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Ionization of covalent immobilized poly(4-vinylphenol) monolayers measured by ellipsometry, QCM and SPR

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ABSTRACT

Covalently immobilized poly(4-vinylphenol) (PVP) monolayer films were fabricated by spin coating PVP on perfluorophenyl azide (PFPA)-functionalized surfaces followed by UV irradiation. The pH-responsive behavior of these PVP ultrathin films was evaluated by ellipsometry, quartz crystal microbalance (QCM) and surface plasmon resonance (SPR). By monitoring the responses of these films to pH *in situ*, the ionization constant of the monolayer thin films was obtained. The apparent pK_a value of these covalently immobilized PVP monolayers, 13.4 by SPR, was 3 units higher than that of the free polymer in aqueous solution.

1. Introduction

Smart polymers [1–4], also known as environmentally sensitive [5], stimuli responsive [6,7], or intelligent polymers [8], undergo large and sharp property changes with small or modest changes in environmental conditions. Through the introduction of structural features and functional groups, polymer responses can be selectively controlled with changes in chemical (e.g., pH, salt concentration), physical (e.g., temperature, electromagnetic radiation, mechanical stress), or biochemical (e.g., antigen, enzyme, ligand) stimuli. In some cases, polymers are constructed in such a way that they can respond to multiple stimuli input [9,10]. The polymer output response may be swelling or collapsing, surface energy changes (hydrophilic to hydrophobic, and vice versa), drug release, conformational changes, dissolution or precipitation, and changes in physical properties such as optical and electrical parameters. These changes can be readily evaluated by sensitive analytical techniques such as ellipsometry, chemical force microscopy, light or fluorescence microscopy, QCM, and SPR. Polymer thin films having responsive surfaces have demonstrated a wide range of applications such as drug delivery, separation, sensors, and microscale actuators [8–11]. Over the past few decades, the need for new chemical and biological applications, such as pH sensors, controlled drug/gene delivery, personal care, industrial coatings, oil exploration, enzyme immobilization, and chemo-mechanical systems that require "smart" functional materials, has rapidly fueled the research development in pH-responsive polymers [12–15].

Polymer thin films can be generated by casting, dipping or spin coating a polymer solution on a solid substrate. Without covalent bonding between the polymer and the substrate, the polymer films are held to the surface by physisorption through non-covalent forces such as hydrogen bonding, hydrophobic interactions, and dipole interactions. These forces are often weak, unlike the more robust and stable covalent bonding that attaches polymers firmly to the surface. Covalently immobilized polymer films can be fabricated by either graft-to or graft-from methods. The graft-to method uses a functionalized polymer, which reacts with the substrate to form covalent bonds [16,17]. The graft-from method starts with a substrate that is functionalized with either a monomer or initiator. *In situ* polymerization generates polymer films directly on the surface with a relatively high grafting density [18–20].

Poly(4-vinylphenol) (PVP) is a weakly acidic polymer that releases protons in alkaline solutions. PVP has found a variety of applications, for example, as photoresist materials in semiconductor industries [21,22], as substitutes for water resistive wood adhesive [23], as dielectric materials for energy storage [24,25], and for enzyme recognition by altering polymer surfaces with biomolecules [26]. Very few studies have been dedicated towards characterizing responsive behavior of PVP ultrathin films to

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external environmental factors [27–30], and there have been no reported studies on the pH swelling behavior of PVP.

We have developed a simple method to photochemically immobilize polymer thin films on a substrate [31–35]. The method utilizes heterobifunctional perfluorophenylazide (PFPA) derivatives as coupling agents to allow for the covalent attachment of polymers to substrate surfaces by way of the CH insertion reaction of the photochemically generated perfluorophenyl nitrene [36]. In this case, the polymer does not need to be chemically derivatized in advance and can be used in its native form. In this work, we fabricated PVP thin films by spin coating PVP solutions onto PFPA-functionalized silicon wafers, followed by UV irradiation, to covalently attach a monolayer PVP film to the wafer surfaces. The pH responsive behavior of the PVP thin films was studied by ellipsometry, QCM and SPR. The apparent pK_a value of the immobilized PVP thin films was estimated.

2. Experimental

2.1. Materials

Poly(4-vinylphenol) (M_w *ca.* 20,000), methyl pentafluorobenzoate, sodium azide (99%), *N*-hydroxysuccinimide (98%), 3-aminopropyltrimethoxysilane (97%), and calcium hydride (90–95%) were used as received from Aldrich. 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDAC) was purchased from TCI America (Portland, OR). 2-Propanol (99.9% ACS certified), ethyl acetate (99.9%, HPLC grade), *n*-butanol (99.4%, ACS certified), acetone (HPLC grade), ethyl ether anhydrous (99.9%, ACS certified), methanol (99.9%, HPLC grade), hexane (99.9%, HPLC grade), chloroform (99.9%, HPLC grade), hydrogen peroxide (30 wt.%, ACS certified), and toluene (99.9%, ACS certified) were purchased from Fisher Scientific and were used as received. Ethanol (95%) was obtained from Aaper Alcohol and Chemical Co. (Shelbyville, KY). Water used was obtained from a Millipore Milli-Q system with at least 18.2 MΩ resistivity. Methylene chloride (DCM, 99.9%, HPLC grade, Fischer Scientific) was distilled from CaH_2 and stored under nitrogen. Silica gel (mesh size 100–200), sodium hydroxide (98.1%, ACS certified), sodium phosphate tribasic (98.9%, ACS certified), and sodium chloride (ACS certified) were used as received from Fisher Scientific. Sodium phosphate monobasic and sodium phosphate dibasic anhydrous were obtained from Mallinckrodt Chemical Works (St. Louis, MO). Sodium sulfate, anhydrous (99%) was acquired from EMD Chemicals (Gibbstown, NJ). Ammonium hydroxide (29.3% NH_3) was obtained from J.T. Baker Chemical Co. (Phillipsburg, NJ). $CDCl_3$ with 1% v/v TMS (99.8%) was purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA). Silicon wafers with a native oxide layer of 10–20 Å were purchased from WaferNet, Inc. (San Jose, CA). A 280 nm long path optical filter was acquired from Schott glass technologies, Inc. (Elmsford, NY). Gold-plated quartz crystals (10 MHz) were purchased from Attana AB (Stockholm, Sweden). *N*-(3-Trimethoxysilylpropyl)-4-azido-2,3,5,6-tetrafluorobenzamide (PFPA-silane) [37] and 2,2′-dithioethyl bis(4-azido-2,3,5,6-tetrafluorobenzoate) (PFPA-disulfide) [33,38] were synthesized according to previously developed procedures. The purified compounds were confirmed by NMR spectroscopy acquired on a Bruker Avance 400 MHz spectrometer.

2.2. Covalent immobilization of PVP thin films

Silicon wafers (1 cm × 1 cm) were cleaned with piranha solution (7:3 v/v 98% sulfuric acid/35% hydrogen peroxide) for 1.5 h at 80–90 °C (Caution: care should be taken when handling the piranha solution as it reacts violently with organic compounds). The wafers were then washed thoroughly with boiling water for 1 h and dried under a stream of nitrogen. The cleaned wafers were soaked overnight in a solution of PFPA-silane in toluene (1.5 mg/mL), and the samples were rinsed thoroughly in toluene several times and dried under nitrogen. The wafers were then cured for 24 h under ambient conditions. A solution of PVP in ethyl acetate (10 mg/mL) was spin coated on a P6204 spin-coater (Specialty Coating Systems, Indianapolis, IN) at 2000 rpm for 60 s onto the cured wafers. The spin coated samples were then exposed to a 450W medium-pressure Hg lamp (Hanovia, ACE Glass Incorporated, Vineland, NJ) in the presence of a 280 nm optical filter on the samples for 5 min under ambient conditions. The intensity of the lamp at the sample location was measured to 2.5 mW/cm^2 using a 254 nm sensor. The 5 min irradiation time includes a 2 min warm-up of the lamp to reach its full intensity. The irradiated samples were left in ethyl acetate for 5 h to remove the unbound polymer film and then dried under a stream of nitrogen.

2.3. Treatment of PVP films with solutions of varying pH

The pH-responsive studies were carried out in two different types of solutions: 10 mM phosphate buffer and dilute NaOH solutions. Phosphate buffer solutions of varying pH were prepared by varying the mass ratio of phosphate salts (Na_2HPO_4, NaH_2PO_4, and Na_3PO_4) in 100 mL of water. The NaOH solutions of varying pH were prepared by diluting the NaOH solution with water. The NaOH solutions were used immediately after they were prepared. The PVP thin films were soaked in solutions of varying pH (7, 8, 9, 10, 11, 12, and 13) for 5 min, and dried under a stream of nitrogen.

2.4. Ellipsometry measurements

Film thicknesses were measured on a Gaertner model L116A ellipsometer with a He/Ne laser at an incident angle of 70°, and also on a model LSE Stokes ellipsometer (Gaertner Scientific Corporation, Skokie, IL) with a 6328 Å He/Ne laser measuring beam at a 70° incidence angle. Refractive index values of 1.465 (SiO_2), 1.600 (PVP), 1.503 (PFPA-silane) were used to determine the film thicknesses. The final film thickness value was obtained by taking the average of three readings on different sample surfaces.

2.5. QCM measurements

Samples for QCM studies were prepared on gold-plated 10 MHz quartz crystals. The surfaces of the crystals were initially cleaned by immersion into a mixture of 1:1:3 v/v/v hydrogen peroxide (30%), ammonium hydroxide (29.3%) and distilled water, and heating at 80 °C for 5 min. The cleaned crystals were thoroughly rinsed several times in distilled water and dried under a stream of nitrogen. The cleaned crystals were soaked in a 14 mM solution of PFPA-disulfide in distilled dichloromethane (DCM) at room temperature in the dark overnight following a previously reported method [33]. The crystals were rinsed several times with DCM to remove excess PFPA-disulfide and dried under a stream of nitrogen. A solution of PVP in ethyl acetate (10 mg/mL) was spincoated at 2000 rpm for 60 s onto the PFPA-functionalized crystals. The samples were then UV-irradiated for 5 min in the presence of 280 nm optical filter with 450 W medium pressure mercury lamp. Finally, the samples were soaked in ethyl acetate for 5 h to remove the un-attached polymer and dried under a stream of nitrogen. The crystals were mounted in the flow-through QCM system on an Attana 100 instrument (Attana AB, Stockholm, Sweden), and the solution flow rate was controlled to 150 μL/min. Measurements were taken after 30 s of exposure to the buffer solution (10 mM) of desired pH. The solution was then switched to pH 7 phosphate buffer to condition the sample before the next buffer solution was introduced. The frequency data were collected at ambient temperature.

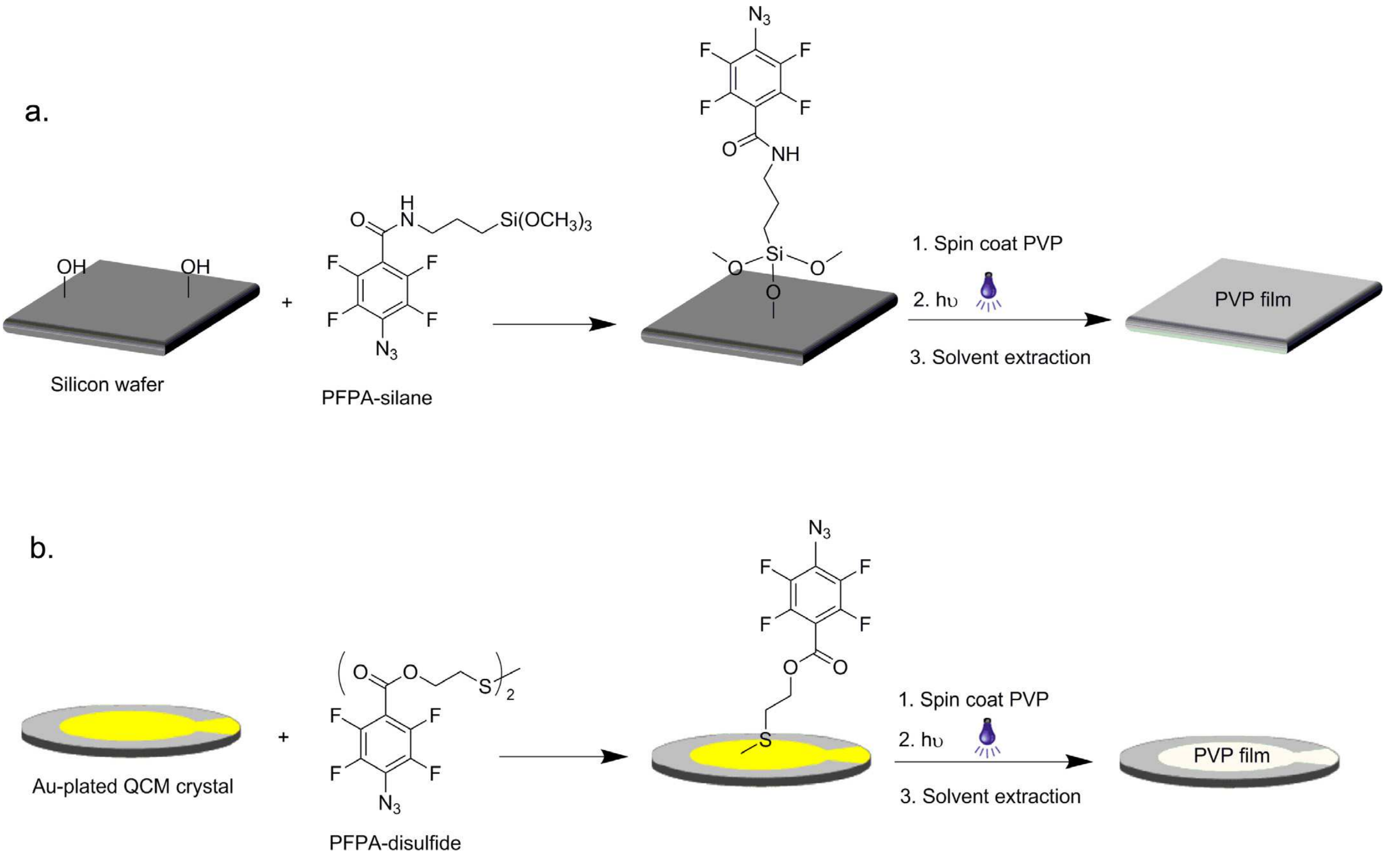
2.6. SPR measurements

Gold substrates used for SPR measurements were 18 × 18 mm SF 10 glass slides, onto which 2 mm thick Ti followed by 45 nm thick gold films were deposited using an electron beam evaporator. Immediately before the fabrication of the PVP films, the gold-coated SPR chips were cleaned in the piranha solution for 30 s. The substrates were then thoroughly washed with boiling water 3 × 20 min each, and dried under a stream of nitrogen. The gold-coated SPR chips were soaked in a solution of PFPA-disulfide in ethanol (5.1 mM) for 3 h, rinsed thoroughly with ethanol to remove excess PFPA-disulfide and dried under a stream of nitrogen [33,38]. A solution of PVP in ethyl acetate (10 mg/mL) was spin-coated at 2000 rpm for 60 s onto the PFPA-functionalized SPR chips. UV irradiation was executed on an OAI 200 mask aligner (OAI, San Jose, CA) using a 260 nm Hg/Xe UV lamp for 50 s. The intensity of the lamp at the sample location was measured to 34 mW/cm^2 using a 260 nm light sensor. The irradiated samples were soaked in ethyl acetate for 5 h to remove the unbound polymer. SPR experiments were performed using an SPR imager II (GWC technologies, Madison, WI), and data were acquired using the associated software. During the SPR experiments, the sample chip was first treated with the running buffer (pH 7) until a stable baseline was reached. The buffer solutions with varying pH were then introduced sequentially. Data were acquired after the signals were stabilized, which normally took 2–8 min. The flow rate was maintained at 100 μL/min throughout the experiment.

3. Results

Covalently immobilized PVP thin films were fabricated following the procedures shown in Scheme 1a. Silicon wafers were first treated with PFPA-silane to introduce PFPA on the wafer surface. PVP was then spin-coated on the surface followed by irradiation using a medium pressure Hg lamp. Irradiation of PVP by deep UV results in the formation of quinone-type structures [39], which are no longer electrolytes and would not have pH responsive properties. Deep UV would also crosslink the polymer [39,40]. To avoid these issues, a 280 nm optical filter was placed on the PVP films during irradiation to remove the deep UV from the light source. The covalent immobilization of PVP was accomplished through CH insertion of the photogenerated singlet perfluorophenyl nitrene to the adjacent polymer chains [31,37,41]. A final solvent extraction in ethyl acetate removed the unbound polymer, after which the PVP thin film remained covalently attached to the wafer surface. The thickness of the films was measured by ellipsometry to be 3.8 ± 0.1 nm. This is consistent with the immobilization chemistry that only the polymer chains in close proximity of the surface PFPA groups would be attached. The un-reacted polymer was removed by solvent extraction, leaving only a monolayer of the polymer on the surface.

The pH-responsiveness of the immobilized PVP thin films was first tested using ellipsometry. As the films swell, the thicknesses of the films increase, which can be monitored by ellipsometry [42]. Phosphate buffer solutions were used to treat the PVP thin films. However, after soaking the PVP films in the buffer solutions and drying, white solids remained on the film surface, which compromised the thickness measurements. Dilute NaOH solutions were then used to treat the PVP films. The solutions were adjusted to different pH and the film thicknesses were measured after the films



Scheme 1. Photochemical immobilization of PVP thin films on (a) silicon wafer, (b) Au-plated QCM crystal.

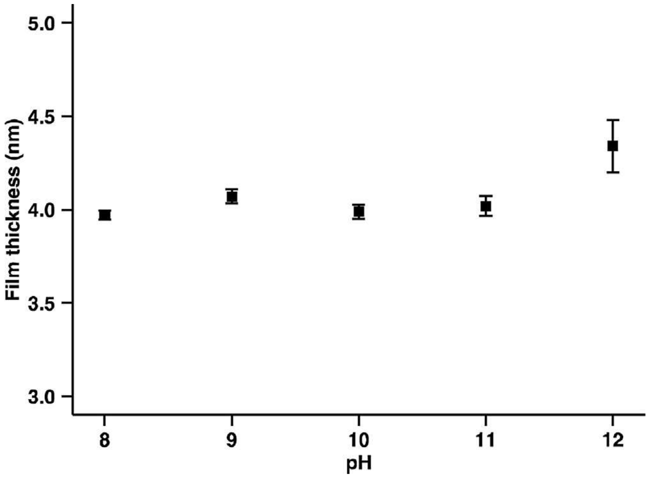


Fig. 1. Thicknesses of PVP films after treatment with NaOH solutions of varying pH.

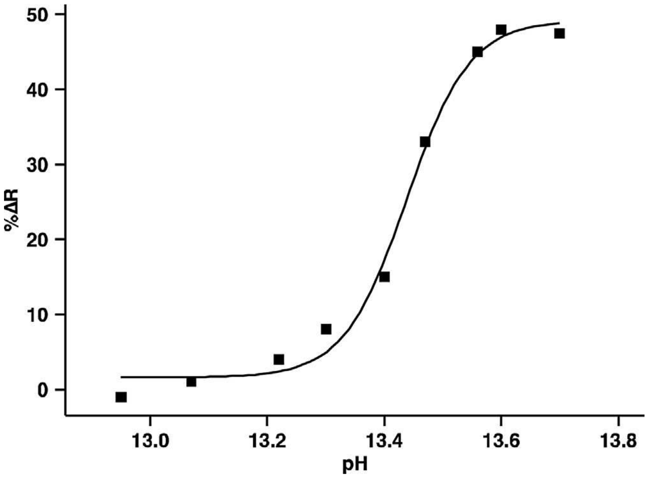


Fig. 3. Percent change in reflectivity (%ΔR) of PVP thin films treated with phosphate buffer solutions of varying pH.

were dried with nitrogen. Results in Fig. 1 showed no significant changes in film thickness from pH 8–11. An increase in film thickness, about 8%, was observed at pH 12. When the films were treated with NaOH solution at pH 13, the films became tarnished and no measurement was possible by ellipsometry.

QCM studies were next conducted. Since QCM generally utilizes gold-plated quartz crystals, the PVP thin films were prepared using PFPA-disulfide as a coupling agent following a previously developed protocol (Scheme 1b) [33]. The gold-plated quartz crystals were first treated with PFPA-disulfide. PVP was then spin-coated, irradiated in the presence of a 280 nm optical filter, and the solvent extracted to remove unattached polymer. The samples were then placed in a QCM flow-through cell, and buffer solutions of varying pH were introduced. The results showed no significant change in the resonance frequency up to pH 11 (Fig. 2). The signal decreased slightly at pH 12, and at pH 13 and beyond, large decreases in the resonance frequency were observed.

SPR analysis was performed to further corroborate the pH response behavior of PVP thin films. The SPR technique measures the refractive index change of the dielectric layer on the gold surface. For the GWC SPR imager II used in this work, the responses are presented as percent change in reflectivity (%ΔR). In this work, an *in situ* flow-through system was used to monitor in real time the %ΔR values when the PVP thin film was treated with solutions of varying pH. Since SPR chips are gold-coated, the PVP thin films were immobilized on SPR chips following the same procedure as those on QCM chips (Scheme 1b). In the SPR experiment, the sample was inserted in the flow-through chamber, and pH 7 phosphate buffer was introduced until a stable baseline was obtained. Phosphate buffer solutions of varying pH were then introduced, and %ΔR was recorded after the signals were stabilized, which typically took 2–8 min. At pH < 13, no significant change in %ΔR was observed. The percent change in reflectivity started to increase from pH 13.1, and levelled off at pH > 13.6 (Fig. 3).

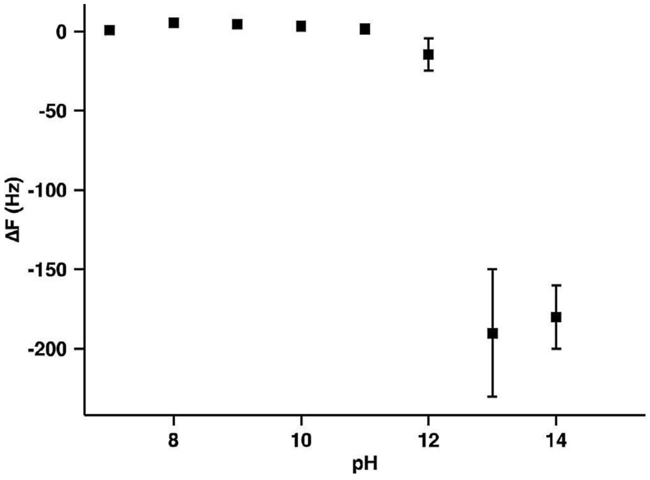


Fig. 2. QCM frequency responses (ΔF) of covalently attached PVP films to phosphate buffer of varying pH.

4. Discussion

PVP is a weak polyprotic acid, and behaves as a weak polyelectrolyte in aqueous solutions. Polyprotic acids contain multiple acidic protons, and can dissociate sequentially with unique acid dissociation constants for each proton, designated as pK_1, pK_2, pK_3 and so on. For weak polyprotic acids such as PVP, their acidity is often expressed as p$K_{a(app)}$, i.e., the apparent acid dissociation (or ionization) constant which reflects the overall degree of ionization of the polymer. The ionization constant is an important parameter in understanding the dissolution behavior of polyelectrolytes. In semiconductor and photoresist applications, the pK_a values aid the selection of developer solutions as well as the design of devices based on these polyelectrolytes.

PVP as a weak polyprotic acid exists in a protonated state at low pH and a deprotonated state at high pH. At the deprotonated state, the phenol groups in PVP film are converted to phenoxide anions which repel each other. These electrostatic interactions generate repulsive forces that cause the film to swell. In this work, the extent of swelling was monitored by three different techniques: ellipsometry, QCM and SPR. In the ellipsometry measurements, the film thickness started to increase at pH 12 but the films became tarnished at pH 13. The QCM and SPR techniques allowed for real-time monitoring of the changes in the polymer thin films as they underwent swelling. The QCM frequency shift had no significant change up to pH 11. It started to decrease at pH 12, and a large change was observed at pH 13 and beyond (Fig. 2). Larger pH values were also associated with larger variances of the data points. The SPR signal, presented as the percent change in reflectivity, %ΔR, underwent a substantial change in the range of pH 13.0–13.6 (Fig. 3). The correlation between the SPR signals and the solution pH results in a titration curve, from which, the acid dissociation (or ionization) constant (K_a) can be derived from the acid-base equilibrium equation as the inflection point on the curve when pH = pK_a. By fitting the data to a logistic function, the apparent acid dissociation constant p$K_{a(app)}$ of the PVP thin film was estimated to be 13.4. This value was similar to the value of p$K_a \geq 12.5$ measured for a phenol-terminated momolayer on silicon wafer [43].

The transition pH ranges obtained from the QCM and SPR analyses differ by about 1 unit. The difference in the results is likely due to the fundamental physical properties that each technique measures. QCM measures the change in frequency of the quartz crystal sensor as a function of the mass on the quartz crystal. The mass-frequency relationship, i.e., the Sauerbrey equation, applies to rigid and uniform thin layers. In our case, the frequency changes are probably caused by the swelling of PVP thin films resulting from the absorption of water/salt into the films. In addition, the swollen films are likely hydrogels rather than rigid films, and therefore, large deviations are expected in this case. In the SPR technique, the surface plasmon wave propagating at the interface between the medium and Au is a function of the dielectric constant of Au and the refractive index of the medium. The swelling of PVP films causes the change in the dielectric constant on the Au surface, which are measured by SPR. With samples firmly fixed in a liquid cell, the films were stable and the SPR signals could be monitored *in situ* with high reproducibility.

Flanagin et al. reported the pK_a of PVP (degree of polymerization = 20) to be between 10 and 10.5 [44]. In our study, the p$K_{a(app)}$ values of immobilized PVP thin films measured by SPR are 3 units higher than that of the bulk polymer measured in the aqueous solutions. The higher p$K_{a(app)}$ value obtained from our system implies the increased stability of the PVP thin film in the protonated state. This can be caused by the hydrogen bonding between the phenol/phenoxide groups in the film, making the protons bond more tightly in the film. Furthermore, deprotonation of a phenol group adjacent to deprotonated phenoxide anions is energetically more difficult than depronating a free phenol due to the charge repulsion of neighboring phenoxide groups. In addition, a Hill coefficient of $\sim$8 was obtained from the fitting curve in Fig. 3, indicating a higher extent of cooperativity among multiple proton sites.

The derivation of the acid-base equilibrium from the bulk solutions has been observed in other organic monolayer systems. For example, the pK_a values of ω-carboxyl alkanethiol on gold were reported to be 0.5–4.5 units larger than that of the free molecule in solution. For the monolayer of $HS(CH_2)_2COOH$ on gold, Bard et al. obtained a pK_a of 7.7 using AFM force measurement [45], and a pK_a value of 6 was reported by Shimazu using QCM [46]. Kakiuchi and coworkers measured a pK_a of 8 for the same system using double-layer-capacitance titration [47]. When the authors increased the number of methylene units in ω-carboxyl alkanethiol to 4, 6, and 10, the pK_a value increased to 8.7, 9.2 and 10.3, respectively. The increase in the ionization constant was attributed to the repulsive forces between the deprotonated groups, the hydrogen bonding interactions, and the heterogeneous environment with a lower dielectric constant in the SAM.

5. Conclusions

In summary, covalently immobilized PVP thin films were conveniently prepared by a simple photocoupling reaction of surface-tethered PFPA with PVP. The films exhibited pH-response behavior, which were monitored by ellipsometry, QCM, and SPR. All results showed the swelling of PVP films at pH > 12, and no obvious swelling between pH 7 and 12. Using SPR in conjunction with a flow through system, the apparent pK_a value of the immobilized PVP monolayer was successfully determined. The result was about 3 units higher than the pK_a value of the bulk polymer in aqueous solution. This can be accounted for by the increased electrostatic repulsion between the ionized phenoxide groups when the polymer is immobilized on the surface.

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Supplementary Information

Supplementary data related to this article can be found at doi:

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