

Fabrication of photoactive self-assembled ultra-thin films from diazoresin and poly(4-vinylphenol) via H-bonding

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Using a self-assembly technique, a type of photoactive multilayer film was successfully fabricated from diazoresin (DR) and poly(4-vinylphenol) (PVPh) followed by UV irradiation. The driving force of the self-assembly was confirmed to be the H-bonding interaction between the diazonium group ($-\text{N}_2^+$) of DR and the phenolic hydroxy group ($-\text{Ph}-\text{OH}$) of PVPh. A linkage conversion from an H-bond to a covalent bond takes place following the decomposition of the $-\text{N}_2^+$ group when the multilayer film undergoes UV irradiation. As a result, the stability of the film towards etching by polar solvents increases dramatically.

Since Decher's pioneering work, the layer-by-layer self-assembly technique used to form organized ultra-thin films has been investigated extensively and reviewed recently in several publications.¹ This technique, which depends on the Coulombic attraction between oppositely charged polymers or multi-ionic components, has attracted more and more attention,^{2–11} and has been applied to prepare unique membranes with desired components such as biomolecules,⁶ chromophoric molecules,⁷ dendritic molecules,⁸ polymer dyes,⁹ conductive polymers¹⁰ and so on.¹¹

The mechanism of film formation and the inner structure of the films have also been developed.¹² Furthermore, the weak attraction of the H-bond has also been used to fabricate molecular-level multilayer films. Stockton and Rubner¹³ reported a number of multilayer ultra-thin films between polyaniline and various water-soluble polymers including poly(vinyl pyrrolidone) (PVP), poly(vinyl alcohol) (PVA), poly(acrylamide) (PA) and poly(ethylene oxide) (PEO) via H-bonding interactions, and Zhang *et al.*,¹⁴ almost at the same time, reported a polyacrylic acid (PAA)–PVP multilayer film formed via an H-bonding interaction.

However, both the Coulombic and the H-bonding attractions are too weak to prevent the etching of the film by polar solvents. Recently, we reported the formation of photoactive multilayer films from DR and anionic polyelectrolytes or phenol–formaldehyde resin, and verified that the films are very stable towards polar solvents after UV irradiation.¹⁵

Poly(4-vinylphenol) (PVPh) has long been an attractive polymer due to its availability in polymer blends¹⁶ and its ability to form H-bonds with many kinds of proton-donating polymers. In this article we report a photoactive ultra-thin film from DR and PVPh and confirmed that the film will change its ionic bond to a covalent bond when it undergoes UV irradiation. As a result, the stability of the film towards polar solvents increases dramatically.

Experimental

Syntheses

4-Methoxystyrene (MS) was synthesized with 4-methoxycinnamic acid (MCA) according to ref. 17 with some modifications.

Preparation of MCA. Anisaldehyde (40.8 g, 0.3 mol), malonic acid (60 g, 0.58 mol), dry pyridine (120 ml) and piperidine (3 ml) were mixed in a 500-ml three-necked bottle equipped with a thermometer and a condenser. The mixture was heated for 2 h at 100 °C, then refluxed gently for 15 min at 120 °C. The mixture, while still hot, was poured into 175 ml of concentrated hydrochloric acid and 300 g of chopped ice under stirring. The precipitate was filtered, washed with 25 ml of 10% hydrochloric acid and water, then dried. Yield: 52.0 g (97.4%); mp: 183–185 °C.

Preparation of MS. MCA (35.6 g, 0.2 mol), anhydrous copper sulfate (3.6 g), hydroquinone (2 g) and dry quinoline (140 g) were charged into a 200-ml three-necked bottle equipped with a thermometer and a stirrer. The mixture was heated to reflux for 30 min; the fraction between 190 and 210 °C was collected by distillation, washed with 150 ml of 10% sulfuric acid and then with water, then dried with anhydrous magnesium sulfate. It was then purified chromatographically on a 200 mesh silica gel column using CH_2Cl_2 as elution agent. The colorless part of the eluent was collected and the CH_2Cl_2 was evaporated, leaving MS as a colorless liquid. Yield: 7.8 g (29.1%). ¹HNMR (200 MHz, CDCl_3) δ : 3.49 (3H, OCH_3); 6.6–7.4 (4H, aromatic); 5.65 (1H, $=\text{CH}$); 5.56 (2H, $=\text{CH}_2$). Anal. found (calc.) for $\text{C}_9\text{H}_{10}\text{O}$ (%): C 79.36 (80.59); H 7.68 (7.46); O 12.43 (11.94).

Preparation of PVPh. PVPh was prepared by elimination of the methoxy group of PMS by treating with trimethylsilyl iodide at room temperature.¹⁸ PMS was prepared by free radical polymerization of MS using AIBN as the initiator in bulk. The number- and weight-average molecular weights of PMS were determined by gel permeation chromatography to be 7.7×10^4 and $10.8 \times 10^4 \text{ g mol}^{-1}$. From the IR spectrum and the elemental analysis of PMS it is believed that there are no methoxy groups in PVPh.

Preparation of DR. Diazoresin was prepared in our laboratory from diphenylamine-4-diazonium salt and paraformaldehyde according to ref. 19: $\eta_{\text{p/c}} = 0.12 \text{ dl g}^{-1}$, $M_n \sim 2.1 \times 10^3 \text{ g mol}^{-1}$.

Film preparation and characterization

DR was dissolved in methanol at a concentration of 0.2 mg ml^{-1} , PVPh was dissolved in acetone at 0.5 mg ml^{-1} . A

quartz wafer, which was treated with 30% H_2O_2 and concentrated sulfuric acid (3 : 7 in volume) at 100°C for 0.5 h, was used as the substrate. The substrate was immersed first in the PVPh acetone solution for 5 min, then rinsed with acetone and dried, then immersed in the methanol solution of DR for 5 min, followed by rinsing with methanol and drying. In each immersion cycle, a bilayer of PVPh-DR was deposited on both sides of the substrate.

UV-vis spectra recorded on a Shimadzu 2100 spectrophotometer were used to monitor the layer-by-layer deposition. The photoreaction occurring in the film was also determined spectrometrically after UV irradiation. IR spectra were obtained on a Bruker Vector 22 FTIR spectrometer of a DR-PVPh film fabricated on a CaF_2 wafer.

Results and discussion

Fig. 1 shows the absorbance of the PVPh-DR multilayer film increasing with bilayer number. The continuous increase in absorbance at 380 and 240 nm, which are the characteristic absorptions of the $-\text{N}_2^+$ and phenyl groups, respectively, indicates that DR and PVPh were successfully deposited on the quartz wafer.

The driving force for layer-by-layer deposition should be ascribed to a hydrogen bond rather than an electrostatic attraction because neither PVPh nor DR is dissociated in acetone or in methanol solution. Although the diazonium group ($-\text{N}_2^+$) is a cation, its two nitrogen atoms are not equivalent. One (connected to the phenyl moiety) is charge deficient and in equilibrium with the counter-ion HSO_4^- , the other is charge rich. Therefore, it is reasonable to consider that the diazonium group can form a hydrogen bond with a strong H-donor such as the phenolic hydroxy group present in PVPh, as shown in Scheme 1.

In order to verify the H-bonding nature in the film structure, a 50-bilayer film from PVPh and DR was fabricated on a CaF_2 wafer to measure the IR spectrum of the film directly. The stretching vibration of the $-\text{N}_2^+$ group of the DR-PVPh film is at 2157 cm^{-1} (Fig. 2, curve a); it is 9 wavenumbers lower than in DR itself, which has the stretching vibration of the $-\text{N}_2^+$ group at 2166 cm^{-1} .^{15a}

Fig. 2 shows the IR spectra of the PVPh-DR film before and after UV irradiation. The 1584 cm^{-1} bond should be attributed to vibration of the phenyl nucleus conjugated with an unsaturated group; it shifts to 1605 cm^{-1} , the normal absorption of the phenyl group,²⁰ after UV irradiation. The 1369 cm^{-1} band is assigned to the in-plane bending vibration of O-H after formation of the H-bond;²⁰ it disappears after UV irradiation. This is further evidence of formation of an H-bond between $-\text{N}_2^+$ and HO-Ph.

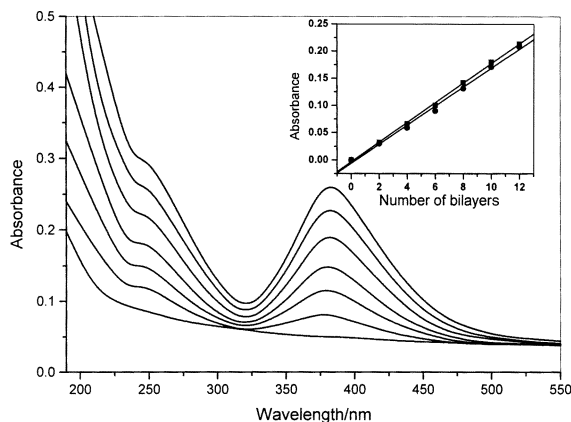
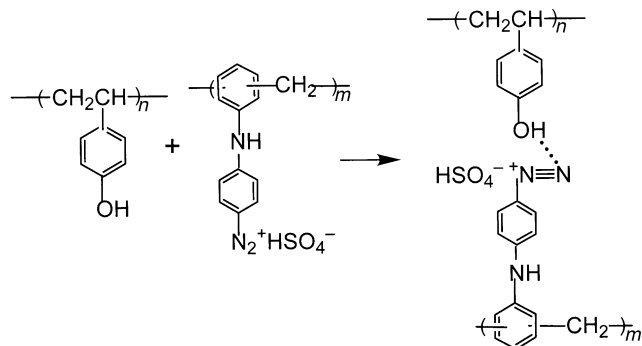


Fig. 1 The UV-vis spectra of PVPh-DR multilayer films with different numbers of bilayers. Bilayer number (bottom to top): 0, 2, 4, 6, 8, 10, 12. The inset plot indicates the linear relationship between absorbance and bilayer number: (■) at 240 nm; (●) at 380 nm.



Scheme 1 PVPh and DR form a complex via H-bonding interaction.

The multilayer film from PVPh and DR is photoactive. With decomposition of the diazoresin group under UV irradiation, the absorbance at 380 nm decreases gradually. Fig. 3 shows the change in the UV-vis spectra of a 12-bilayer film of PVPh-DR with irradiation time. It shows that the diazonium group decomposes quickly and almost completely in 5 min under the experimental conditions. The insert plot of Fig. 3 shows that the decomposition follows first-order reaction kinetics.

The photoreaction taking place in the PVPh-DR film under exposure to UV light may be similar to that occurring in a film of DR and poly(sodium acrylate) (PSA),²¹ in which the electrostatic $-\text{C}-\text{N}_2^+\text{OOC}^-$ bond converts to an ester

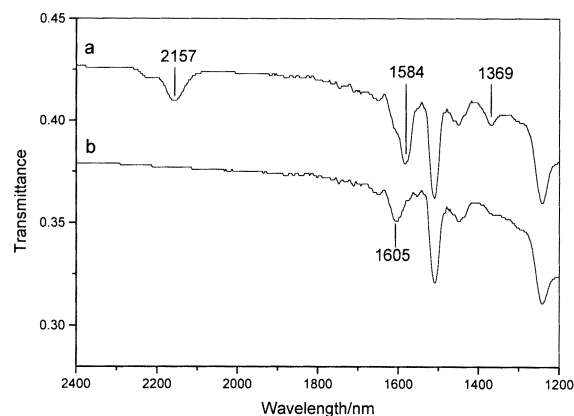


Fig. 2 FT-IR spectra of PVPh-DR multilayer film: (a) before irradiation; (b) after irradiation. Irradiation intensity (at 360 nm): $230\text{ }\mu\text{W cm}^{-2}$; irradiation time: 10 min.

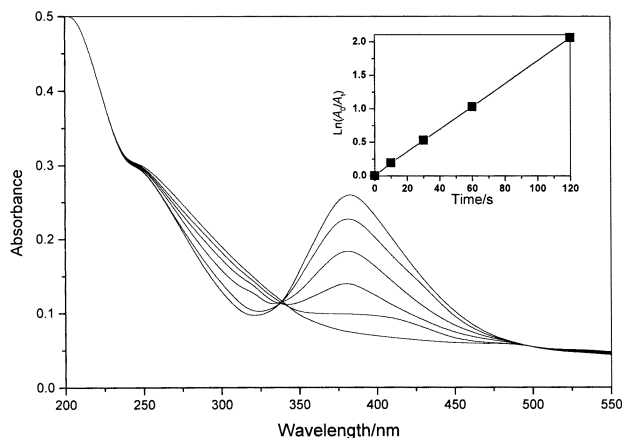
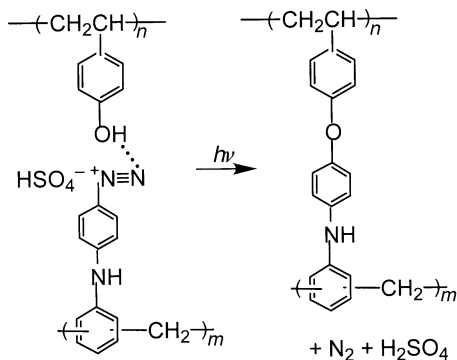


Fig. 3 The UV-vis spectra of a PVPh-DR multilayer (12 bilayers) film with different irradiation times (from top to bottom at 380 nm): 0, 10, 30, 60, 120, 300 s. Irradiation intensity (at 360 nm): $230\text{ }\mu\text{W cm}^{-2}$.



Scheme 2 One of the photoreactions taking place in a PVPh-DR multilayer film, in which the H-bond converts to an ether bond.

bond, $-\text{COOC}-$, under UV irradiation. The hydrogen bond, $-\text{ph}-\text{N}_2^+\cdots\text{HO}-\text{Ph}-$, in the DR-PVPh film structure converts to a covalent ether bond, following decomposition of the $-\text{N}_2^+$ group, represented in Scheme 2.

The reaction of the intermediate (cation or free radical) formed from decomposition of the $-\text{N}_2^+$ group is rather complex.²² It can react with $-\text{OH}$ to form an ether bond or it can react with the phenyl moiety of PVPh *via* electrophilic substitution to form a C-C bond, and so on. However, it is difficult to detect these bonds directly in the film structure because the film thickness is only of nanometre magnitude.

After UV irradiation, the stability of the film towards etching by polar solvents increases dramatically. The un-irradiated film was dissolved completely after immersion in DMF for 5 min, but the irradiated film showed no changes after immersion in DMF for 24 h; that is, the absorbance of the irradiated film did not exhibit any decrease after immersion in DMF as compared with that before immersion (hence the UV-vis spectra have been abbreviated). This should provide evidence that under UV irradiation the H-bonding structure, which dissociates easily in strong polar solvents, converts to a covalent bond.

Conclusion

In conclusion, a multilayer ultra-thin self-assembled film was fabricated from diazoresin (DR) and poly(4-vinylphenol) (PVPh) *via* H-bonding interactions. Under irradiation by UV light the H-bonds between the layers of the films convert to covalent bonds. The stability of the film towards etching by polar solvents increases strongly after UV irradiation.

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