UV-Cross-Linked Poly(vinylpyridine) Thin Films as Reversibly Responsive Surfaces

Bernadette Harnish,† Joshua T. Robinson,† Zhichao Pei,‡ Olof Ramström,*,‡ and Mingdi Yan*,†

Department of Chemistry, Portland State University, P.O. Box 751, Portland, Oregon 97207-0751, and Department of Chemistry, Royal Institute of Technology, Teknikringen 30, S-10044 Stockholm, Sweden

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We report that UV-cross-linked poly(4-vinylpyridine) (P4VP) films acted as reversibly responsive coatings that controlled surface wettability and swelling toward external stimuli: solvent and pH. The polymer films were prepared simply by spin-coating a solution of P4VP followed by UV irradiation. These cross-linked films, when treated with chloroform, showed ∼31% increase in film thickness whereas films extracted with methylene chloride or *n*-butanol exhibited a slight decrease. The increase in film thickness was due to the protonation of pyridyl groups by hydrogen chloride resulting from the photodegeneration of chloroform. The film expanded to minimize repulsion around the charged centers. This hypothesis was further confirmed by exposing the cross-linked film to hydrogen chloride vapor. The film expanded ∼37% whereas no thickness increase was observed for films exposed to ammonia or methanol vapors. The extent of swelling was monitored in situ using a quartz crystal microbalance sensor. Large oscillation frequency shifts were detected when the UV-cross-linked P4VP film was exposed to acidic buffer solutions. The changes were rapid, and the effect was reversible.

Introduction

The development of electronic, analytical, and biomedical devices demands for new materials that produce functions in a controlled fashion.[1−5] Of particular interest are materials that exhibit different molecular states or phase transitions in response to the environment. As a result, properties such as wettability[1,6,7] or swelling behaviors[8,9] change upon stimulation by heat, light, pH, electric field, temperature, or solvents. This phenomenon has been used for novel design of separation,[10] drug delivery,[11] sensing,[12] and microfluidic devices.[13−16]

Responsive surfaces documented in the literature are commonly prepared using self-assembled monolayers (SAMs) or polymer thin films. For example, Langer and co-workers used SAMs on Au to create surfaces that could reversibly switch from hydrophilic to hydrophobic by applying an electric potential.[17] The design feature of the system is a low density SAM that has a negatively charged terminus and a carefully controlled intermolecular spacing. When a negative electric potential was applied, the SAM extended, thus, exposing the negatively charged terminus. With a positive electric potential, the Au surface attracted the negatively charged end groups, bending the SAM molecules and, thus, exposing the interior hydrophobic moieties. The surface properties were, therefore, controlled and could be reversibly switched by alternating the applied potential. This strategy has been employed to induce mechanical motions of molecules[18] and to control protein assembly.[19,20]

Polymer thin films have been used to create responsive surfaces for a wide range of applications. Most of such polymer films are created by chemical grafting. For example, surface-bound poly(*N*-isopropylacrylamide) (pNIPAAm) films were prepared by conjugating a carboxyl-functionalized pNIPAAm to an aminated glass surface[21,22] or by in situ

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* Corresponding authors. Prof. Mingdi Yan: e-mail, yanm@pdx.edu; fax, 503 7259525. Dr. Olof Ramström: e-mail, ramstrom@kth.se; fax, +46 8 7912333.

† Portland State University.

‡ Royal Institute of Technology.

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polymerization of *N*-isopropylacrylamide onto a functionalized surface via atom transfer radical polymerization,[23] plasma polymerization,[24] or photopolymerization.[25] pNIPAAm is a well-studied responsive material that undergoes reversible phase transition between an extended conformational state (hydrated and hydrophilic) and a collapsed conformation (hydrophobic) with the change of temperature[26] or solvent.[26,27] Responsive polymer films can also be prepared from polyelectrolytes. These films are created by sequentially depositing oppositely charged polyelectrolytes onto a substrate. The resulting multilayers have shown swelling responses to ionic strength and pH.[28]

We have previously developed a method for the direct attachment of polymer films onto solid substrates simply by UV irradiation.[29] The immobilization was a result of photochemically induced cross-linking of the polymer leading to the attachment of the polymer film to the substrate. Herein, we report an application of this strategy, showing that UV-cross-linked poly(4-vinylpyridine) (P4VP) thin films act as responsive coatings that control surface wettability and swelling toward external stimuli: solvent and pH.

Experimental Section

Chemicals. P4VP (molecular weight ca. 160 000), poly(vinylpyrrolidone) (PNVP; molecular weight ca. 360 000), methanol (99.9%), and dichloromethane (99.8% anhydrous) were used as received from Aldrich. Hydrochloric acid (HCl, 36.7%) and *n*-butanol (99.9%) were purchased from EM Science (Cherry Hill, NJ). Ammonium hydroxide (29.3% ammonia, NH_3) was acquired from J. T. Baker Chemical Co. (Phillipsburg, NJ). Chloroform (stabilized with ethanol), hydrogen peroxide (35 wt %), 2-propanol (HPLC grade), and sulfuric acid (98%, technical grade) were purchased from Fisher Scientific. Purified chloroform was prepared by refluxing with P_2O_5 for 2 h and distilled.

Preparation of Polymer Films. Silicon wafers were cleaned by sonication in 2-propanol for 10 min followed by heating in the piranha solution (3:7 v/v 98% sulfuric acid/35% hydrogen peroxide) for 1 h at 80−90 °C. They were then washed thoroughly with boiling water for 1 h and dried under a stream of nitrogen. A 10 mg/mL solution of P4VP in chloroform, dichloromethane, or *n*-butanol was spin-coated onto the cleaned wafer at 2000 rpm for 60 s. The film was irradiated with a 450-W medium-pressure Hg lamp at ambient conditions for 5 min. The intensity of the lamp at the location of the sample was measured to be 12.3 mW/cm^2 using a 254-nm sensor. The 5-min irradiation time included a 2-min warm-up for the lamp to reach its full intensity. The unbound polymer was removed by soaking the sample in the corresponding solvent (chloroform, dichloromethane, or *n*-butanol) for 24 h.

Samples for quartz crystal microbalance (QCM) experiments were prepared in a similar manner as described above from a 10 mg/mL solution of P4VP in dichloromethane or PNVP in chloroform. The irradiated films were extracted with the corresponding solvent for 3 h and dried with nitrogen. QCM crystals were sonicated with 2-propanol for 5 min and dried with nitrogen immediately before coating. Crystals coated with polystyrene (PS) were prepared as previously reported.[30]

Corss-linked P4VP films used for the vapor exposure experiments were prepared and extracted with dichloromethane as the solvent. The films were placed in a sealed container together with a beaker containing 20 mL of 36.7% hydrochloric acid, ammonium hydroxide (29.3% NH_3), or methanol. After exposure to the vapor for 2 h, the thickness of the resulting film was measured. For the swelling experiments, buffer solutions (0.1 M) of varying pH were prepared from NaH_2PO_4 and Na_2HPO_4 at different mole ratios. Cross-linked P4VP films were incubated in the buffer for 10 min and dried with nitrogen.

Ellipsometry. Film thickness was measured on a Gaertner model L116A ellipsometer with a He/Ne laser (2 mW, Melles Griot) at an incident angle of 70°. The following refractive indices were used for film thickness calculation: SiO_2, 1.465, and P4VP, 1.581.[31] Measurements were taken at three different areas of each sample and were averaged.

Fourier Transform Infrared (FTIR) Measurements. Samples for infrared analysis were prepared on NaCl plates, and the spectra were recorded with a Perkin-Elmer Series 2000 FTIR spectrometer at 2.0 cm^{-1} resolution. The static contact angle was measured using 2 μL of distilled water by the sessile drop method. Measurements were taken at ∼10 s after the initial contact.

Contact Angle Measurements. Contact angles were determined on an apparatus consisting of an Intel QX3 200x microscope, a digital camera, and image analysis software.

QCM Measurements. QCM experiments were conducted with an Attana 100 sensor (Attana AB, Stockholm, Sweden), equipped with a flow-through system set at 50 μL/min and a 5-μL sensing chamber. Gold-plated 10-MHz quartz crystals (Attana) were used to prepare P4VP, PNVP, and PS films. Buffers for QCM measurements were either phosphate-buffered salines (PBSs) prepared from a standard solution (10 mM, pH 7.4, Sigma), the corresponding NaCl/KCl-free phosphate buffers, or formate buffered salines.

Prepared QCM crystals were mounted in the instrument, and the system was allowed to equilibrate in deionized water until a stable baseline was obtained. Deionized water was generally used as the running fluid throughout the study. The sample buffer solution was then injected to the sensor (sample size: 50 μL), and frequency data were collected at ambient temperature. All samples were analyzed in triplicate with each measurement reaching a stable baseline before the next injection. Note that the system was running deionized water as the background; therefore, the buffer was gradually replaced by deionized water until it was completely depleted. Changes were monitored by frequency logging using Attester 1.1 (Attana) and were recorded as the corresponding frequency shifts (Δf).

Apparent dissociation constant (pK_{app}) data were recorded correspondingly, where frequency changes were recorded in triplicate from pH 1.0−7.0, as well as from pH 7.0−1.0. The program GraphPad Prism (GraphPad Software, San Diego, CA) was adopted for nonlinear regression analysis to determine the apparent pK_a according to eq 1, where Δf_{min} is the minimum frequency difference and Δf_{max} is the maximum frequency difference.

$$\Delta f = \Delta f_{min} + (\Delta f_{max} - \Delta f_{min})/(1 + 10^{pK_{app} - pH}) \qquad (1)$$

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Table 1. P4VP Film Thicknesses[a] at Different Stages of the Preparation Process[b]

	n-butanol	dichloromethane	chloroform
initial spin-coated film	48.3 ± 0.3 nm	109.5 ± 1.4 nm	81.0 ± 0.4 nm
after irradiation	47.2 ± 0.1 nm	110.8 ± 0.9 nm	82.3 ± 0.5 nm
after solvent extraction	44.5 ± 0.1 nm	106.0 ± 0.5 nm	108.7 ± 0.7 nm
increase in film thickness	−7.9%	−3.2%	31.2%

[a] Film thicknesses were measured at three different areas on each sample and were averaged. [b] Films were prepared and extracted in the same solvent as indicated.

Results and Discussion

We have developed an alternative method for the direct attachment of polymer films onto solid substrates by UV irradiation.[29] The process involves spin-coating a polymer film followed by UV irradiation. After extraction with a solvent, a thin film remains on the substrate. We confirmed that the immobilization was a result of photochemically induced cross-linking of the polymer leading to enhanced van der Waals interactions of the polymer films with the substrate surface. These films could withstand extensive solvent extraction at elevated temperatures. Polymers that undergo this immobilization mechanism include PS, poly(vinyl chloride), polypropylene, P4VP, and PNVP.

Cross-linked P4VP films were prepared by spin-coating the polymer onto clean silicon wafers, irradiating the films with UV for 5 min, and extracting with the solvent to remove the unbound polymer. The thickness of the resulting film was measured by ellipsometry (Table 1). Films extracted with dichloromethane or *n*-butanol showed a slight decrease in the film thickness. This was expected due to the removal of the un-cross-linked polymer.[29] When the cross-linked P4VP film was extracted with chloroform, however, the film thickness increased by 31% in comparison to the initial spin-coated film. Samples that were first prepared and extracted in dichloromethane or *n*-butanol also showed ~30% increase in film thickness when the films were then extracted with chloroform.

In the presence of oxygen and light, chloroform is known to break down to phosgene, chlorine gas, and hydrogen chloride.[32] When the P4VP film was exposed to chloroform, the acidic hydrogen chloride would protonate the pyridyl groups, causing the cross-linked film to swell. The ability of chloroform to photodecompose was recently employed by Scolaro and co-workers to create porphyrin aggregates and crystals by UV irradiation of a chloroform solution of porphyrin.[33] The authors proposed that the rapid protonation of the porphyrin by photogenerated hydrogen chloride was responsible for the formation of the observed mesostructures. In a control experiment, the commercially acquired chloroform was purified by distillation. When the cross-linked P4VP films were extracted in distilled chloroform, no increase in film thickness was observed.

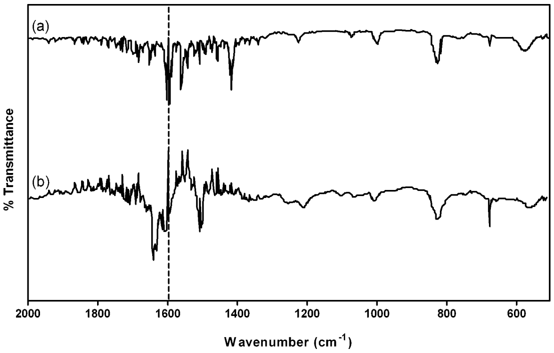

Figure 1. IR spectra of a P4VP film (a) before and (b) after extraction with chloroform. The dotted line is drawn at the location of the pyridyl 1597 cm^{-1} band which shifted to 1640 cm^{-1} after extraction in chloroform.

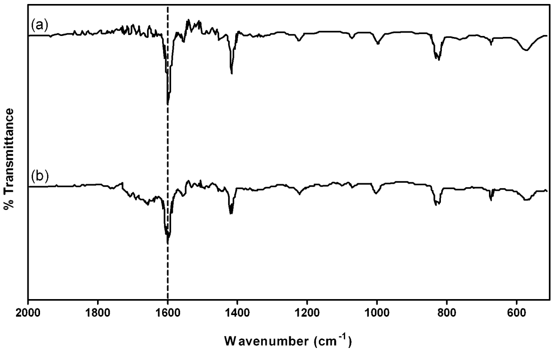

Figure 2. IR spectra of a P4VP film (a) before and (b) after extraction with dichloromethane. The dotted line was drawn at the frequency band of 1597 cm^{-1}.

The protonation of the pyridyl groups can be conveniently monitored by infrared spectroscopy. Frequency bands at 1597, 1558, and 1416 cm^{-1} are characteristic of the pyridyl ring-stretching modes[34,35] and are known to shift to higher frequencies upon hydrogen bonding or protonation. Hydrogen bonding between polar molecules and the pyridyl group in P4VP shifts these bands to higher frequencies by approximately 6 cm^{-1}.[36] In the studies of Takahashi et al., chloroform was included as a hydrogen donating solvent where a vibrational frequency shift of 4 cm^{-1} by chloroform was observed for the pyridyl group.[37] When the pyridyl groups are protonated, however, these three bands shift to higher frequencies by approximately 30−40 cm^{-1}.[36] Figure 1a is the IR spectrum of the spin-coated P4VP film showing the expected pyridyl ring-stretching vibrations at 1597, 1558, and 1416 cm^{-1}. When the film was extracted in chloroform, the bands shifted to 1640, 1613, and 1502 cm^{-1}, respectively (Figure 1b). These absorption bands are characteristic of the pyridinium group,[35] indicating that the pyridyl groups in the P4VP film had been protonated. When the cross-linked P4VP film was extracted in dichloromethane, however, shifts in these frequency bands did not occur (Figure 2).

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Table 2. Water Contact Angles of P4VP Films[a]

	chloroform	dichloromethane
initial spin-coated film	∼45°	∼55°
after UV and solvent extraction	∼5−10°	∼40°
after UV, solvent extraction, and 10-min soaking in triethylamine	∼41°	∼40°

[a] For samples that had been soaked in triethylamine, the films were rinsed with toluene and dried before the measurements were taken.

Table 3. Thicknesses of P4VP Films Exposed to Various Solvent Vapors[a]

	methanol	NH_3	HCl
initial spin-coated film	113.6 ± 0.4 nm	114.1 ± 0.2 nm	98.8 ± 0.6 nm
after extraction in dichloromethane	108.0 ± 0.5 nm	108.3 ± 0.8 nm	87.5 ± 0.3 nm
after vapor exposure for 2 h	108.4 ± 0.4 nm	108.6 ± 0.4 nm	132.6 ± 0.4 nm
increase in film thickness	−4.6%	−4.8%	36.9%

[a] Film thicknesses were measured at three different areas on each sample and were averaged.

When the cross-linked P4VP film was extracted in chloroform, the film became hydrophilic, as evidenced by a lower water contact angle compared to that of the spin-coated film (Table 2). The film was then treated with triethylamine, and the contact angle returned to roughly the original value. On the other hand, for films extracted in dichloromethane, such changes in the contact angle were not observed (Table 2). The decrease in water contact angle for the chloroform-treated film can be attributed to the protonation of pyridyl groups yielding the pyridinium groups, thus, making the film hydrophilic. When the film was treated with the basic triethylamine, it neutralized the charges and, therefore, made the film more hydrophobic.

To test the possibility of hydrogen bonding interactions leading to film swelling, the films were treated with ammonia and methanol. P4VP films that had been irradiated and extracted in dichloromethane were exposed to ammonia or methanol vapor for 2 h. The thicknesses of the resulting films, measured by ellipsometry, decreased slightly (Table 3). When the cross-linked P4VP film was exposed to hydrochloric acid vapor, however, the film thickness increased by ∼37% (Table 3). This is comparable to the extent of expansion when the film was extracted in chloroform (∼31%, Table 1). These results strongly suggest that protonation of the pyridyl groups by hydrogen chloride be responsible for the increase in film thickness.

The increase in film thickness was pH-dependent. Irradiated P4VP films extracted in dichloromethane were incubated in phosphate buffer solutions at varying pH for 10 min. The thicknesses of the resulting films were measured and were compared with the initially spin-coated film. The film thickness increased at a pH below 6, and the increase reached ∼33% at pH 3 (Figure 3). At a pH below 3, the film started to deteriorate in the buffer solution.

To further test the characteristics of these responsive thin films, a QCM setup was adopted. QCM crystals were coated with cross-linked P4VP films from dichloromethane, and the responsive properties were monitored in real time using a flow-through system. Buffers with pHs ranging from 1.0 to 7.0 were injected over the crystal surfaces, and the resulting frequency differences (Δf) were recorded. A typical frequency response graph is displayed in Figure 4, where a series of buffers has been injected sequentially from low to neutral pH. The response followed essentially the same pattern as for the ellipsometry studies, with increasing frequency shift at progressively lower pH. Upon injection of acidic buffers below 2.0, the frequency response was very high, amounting to approximately 2700 Hz. As a comparison, adsorption of a 28-nm-thick PS film on the crystal surface typically amounts to approximately 650 Hz.[30] The reason for this strong effect can only be related to the very high swelling of the polymers. When expanding, the water and/or ion absorption in the polymer film becomes higher, resulting in a decreased oscillation of the quartz crystal. To further test this hypothesis, several control experiments were performed. Thus, the salt effect was evaluated using injec-

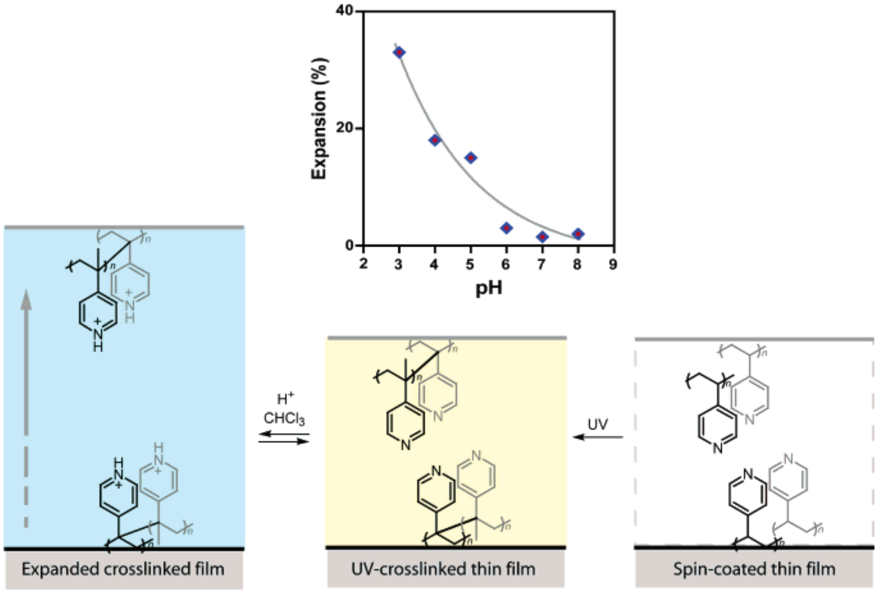

Figure 3. Schematic preparation of stimuli-responsive UV-cross-linked P4VP thin films, resulting in pH-dependent changes in film thickness measured by ellipsometry.

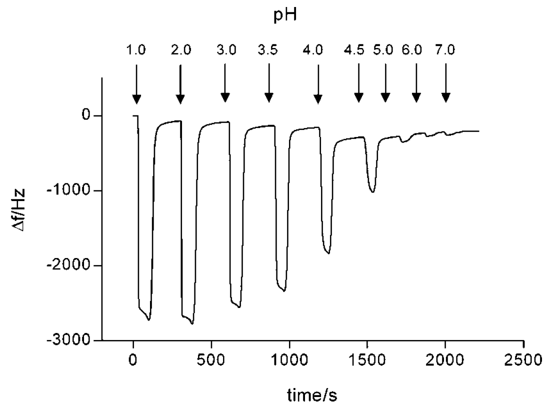

Figure 4. Frequency response effects from sequential injection of PBSs over P4VP-coated quartz crystals.

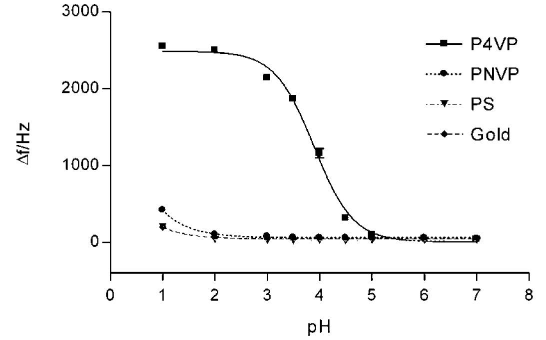

Figure 5. pH-dependent frequency responses of polymer-coated and uncoated gold-plated quartz crystals.

tions of either PBS or common phosphate buffer of the same pH over the entire pH range. The PBS contains a high concentration of chloride (138 mM), whereas this is absent in the phosphate buffer. No significant difference in frequency changes between the buffers could be recorded, indicating that NaCl/KCl was not specifically absorbed by the expanded layer. The negligible effect of the high concentration of chloride ions also suggests that phosphate counterions (10 mM) were nonessential for mass increase. Furthermore, the use of formate-buffered saline instead of PBS did not result in any differences in frequency response, indicating that the formate anions behave the same as the phosphate ions. These results suggest that water is absorbed into the layer, being the main reason for the high-frequency shifts. The cross-linked P4VP films behave like hydrogels where the charged polymer swells by incorporating solvent molecules to minimize Coulombic repulsion between the charged centers.

For comparison, three other surfaces were also tested with the QCM setup; uncoated gold crystals, PS-coated crystals, and PNVP-coated crystals (Figure 5). As expected, the bare gold surfaces were generally devoid of any mass change responses upon injection of buffers. However, at very low pH (pH 1.0) a small effect of unknown origin was recorded. Two polymer-coated surfaces were also tested, lipophilic PS-coated crystals and hydrophilic PNVP-coated crystals. In both cases, however, similar response patterns as for bare gold surfaces were observed, with no or very small frequency differences. The PS-coated crystals displayed essentially the same behavior as the bare gold surfaces, and a small frequency difference was recorded at pH 1.0. The PNVP crystals displayed a slight frequency response starting from pH 2.0. This effect is likely due to protonation of the amide nitrogen, the pK_a value for *N*-methylpyrrolidinone being close to zero.[38]

The successive pH response of the P4VP-coated crystals could be fitted to a standard pH titration model, allowing the estimation of the apparent dissociation constant (pK_{app}) of the P4VP films. The resulting apparent pK_{app} amounted to 3.9, which is in agreement with literature measurements on immobilized P4VP using standard pH meters.[39]

Conclusion

We report a simple method for the preparation of responsive coatings by spin-coating P4VP followed by UV irradiation. This procedure produced cross-linked P4VP thin films that swell upon protonation. The film is very sensitive, producing comparable responses from either the hydrochloric acid vapor or the minute amount of acid generated in chloroform. The films became hydrophilic upon exposure to chloroform or an acidic condition. Subsequent treatment with a base returned the films close to their original hydrophobicity. These conditions can be conveniently used to control the wettability of surfaces. Upon swelling in acidic buffered solutions, a large shift in the QCM resonant frequency was observed, with the greatest changes occurring in the pH range of 4.5−3. This large frequency shift is due to the absorption of water molecules into the swollen polymer for the protonated pyridyl groups to minimize charge repulsion. Sensors based on this design may be suited for detecting the threshold pH or pH changes. Moreover, these films are robust and have exhibited reversible and reproducible responses when tested continuously at varying pH. An attractive feature of this system is ease of preparation. The films are conveniently prepared simply by spin-coating followed by UV irradiation. No chemical derivatization is needed for either the substrate or the polymer. In addition, the film thickness and, thus, the extent of responses can be easily controlled.

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