazo]benzoic acid] (ER) was obtained from Aldrich. Aqueous solutions

of polyion concentration 10^{-2} M per repeat unit were prepared using Milli-Q water (18 MΩ resistivity) and the pH of both solutions were adjusted and matched (from pH = 4 to pH = 11) with HCl and NaOH. Unless otherwise stated, multi-layering was performed using pH 9 solutions. Various metallic and inorganic substrates, including Al, Au, Ag, Cu, mica, Mo, Ni, quartz, SiO₂ microscope glass slides, stainless steel, V, and 100–150 nm diameter colloidal SiO₂, were cleaned by 12 h immersion in 10^{-3} M H₂SO₄. Ellipsometry and optical absorbance measurements were conducted on Si wafer substrates (Wafernet; crystallographic orientation < 100 >) and Fisherbrand microscope glass slides, respectively, which were similarly treated for 12 h in a bath of 75% H₂SO₄ and 25% H₂CrO₄. Subsequent washing of all substrates with neutral Milli-Q water (pH 7.5 ± 5%) was performed in preparation for electrostatic multi-layer deposition.

2.2 Methods for multi-layer coating

Multi-layering was initiated by immersion of the cleaned substrates (with a hydroxylated surface) into the 10^{-2} M polycation solution for 12.5 min. This adsorption was then followed by washing of non-adsorbed polyion through two immersions in separate neutral Milli-Q H₂O baths for a total of 5 min. Next, a similar dipping protocol was used for adsorption of the polyanion at similar solution concentration and dipping time, with subsequent rinsing of unadsorbed polyion. This procedure was repeated until the desired number of layers was obtained. On the conclusion of the aqueous adsorption cycles, layered samples were dried in an oven at 65 °C for 2 h, and allowed to return to room temperature before measurements. Additionally, a similar multi-layering scheme was applied to alternate geometries of adsorption. Three different geometries were chosen for testing the versatility of L-B-L multi-layering: (1) high curvature surfaces, (2) confined geometries, and (3) spin-coating.

Layering on a high curvature surface was demonstrated by cyclic immersion of SiO₂ colloidal particles in alternately charged polyelectrolyte solutions. Specifically, ISAM growth on silica colloids was implemented using a procedure reported by Donath and co-workers.[13,14] Colloids (3 g) were dispersed in 500 mL of polyion solution for 30 min. This was followed by 1 h of centrifugation at 4300 rpm and removal of supernatant. Three separate washing cycles (each with 500 mL of Milli-Q H₂O), sequentially consisting of 25 min sonication, 1 h centrifugation and extraction of supernatant liquid, was then performed to remove unadsorbed polyions. Silica particles were sonicated in solution at each washing step to prevent aggregation and to exploit maximum surface area for subsequent polyelectrolyte deposition. The above procedure was then repeated for polyion deposition of the opposite charge, thereby

constructing a bi-layer. The presence of the layers was confirmed through ζ potential measurements and solid-state NMR spectroscopy.[15]

Multi-layering was also attempted in a confined geometry, using 30 sequential and repetitive flow cycles of polyelectrolyte through a glass tube (< 1 mm diameter and flow rate ~ 0.3 mL s⁻¹ for 5 s). Between flow depositions of oppositely charged polyions, three intermittent flow-rinsing cycles were implemented (each of 5 s duration). Successful layering of dye-containing polyelectrolyte was confirmed optically.

Films of 30 spin-cast multi-layers were also constructed by introducing polyion droplets (0.1 mL) on a flat Si surface or microscope slide, immediately followed by rapid spinning (at 4000 rpm) using a spin coater (Precision Scientific). Similarly, three individual spin washing cycles (each of 0.5 mL H₂O) separated each subsequent layer deposition.

2.3 Film thickness measurements

The optical absorption of PAH/P-Azo multi-layer films was probed by transmission studies through microscope glass slides (Varian Cary 300-Bio Spectrophotometer; scan rate of 100 nm min⁻¹). Unless otherwise stated, reflective measurements of Si films were obtained using a Gaertner Ellipsometer (with a HeNe laser at 633 nm and fitted for both layer thickness and refractive index). All ellipsometric determinations of total layer thickness are reported as the statistical mean of 13 measurements after subtraction of surface oxide layer thickness (measured average of 27 ± 3 Å).

3. Results and discussion

3.1 Physical control of thickness

In order to incorporate a desired number of sensor groups in contact with a unit area of surface, it is necessary to control the total thickness of the sensor-containing polymer layers. Fig. 2 depicts a series of typical UV-Vis absorption profiles (studied on a glass slide surface) showing build-up of multi-layers obtained for the PAH/P-Azo system at unaltered pH of polyelectrolyte dipping solution (measured as pH = 4.2 and pH = 8.5 for polycation and polyanion respectively). Optical measurements were taken for the $\pi \rightarrow \pi^*$ absorbance maximum centered at 365 nm for the *trans* azobenzene isomer. No appreciable variation in λ_{max} was observed throughout the layering, suggesting that the chromophore sensors are not significantly altered by the layering process. This suggests that films of a desired total thickness can be achieved by appropriate selection of the total number of layers deposited (N_L). These
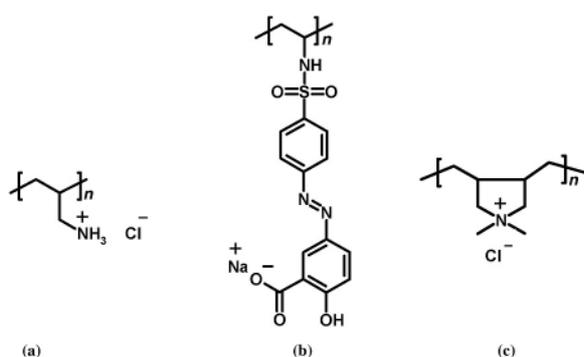
Fig. 1 Repeat unit structures of polyelectrolytes used for multi-layering: (a) PAH (weak polycation), (b) P-Azo (weak polyanion), and (c) P-DAC (strong polycation).
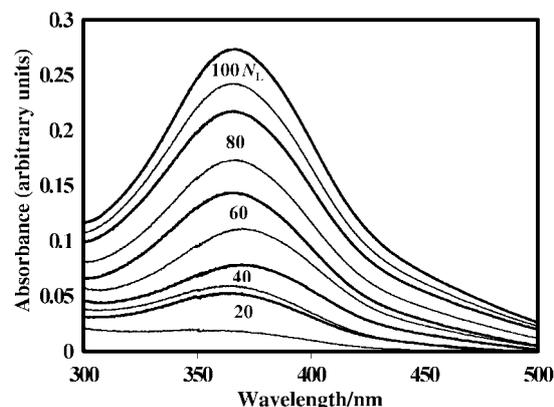
Fig. 2 UV-Vis absorbance for layer-by-layer build-up of a PAH/P-Azo multi-layer film measured successively at 10 layer (N_L) intervals.

results concur with previous demonstrations of physical manipulation of thickness for P-DAC/P-Azo films as reported up to $100N_L$.[16] The upper limits for multi-layering the same polyelectrolyte system deposited at pH 9 were similarly examined by spectroscopically tracking an off-maximum absorbance of the azobenzene moiety. Beyond an absorbance of 3 (approximately at $350N_L$), an off-maximum probe of $\lambda = 440$ nm was used to prevent detector saturation. The measured optical absorbance is shown every $50N_L$ up to $1000N_L$ in Fig. 3 (inset) and indicates continued linear growth behaviour in the L-B-L build-up for the same polyelectrolyte system. The absence of observable film desorption from the glass surface suggests stable L-B-L growth as tested to $1000N_L$. A corresponding optically determined thickness of 547 nm indicates that uniformly thick films, in the micron regime may easily be fabricated using the ISAM method. These results suggest that choice of total layer number can be considered a simple physical approach for film fabrication to a predetermined thickness, from the angstrom to the sub-micron level.

3.2 Chemical control of thickness

The total layer thickness can also be controlled through varying the solution conditions of the adsorption baths. In agreement with previous investigations of ionic effects on film structure using strong polyelectrolytes,[17] the thickness of layers deposited was shown to be strongly dependent on the charge density of the ionic functionalities incorporated in the polymer chain. Specifically, recent studies have indicated that multi-layer thickness and interpenetration can be altered by manipulation of polyelectrolyte ionic strength *via* addition of salt or adjustment of the solution pH during the layering process.[4,18] Here, the effects of charge density with variable pH experiments were examined for the two weakly charged polyelectrolytes, PAH and P-Azo. Fig. 3 displays a plot of absorbance as a function of N_L for the probed pH regimes of assembly dipping solutions (pH = 4 to pH = 11), which were matched for both polyelectrolytes. Comparison of the two pH extremes revealed a near 20-fold increase in optical density between a fully charged (pH = 4) *vs.* weakly charged (pH = 11) case (the pK_a of PAH = 8.7).[19] The corresponding P-Azo thickness was determined as 1 Å per layer and 18 Å per layer for pH = 4 and pH = 11 adsorption environments, respectively. This suggests significant contribution of polyelectrolyte pH in the weak–weak PAH/P-Azo system with respect to film thickness. Therefore, exploiting the polyion charge fraction can provide a more straightforward chemical means for obtaining control over the extent of polyion deposition through dipping bath parameters. The advantage is that a good command over ISAM film structure is achievable over a large pH range. Specifically, dipping solution conditions in L-B-L assembly can appropriately be set over 7 pH units, ranging from acidic to strongly basic. Sufficient polarity arising from the weakly charged polycation PAH allows for thick multi-layer self-assembly at pH 9, as demonstrated experimentally by ellipsometry and UV-Vis spectrophotometry (Fig. 3). Although both weak polyelectrolytes exhibit good aqueous solubility under highly alkaline conditions (pH = 12), ideal for thick film fabrication, gradual precipitation of PAH with increasing pH represents an upper limit for achieving films of a thickness greater than 20 Å per layer.
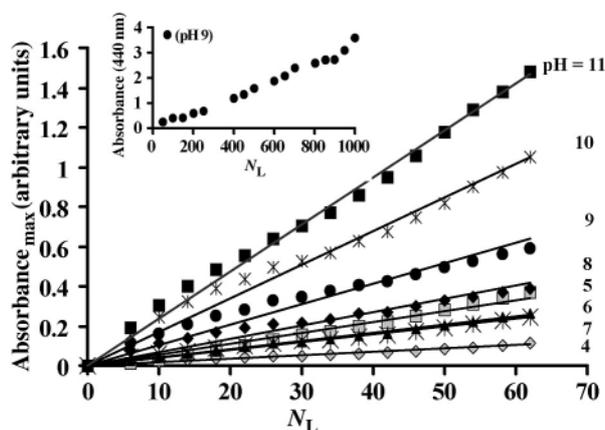
ISAMs made from weakly charged polyelectrolytes (where ionizable repeat units are not fully charged) also behave analogously to strongly charged polymers under suitable pH conditions. Evidence of this is offered by the observation of a similar film optical thickness (within 6%) for P-Azo multi-layer films constructed with either strongly charged polycation P-DAC, or a weak polycation PAH, converted to the fully charged state upon altering the acidity of both the polycation and polyanion solutions to pH = 3.

3.3 Practical considerations

3.3a Suitability of substrates. Recent comprehensive studies of ISAMs films have mainly employed glass and Si substrates for multi-layer film fabrication. This is primarily due to the ease and well-established tools that exist for reflective or absorptive spectroscopic optical measurements on these standard substrates. Both glass and Si are relatively inexpensive, are resistant to harsh cleaning protocols and extreme pH/salt conditions, and are readily available. Additionally, it has been repeatedly demonstrated that these surfaces are highly suitable for investigations of azobenzene-containing films for application as photo-sensors and electro-optic films.[20–22] For sensor modification purposes, it is of interest to examine substrate variability with respect to the electrostatic multi-layering technique by: (a) investigating the range of alternative metal oxides and native metals available and (b) testing a range of geometries available for layering.

The PAH/P-Azo deposition parameters described were implemented to build 30 layers on cleaned Al, Ag, Au, Cu, Mo, Ni, Ti, V, mica, and quartz substrates. Successful L-B-L physisorption was demonstrated for all tested surfaces through comparison of the multi-layered thin films to the initially clean surface. The presence of adsorbed multi-layers for all surfaces was optically confirmed by qualitative observation of the characteristic P-Azo absorption at $\lambda = 365$ nm. These results suggest no restrictions with respect to choice of metal oxide surface used for electrostatic self-assembly. All films exhibited stability to repeated washing cycles, and were also resistant to de-wetting when heated in an oven for > 24 h at 70 °C. Similar to the results obtained for SiO_2, no indication of physical limitations on the number of layers deposited was observed for the metallic substrates, as demonstrated by multi-layering $1000N_L$ of PAH/P-Azo on a stainless steel surface.

3.3b Suitability of various geometries. The applicability of the ISAM method to various geometries of adsorption was also investigated for the PAH/P-Azo system. L-B-L adsorption was optically demonstrated for three adsorption geometry cases tested including: (a) spin-cast polycation/polyanion droplets on a flat glass or Si, (b) polyelectrolytes deposited on high curvature colloidal SiO_2, and (c) flow-based ISAM fabrication within a cylindrical glass tube. To determine the nature of polyion–substrate interaction, we compared optical measurements of the L-B-L spin-cast system of $30N_L$ to the homopolymer spin coated films generated solely using PAH or P-Azo homopolymer. Both resultant films were rinsed well with water.

Fig. 3 UV-Vis absorbance of PAH/P-Azo multi-layers assembled under various pH matched adsorption bath conditions from 0 to 62 layers, and from 50 to 1000 layers (inset).

Table 1 summarizes the results for UV-Vis P-Azo optical density and calculated average per layer thickness obtained by ellipsometry for the two systems. Evidence of multi-layer physisorption in the case of L-B-L polyion spinning on a surface is supported by the absence of aqueous desorption observed for the 39 Å per N_L ISAM film (case G). After 24 h rinsing of the film in solvent, ellipsometry indicated a negligible difference in the layer thickness, measured as 38 Å (case H). In contrast, the spin-deposited homopolymers, PAH and P-Azo, readily and completely de-wetted from the surfaces after 2 min immersion in water, suggesting only a weak electrostatic interaction of the polyion with the surface (cases C and F). For the spin-deposited PAH, the measured de-wetting of the homopolymer was likely due to the formation of only a mono-layer, below the detection limit of the ellipsometer. Identical results were obtained for multi-layering *via* flow of polyion through the capillary, where 30 stable layers were successfully deposited on the interior surface of a 1 mm diameter glass tube. ISAM stability within the flow cell was also confirmed by exposing the internal coating to constant aqueous washing for several minutes and film resistance to immersion in a 70 °C water bath for 2.5 h. Layering on high curvature surfaces was demonstrated by washing 100–150 nm diameter colloidal SiO$_2$ with alternately charged polyelectrolyte solutions, similar to previous reports on latex particles.[13,23] Results from ζ potential measurements and solid-state ^{1}H-NMR spectroscopy confirm the existence of these stable deposited layers.[15] The demonstrated suitability of the ISAM technique to a variety of film casting methods such as spin-coating and flow cells, and to high curvature surfaces such as colloids, suggests that this technique can in principle be applied to sensor layering through a wide variety of processes and in three dimensions on the nanometer scale.

3.3c Film stability. The stability of constructed PAH/P-Azo ISAMs to prolonged exposure in various solvent environments was tested. Fig. 4 displays the measured changes in film thickness after 2.5 h heating cycles of $30N_L$ films in water. A near-constant average layer thickness of 40 ± 2 Å was observed for films exposed to water baths at temperatures ranging between 25 and 90 °C, indicating resistance to any desorption up to boiling temperatures. At 100 °C, the average layer thickness was reduced to 50%, but complete de-wetting of the film was still not observed in the temperature range examined. PAH/P-Azo films were also subject to a 14 h immersion in solution environments of widely varying polarities, using a diverse range of 18 common organic solvents. The resulting difference in film optical density was calculated from UV-Vis data after films were submerged in acetone, acetonitrile,

glycerol, 1,4-dioxane, DMSO, toluene, ethyl acetate, methylethyl ketone, heptane, THF, benzene, nitrobenzene, propan-2-ol, ethyl alcohol, hexanes, ethyl ether, chloroform, and methylene chloride. No measurable degradation in film thickness was observed in any case. Additionally, the films were exposed to aqueous solutions of a wide range of salt concentrations, from 0.001 to 2 M, of both NaCl and NaBr. Multi-layered films again remained fully intact, showing no desorption on immersion in either saturated salt solution. Desorption was only observed when the films were subject to highly acidic salt water (2 M at pH = 1).

As an important demonstration of the films' ability to withstand common cleaning protocols, constructed films were also shown to withstand 1 h sonication in a high salt and extreme pH environment. Measurements of the percentage difference in UV-Vis absorbance of PAH/P-Azo multi-layers were made on films before and after sonication in various solutions. The films revealed good resistance to sonication with solutions of: (a) Milli-Q water, (b) 1 M NaCl, and (c) pH 12 water, yielding only a 2, 9, and 14% reduction in optical thickness, respectively. Only after sonication in a combined solution of pH 12 and 1 M salt, did experiments show some appreciable film desorption, with an associated optical absorbance reduction of 59%. The results of film stability tests performed for varying concentrations of salt suggest that this effect may well be attributed solely to the combined and unusually harsh solvent environment, rather than the sonication process itself.

3.3d Example application. While this research seeks to study the general suitability of ISAM layers as a promising sensor host material independent of individual applications, one example sensor system was investigated as proof-of-principle. ISAM films functionalized with azobenzene chromophores can make use of the readily-induced and reversible photoisomerization between the two geometric forms of *trans* and *cis*.[24,25] Under irradiation at an absorbing wavelength in the blue visible or near-UV, the more stable *trans* form is converted to the less stable *cis*, to an extent that depends on the irradiation intensity. The *cis* state then decays back to the *trans* form either photochemically, or thermally. The thermal rate constant varies widely depending on the azo chromophore, but in general varies from milliseconds to hours.[25] The absorption coefficient of the azobenzene can change dramatically on isomerization from *trans* to *cis*, which can be easily monitored by absorption spectroscopy near the λ_{max} to determine the first order rate constant. A typical *trans–cis–trans* isomerization cycle (of ER azo chromophore) is presented in Fig. 5 (inset) where the transmission at λ_{max} is monitored over time, while a high intensity pump laser is introduced at time $t = 1$ s for a duration of 1 s. As the photo-generated *cis* isomer has a lower visible absorption coefficient than the *trans* isomer, the probe beam transmission signal intensity increases substantially while the pump beam is on and a photo-stationary state containing an equilibrium of both isomers is generated and maintained. With the pump beam turned off, the *cis* relaxes thermally back to the

Table 1 Optical density and per layer film thickness of PAH and P-Azo homopolymers, and PAH/P-Azo multi-layers spin-cast on glass and Si surfaces

Case	Surface description	Total UV-Vis Abs$_{max}$	Ellipsometric height per layer/Å
A	Bare glass substrate	$< 0.01^a$	—
B	Spin-cast on glass P-Azo homopolymer/10^{-1} M	0.239	—
C	Sample B and 2 min subsequent H$_2$O wash	$< 0.01^a$	—
D	Bare Si surface	—	0
E	Spin-cast on glass PAH homopolymer/10^{-1} M	—	103
F	Sample E and 2 min subsequent H$_2$O wash	—	0
G	Spin-cast $30N_L$ PAH/P-Azo/10^{-2} M	—	39
H	Sample G and subsequent 25 h H$_2$O wash	—	38

^{a} Below detectable threshold.
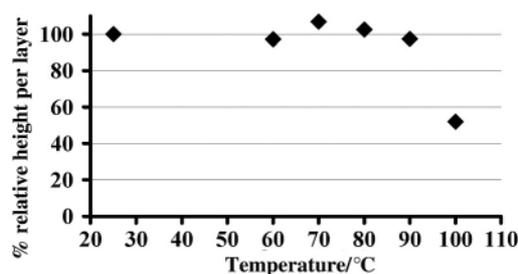
Fig. 4 Layer thickness from ellipsometry of PAH/P-Azo films after 2 h immersion in temperature-controlled water baths.

trans form, and the signal intensity decays exponentially. This signal decay is monoexponential, and thus a first order rate constant can be determined for the process.

This first order rate constant can depend strongly on the local solvent however, as depicted in Fig. 5 for the isomerization taking place in aqueous solution over a range of pH values from pH = 9.5 to pH = 12.[26] The thermal isomerization rate constant varies linearly over two orders of magnitude in this range, with a time constant (inverse rate constant) ranging from 30 ms at pH = 9.5 to more than 3 s at pH = 12. This therefore represents an effective and sensitive hydroxide ion sensor, which can function at high pH, of interest to many wastewater applications.[27] Although this hydroxide ion sensor relies on a spectroscopic determination of a rate constant, one could readily develop a practical sensor based on this technique using routine fibre optics, whereby the sensor layers are adsorbed either directly on a light-guiding fibre, or on top of a wave-guiding layer over a support, provided appropriate refractive index contrast exists between material layers. With a reflective coating at the end of this cylindrical sensor, the polymer material's absorbance could be continually monitored through reflected evanescent wave absorption with a low power probe laser, monitored at source through fibre optics. The 'pump' flash could be delivered with the same wavelength at higher power, and then the first-order return of the absorbance monitored for a few seconds to determine the rate constant, and hence the local pH. The versatility and stability of the multi-layer host material, described previously in this paper, then suggests that a sensor of this type would be suitable for pH determination in highly alkaline media, and be easily cleaned with solvents and sonication without harm to the sensor material. One can envisage a wide variety of sensor groups incorporated into ISAM layers such as these (electrochemical or spectroscopic), or even multiple sensors incorporated in various layers to comprise a stable multifunctional probe, assembled easily in aqueous baths by appropriate adsorption.
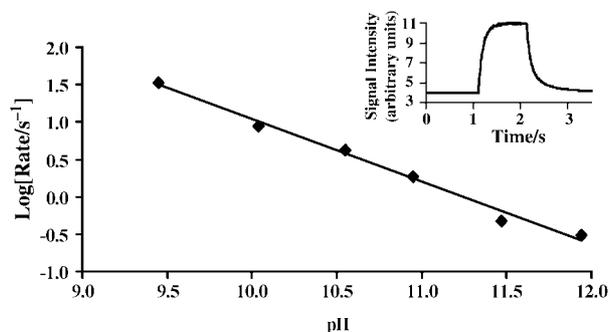
Fig. 5 Optical transmission during photoisomerization (inset) and the resulting *trans–cis–trans* thermal isomerization rate constant as a function of pH for ER azobenzene chromophores.

Conclusions

SAM films constructed from weak–weak polyelectrolyte systems containing chromophores can be physically and chemically controlled during self-assembly, making them promising candidates as host layers for sensor applications. PAH/P-Azo multi-layer films were shown to be adsorbed under a range of layering conditions and geometries and exhibit good stability toward heat and a range of harsh solvent environments.

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