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Polymer 48 (2007) 1455–1458
polymer
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Polymer Communication

Covalently cross-linked multilayer thin films composed of diazoresin and brilliant yellow for an optical pH sensor

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Received 2 November 2006; received in revised form 24 January 2007; accepted 30 January 2007
Available online 2 February 2007

Abstract

The multilayered thin films composed diazoresin (DR) and brilliant yellow (BY) were fabricated by a layer-by-layer (LbL) deposition technique, and the ionic bonds between diazonium ion in DR and sulfonate residues in BY were converted to covalent bonds by UV light irradiation. The cross-linking between BY and DR prevented BY from desorption even in a pH 13 solution. The cross-linked $(DR/BY)_{10}DR$ film exhibited pH-dependent absorption spectra in pH 9–13, and the response was repeatable and quick. The pH response time of the films was within a few seconds upon change from pH 9.0 to 13.0, and *ca*. 40 s upon change from pH 13.0 to 9.0.

Keywords: Diazoresin; Layer-by-layer; pH sensor

1. Introduction

A layer-by-layer (LbL) deposition technique has attracted much attention because of such advantages over the other methods for thin film fabrication as ease of fabrication and a wide application [1–7]. This method is generally based on repeated adsorptions of two components that have opposite charges. The components are dissolved in solution separately, and a solid substrate is alternately immersed in the two solutions. Polymeric materials are commonly used for the LbL deposition. Recent reports, however, show that other materials are adaptable to the LbL deposition [8–11]. The combinations of low-molecular weight compounds and polymer are the subjects of growing interest because functionalities of low-molecular weight compounds can be introduced directly in the solid surface [12–16].

pH indicators have been immobilized on the surface of optic devices for the applications to optical pH sensors [17–21]. In this context, we have previously fabricated LbL films composed of brilliant yellow (BY) and poly(allylamine) (PAA) [22]. The PAA/BY film showed a drastic change in the UV–visible absorption spectra depending upon the shift of pH of the solution. Thus, the PAA/BY film exhibited pH-dependent absorption spectra in pH 5–10. A drawback of the film was that BY molecules were desorbed from the film at high pH as a result of a loss of the positive charges in PAA.

In this study, we have used diazoresin (DR) to prevent BY from desorption. DR is a photosensitive polycation, and the ionic bonds between diazonium ion in DR and sulfonate residues in BY may be converted to covalent bonds by UV light irradiation (Fig. 1) [23–29]. The stability of the cross-linked DR/BY film was investigated in high pH solution. Finally, we evaluated the cross-linked DR/BY films as an optical pH sensor.

2. Experimental section

2.1. Materials

BY was obtained from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). DR (condensation product between 4-diazodiphenylamine and formaldehyde, isolated as phosphate) is kindly supplied by Respe Chemical Co., Ltd. (Tokyo, Japan). All other chemicals used in this study were of the highest grade available and were used without further purification.

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doi:10.1016/j.polymer.2007.01.065

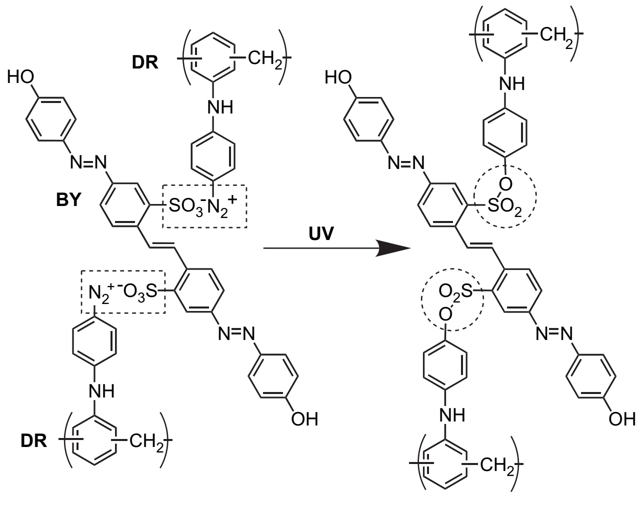

Fig. 1. Photochemical reaction between DR and BY.

2.2. Apparatus

UV–visible absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer (Kyoto, Japan). The pH value was monitored by DKK IOL-50 (Tokyo, Japan). UV light irradiation was carried out with Handy UV lamp SLUV-6 (As One Co., Osaka, Japan).

2.3. Preparation of the cross-linked $(DR/BY)_{10}DR$ film

Multilayer films were prepared on the surface of a quartz slide (5 × 1 × 0.1 cm). The quartz slide was first treated in dichlorodimethylsilane (5% solution in toluene) overnight at room temperature to make the surface hydrophobic and then the slide was washed with acetone and distilled water. To prepare DR/BY film, the hydrophobic quartz slide was immersed in a DR solution ($0.10\ mg\ mL^{-1}$ in 150 mM NaCl aqueous solution) for 5 min to deposit the first DR layer. It was then immersed in water for 5 min to remove excess DR and then was subsequently immersed in a BY solution (0.20 mM in 150 mM NaCl aqueous solution) for 5 min to deposit BY, and then rinsed in water for 5 min. These processes were repeated to build up multilayer films. The film thus prepared was exposed to UV light (irradiation intensity: $1112\ \mu W\ cm^{-2}$ at 365 nm). Following the UV irradiation, the cross-linked $(DR/BY)_{10}DR$ film was immersed in pH 13 solution to remove unreacted BY.

2.4. pH response of the cross-linked $(DR/BY)_{10}DR$ film

The cross-linked $(DR/BY)_{10}DR$ film was used for the evaluation of pH response. The film was cross-linked by UV irradiation for 20 min, and the absorption spectra of the cross-linked film were recorded in aqueous solutions with varying pH. The pH of the solutions containing 10 mM KH_2PO_4 was adjusted with a small amount of HCl or NaOH solution.

To study the response time of the cross-linked $(DR/BY)_{10}DR$, the quartz slide modified with the film was alternately immersed in pH 13.0 and pH 9.0 solutions. The solution was stirred using a small magnetic stirring bar to reduce aqueous diffusion layer thickness. All experiments were carried out at room temperature (*ca.* 20 °C).

3. Results and discussion

3.1. Preparation of the cross-linked $(DR/BY)_{10}DR$ film

Fig. 2 shows typical absorption spectra for the deposition of the $(DR/BY)_{10}DR$ film. These spectra were recorded after depositions of DR. The absorbance at 384 nm increased with the number of depositions of DR and BY. An increase in absorbance at 384 nm per one DR deposition was 0.0124 in average. The amount of bound DR was estimated to be $8.4 \times 10^{-10}\ mol\ cm^{-2}$ ($1.8 \times 10^{-7}\ g\ cm^{-2}$) in monomer unit by using a molar extinction coefficient of $1.48 \times 10^4\ cm^{-1}\ M^{-1}$ for DR in solution at 384 nm. To estimate the amount of BY bound in the film structure, the absorbance at 434 nm that was the isosbestic point of BY in solution was used because the absorbance of BY was drastically changed by pH shift. An increase in absorbance at 434 nm per one BY deposition was 0.0064. The amount of bound BY is calculated to be $1.8 \times 10^{-10}\ mol\ cm^{-2}$ ($8.7 \times 10^{-7}\ g\ cm^{-2}$), using a molar extinction coefficient of $3.66 \times 10^4\ cm^{-1}\ M^{-1}$ for BY in solution at 434 nm. Thus, the molar ratio of DR to BY in the film structure is about 5. The thicknesses of the $(DR/BY)_{10}DR$ film can be estimated to be *ca.* 25 nm by assuming that the density of the organic materials in the film is $1.2–1.3\ g\ cm^{-3}$ according to the literature [12,13].

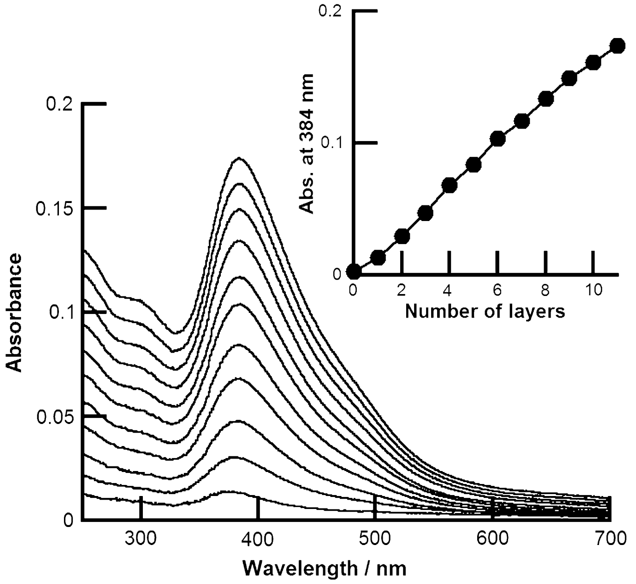

Fig. 2. UV–visible absorption spectra for the deposition of $(DR/BY)_{10}DR$ film, recorded after DR depositions. The inset is the absorbance of the DR/BY film at 384 nm against the number of DR depositions.

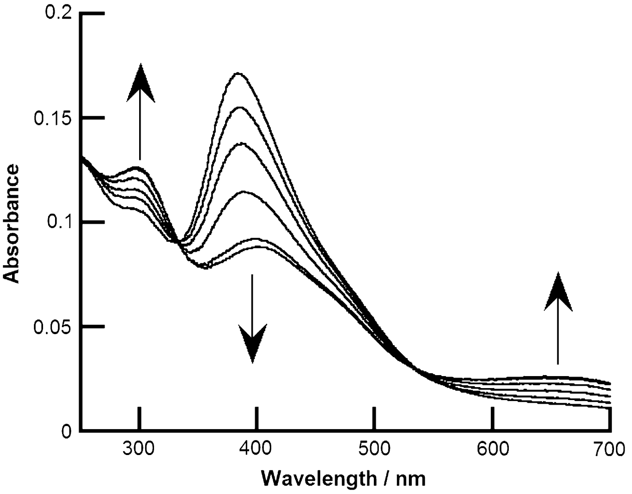

Fig. 3. UV–visible absorption spectra of $(DR/BY)_{10}DR$ film upon UV irradiation for different times. Irradiation time: 0, 1, 2, 4, 10, and 20 min. Irradiation intensity at 365 nm: 1112 μW cm^{-2}.

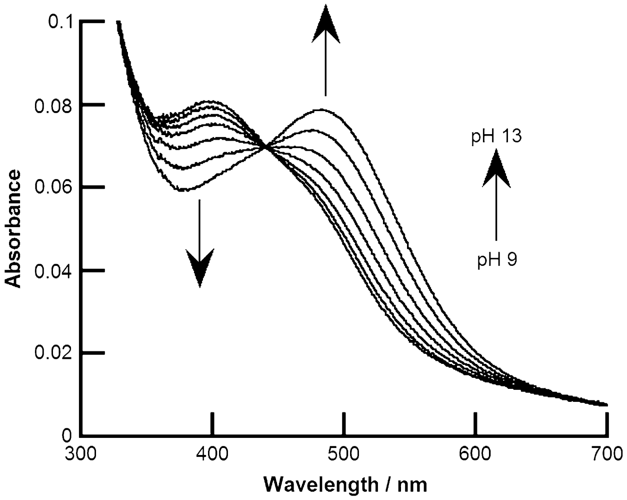

Fig. 4. UV–visible absorption spectra of the cross-linked $(DR/BY)_{10}DR$ film in different pH solutions.

Fig. 3 shows the spectra of $(DR/BY)_{10}DR$ film at different irradiation times. The absorbance at around 400 nm was decreased, which corresponded to disappearance of the diazonium group of DR [25,29]. The change of absorbance reached a steady state after 20 min irradiation. BY was desorbed in part from the cross-linked $(DR/BY)_{10}DR$ after rinsing in an aqueous solution of pH 13, but more than 90% of BY was remained in the film structure. This is a clear contrast to the fact that, before cross-linking, BY is completely desorbed from the PAA/BY film in the high pH solution because of a loss of the positive charges in PAA [22].

In order to understand the cross-linking process, we tried to obtain the FT-IR spectrum of the $(DR/BY)_{10}DR$ on a As_2Se_3 plate which had no IR absorption in measurement range. However, the experiment was not successful because the adsorption amount of DR and BY was too low. In this situation, we prepared a $(DR/PSS)_{10}$ film using poly(styrenesulfonic acid), which was investigated with FT-IR in cross-linking process by Qin et al. [29]. As in the case of the previous report, the absorption at 1580 cm^{-1} corresponding to the vibration of the arene ring conjugated with an unsaturated group was observed in the $(DR/PSS)_{10}$ film. After 20 min UV light irradiation, the absorbance at 1580 cm^{-1} was shifted to 1606 cm^{-1} which corresponded to the absorption of normal arenes. The results show that the diazonium in $(DR/PSS)_{10}$ film was completely converted in 20 min UV irradiation. Thus, the $(DR/BY)_{10}DR$ film was probably cross-linked under the experimental conditions. However, the degree of cross-linking *i.e.* the amount of covalent bond between DR and BY could not be estimated in FT-IR. Further research is needed to characterize $(DR/BY)_{10}DR$.

3.2. pH response of the cross-linked $(DR/BY)_{10}DR$ film

Fig. 4 shows UV–visible absorption spectra of the cross-linked $(DR/BY)_{10}DR$ film. The spectra were changed depending upon the pH value of the solution in which the film-coated slide was immersed. The pH response of BY was retained satisfactorily in the film. The maximum absorption wavelengths in pH 9 and pH 13 were 398 nm and 483 nm, respectively, with an isosbestic point at 438 nm. For free BY in solution, the maximum absorptions were found at 395 nm in pH 5 and 486 nm in pH 10, and an isosbestic point was observed at 434 nm. The maximum absorption and isosbestic point of BY slightly shifted in the cross-linked $(DR/BY)_{10}DR$ film. The pK_a value of immobilized BY was determined to be 11.9 by curve fitting analysis. Meanwhile the pK_a values of free BY in solution and BY immobilized in PAA/BY film were determined to be 8.2 and 8.4, respectively [22]. The pK_a value of BY in the cross-linked $(DR/BY)_{10}DR$ film was raised by the cross-linking due to a change of chemical structure of BY.

Fig. 5 gives the absorbance of the cross-linked $(DR/BY)_{10}DR$ film at 483 nm (a) and 398 nm (b) when the film is alternately immersed in pH 13.0 and pH 9.0 solutions. The absorbance at 483 nm in the pH 13 solution, shown in Fig. 4, is not consistent with that in Fig. 5. The reason for this inconsistency was due to variability of the adsorption amount of BY in the LbL deposition process. In Fig. 5, the absorbance was changed depending upon the pH value of the solution. The absorbance of the cross-linked $(DR/BY)_{10}DR$ film was not decreased by repeated immersion of the film in pH 13.0 and pH 9.0. Therefore, desorption of BY from the cross-linked $(DR/BY)_{10}DR$ film did not occur. The absorbance at 483 nm in pH 13 solutions was 0.0925 in average, and the relative standard deviation was 0.9%. The results show that the cross-linked $(DR/BY)_{10}DR$ film has excellent reusability and reproducibility. Additionally, the cross-linked $(DR/BY)_{10}DR$ film showed a quick response; the response time was within a few seconds upon change from pH 9.0 to 13.0, and *ca.* 40 s was needed for reaching the steady state upon change from pH 13.0 to 9.0. We investigated the pH response and reusability of $(DR/BY)_5DR$ film, and found

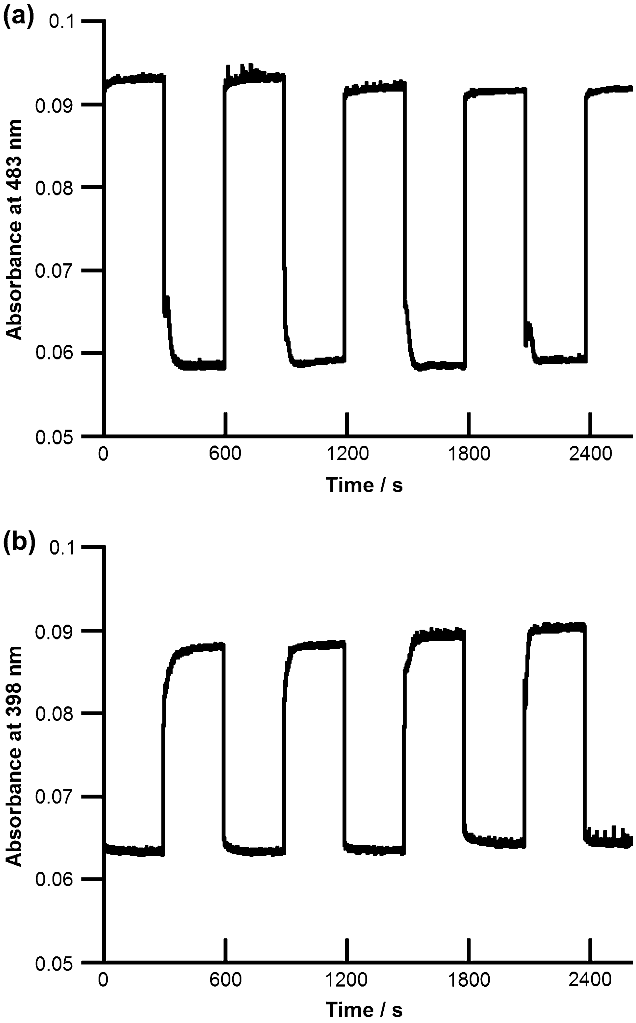

Fig. 5. The changes in absorbance of the cross-linked $(DR/BY)_{10}DR$ film at 483 nm (a) and 398 nm (b) when the film was alternately immersed in pH 13.0 (0–300 s) and pH 9.0 solutions (300–600 s). The data during the replacing of solutions are omitted for clarity.

that the response characteristics of the $(DR/BY)_5DR$ film were almost the same as that of the $(DR/BY)_{10}DR$ films. The results show that the increase of film thickness does not cause adverse effects on the response of the (DR/BY) films.

4. Conclusions

The cross-linked multilayered thin films composed DR and BY were fabricated. The cross-linking between BY and DR prevented BY from desorption even in a pH 13 solution. The cross-linked $(DR/BY)_{10}DR$ film exhibited pH-dependent absorption spectra in pH 9–13. It was confirmed that the absorbance of the cross-linked $(DR/BY)_{10}DR$ film was not decreased by repeated immersion of the film in pH 13.0 and pH 9.0. The pH response time of the films was within a few seconds upon change from pH 9.0 to 13.0, and *ca*. 40 s upon change from pH 13.0 to 9.0. The excellent reusability, reproducibility, and quick response time of the cross-linked $(DR/BY)_{10}DR$ film are ideally suited for an optical pH sensor.

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