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# Stable Self-Assembled Multilayer Films of Diazo Resin and Poly(maleic anhydride-*co*-styrene) Based on Charge-Transfer Interaction

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Received March 1, 2001. In Final Form: May 2, 2001

Diazo resin (DR) and poly(maleic anhydride-*co*-styrene) (PMS) can form a charge-transfer complex in methanol. A multilayer film was fabricated successfully from DR and PMS based on the charge-transfer interaction. After UV irradiation, the stability of the film toward polar solvents increases significantly due to the formation of covalent bonds between DR and PMS.

## Introduction

In the past decade, the "layer-by-layer" self-assembly technique for the fabrication of ultrathin polymer films has received more and more attention due to its striking simplicity and versatility.<sup>1–3</sup> It is considered as an alternative to the Langmuir–Blodgett, spin-coating, and chemical vapor deposition techniques. Besides electrostatic attraction,<sup>1</sup> H-bonding,<sup>4</sup> coordination interaction,<sup>5</sup> and charge-transfer interaction<sup>6</sup> have also been exploited for this object. While the deposition mechanism and the structure of the film are still under investigation,<sup>7–9</sup> potential applications in fields such as biosensors, separation, and electronics have been proposed.<sup>10–12</sup> However, the resulting ultrathin films are usually easily destroyed when exposed to polar solvent, especially when weak interaction such as H-bonding or charge-transfer is applied as the driving force in the assembly process. The stability of the films can be improved by forming covalent linkages between the layers.<sup>13–15</sup> The photosensitive diazo resin (DR) has been used as a cationic polyelectrolyte<sup>16</sup> or a H-acceptor<sup>17</sup> to fabricate ultrathin films via electrostatic or H-bonding attraction, respectively. Under UV irradiation, following the decomposition of diazonium groups,

the covalent bonds form in the film structure and the stability of the film toward polar solvent increases substantially. Here we report that charge-transfer interaction occurs between DR and poly(maleic anhydride-*co*-styrene) (PMS) in methanol. On this basis an ultrathin film was fabricated successfully. While the resulting film is rather unstable toward polar solvents, its stability increases significantly after UV irradiation.

## Experimental Section

**Materials.** Diphenylamine-4-diazonium chloride ( $1/2\text{ZnCl}_2$  complex, DS) was purified by being dissolved in ethanol and then precipitated from ether twice and then dried in the dark at room temperature. Diphenylamine (DPA) and methanol were analytical agents and used without further purification. DR was prepared by polycondensation of DS with paraformaldehyde in concentrated sulfuric acid according to ref 18 ( $\eta_{sp}/C = 0.15\text{ dL/g}$ ,  $M_n = 2600\text{ g/mol}$ ). Copolymerization of an equal molar ratio of maleic anhydride and styrene was carried out in toluene at 80 °C. AIBN was used as initiator. The  $M_w$  of the resulting copolymer (PMS) was measured to be  $1.57 \times 10^6$  by GPC.

**Fabrication of Multilayer Films.** To fabricate the self-assembly multilayers from DR and PMS, a quartz wafer was used as the substrate that was washed in a boiling  $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$  (3:7) mixture for 30 min before use. It was first immersed in a methanol solution of DR ( $0.2\text{ mg mL}^{-1}$ ) for 4 min, washed with methanol, and air-dried. Then it was immersed in a methanol solution of PMS ( $0.5\text{ mg mL}^{-1}$ ) for 4 min, washed with methanol, and air-dried to complete a fabrication cycle. The cycle was repeated until the expected number of cycles was reached. The whole process was carried out in the dark.

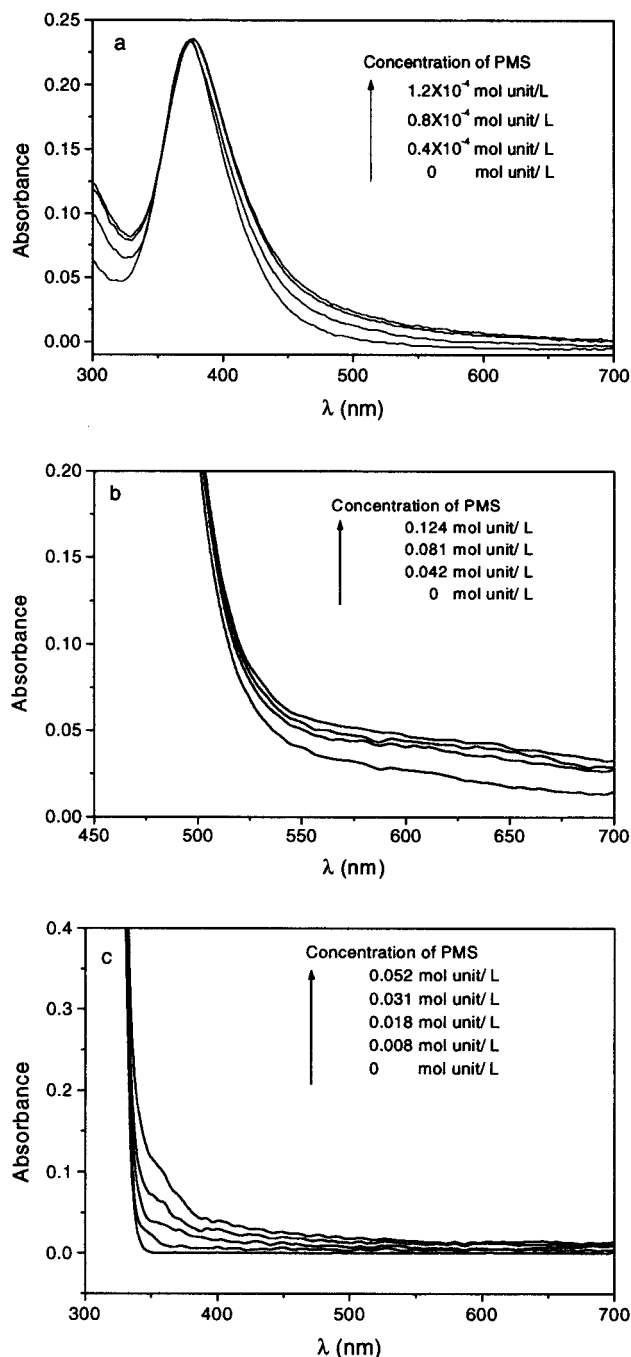
**Measurement.** The absorption spectra were measured on a Shimadzu UV-2100 spectrophotometer. Infrared spectra were recorded on a Bruker Vector 22 FTIR spectrometer.

## Results and Discussion

**Interaction between PMS and DR.** It is known that charge-transfer interaction occurs between poly(maleic anhydride) (or PMS) (as charge acceptor) and organic amines (as charge donor).<sup>19,20</sup> DR as an amine may also form a charge-transfer complex with PMS. Figure 1 shows the absorption spectra of the mixed solutions of (a) DR

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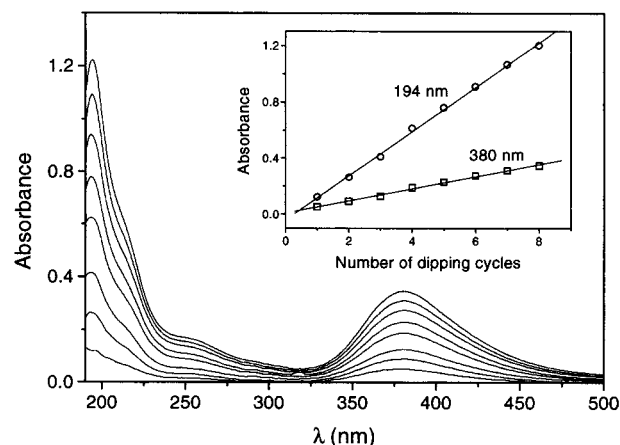
**Figure 1.** Absorption spectra of (a) DR, (b) DS, and (c) DPA in the presence of PMS in methanol. [DR] =  $1 \times 10^{-5}$  mol unit/L, [DS] =  $2 \times 10^{-3}$  M, [DPA] =  $5 \times 10^{-3}$  M, and the concentrations of PMS are shown in the figures.

and PMS, (b) DS and PMS, and (c) DPA and PMS in methanol in which the concentration of DR (DS or DPA) is kept constant. The absorption bands at 280 and 380 nm are assigned to the absorption of the  $-\text{NH}-$  group of diphenylamine and the  $-\text{N}_2^+$  group of DS and DR, respectively. Although there is no distinct charge-transfer band, the spectrum expansion toward longer wavelength in the presence of PMS was found in all cases. Similar spectrum changes were observed for the system of poly-[2-(9-carbazolyl)ethyl methacrylate] and poly [2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate]<sup>6</sup> and the system of C<sub>60</sub> and amines.<sup>21</sup> We believe the broadening originates from the formation of a charge-transfer complex in these

**Table 1.** Charge Transfer Complex Formation Constants ( $K_a$ ) of PMS with DR, DS, and DPA<sup>a</sup>

	DR/PMS	DS/PMS	DPA/PMS
$K_a/\text{M}^{-1}$	$5.6 \times 10^3$ (500 nm)	12.6 (550 nm)	5.36 (360 nm)

<sup>a</sup> Wavelengths used for absorbance measurements are included in parentheses.



**Figure 2.** UV-vis spectra of DR/PMS multilayer films with various numbers of dipping cycles (bottom to top, the dipping cycle number 1-8). Inset: absorbance at 380 and 194 nm.

systems in which PMS acts as charge acceptor and DR, DS, and DPA as charge donor. The formation constants  $K_a$  can be obtained according to the Benesi-Hildebrand equation:<sup>22</sup>

$$\frac{1}{\Delta A} = \frac{1}{K_a \Delta \epsilon [D]_t [A]_t} + \frac{1}{\Delta \epsilon [D]_t}$$

where  $[A]_t$  and  $[D]_t$  represent the total concentrations of the acceptor (PMS) and the donor (DR, DS, or DPA) in the solution and  $\Delta A$  and  $\Delta \epsilon$  represent the change in absorbance and the difference between the molar extinction coefficients of complexed and free donors, respectively.

$K_a$  values obtained are collected in Table 1. The  $K_a$  value for DR is much larger than that of DS and DPA, which can be explained by the "zipping effect" in the polymeric system,<sup>23</sup> i.e., the CT complexes between adjacent groups will form preferentially.

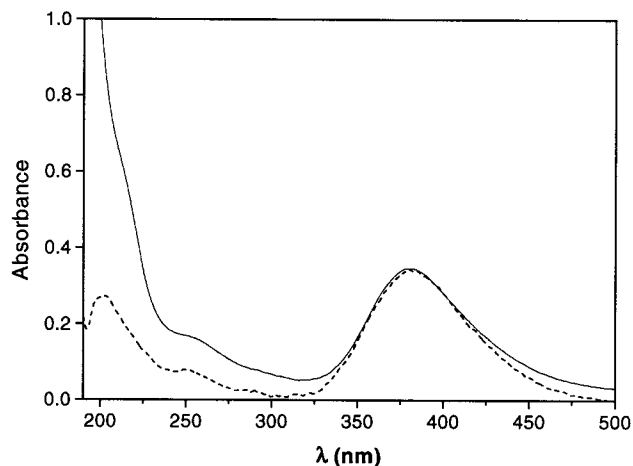
**Multilayer Film Self-Assembled from PMS and DR.** The fabrication of a DR/PMS multilayer was monitored spectrometrically, and the UV-vis spectra of the films with different numbers of dipping cycles are shown in Figure 2. Peaks at 380 and 194 nm are assigned to the absorption of the diazonium group of DR and the phenyl group of PMS, respectively. The good linear relationship between the absorbance both at 380 and 194 nm and the number of dipping cycles (inset plot in Figure 2) reveals that the layer-by-layer fabrication proceeded smoothly. The increasing absorbance at 380 nm for every dipping cycle is about 0.046, which is greater than that of the self-assembled multilayer film from DR based on electrostatic interaction (about 0.035).<sup>24</sup> The difference may be related to the different conformation of DR adopted in different solutions. Figure 3 shows the absorption spectra

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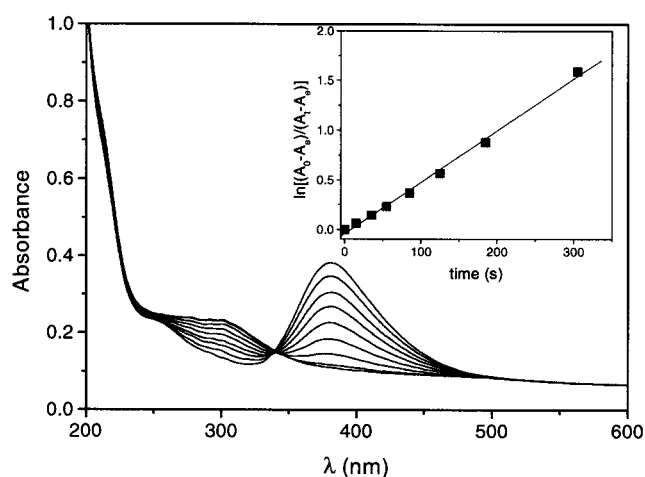
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**Figure 3.** UV-vis spectra of a self-assembly 16-bilayer DR/PMS film (solid line) and a DR film coating on a quartz wafer (dash line).

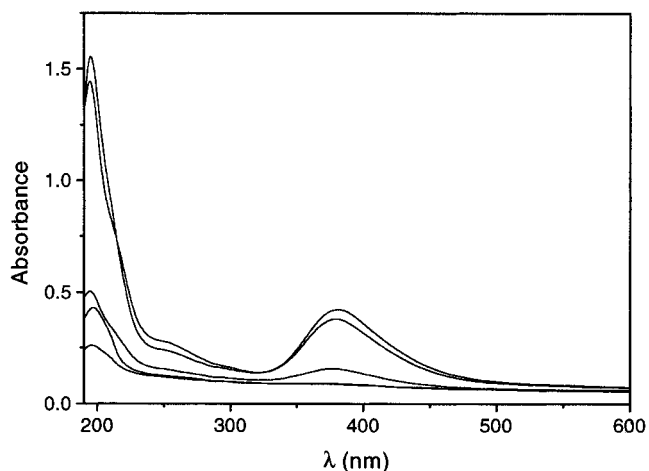


**Figure 4.** UV-vis spectra of a 16-bilayer film with different UV irradiation time. Irradiation intensity:  $300 \mu\text{W}/\text{cm}^2$  at 360 nm. Irradiation time(s) (top to bottom): 0, 15, 35, 55, 85, 125, 185, 305, 545. Inset: plot of  $\ln[(A_0 - A_e)/(A_t - A_e)]$  against time  $t$ .

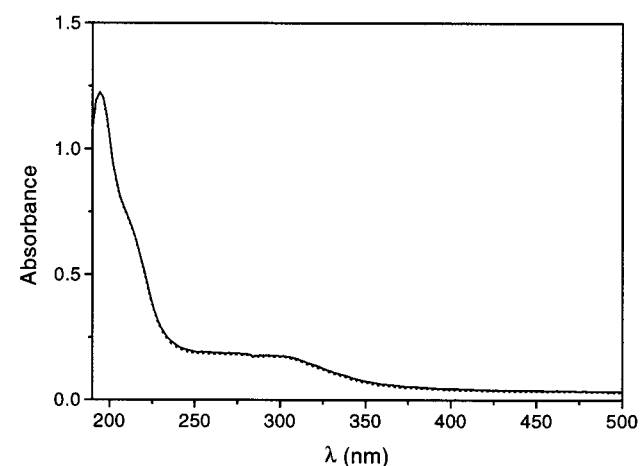
of the DR/PMS self-assembly film and a DR coating film with the same absorbance band at 380 nm. The expansion of the absorption of the diazonium group toward longer wavelength clearly indicates the formation of CT complex between DR and PMS in the self-assembly film. In other words, the charge-transfer interaction between the two components is the driving force for the film build-up.

DR is sensitive to UV light. The UV-vis spectra of a 16-bilayer DR/PMS film with different irradiation time were recorded (Figure 4). The absorption band at 380 nm characteristic of the diazonium group decreases rapidly under UV irradiation. The photodecomposition is almost complete within 2.5 min under the experimental conditions ( $300 \mu\text{W}/\text{cm}^2$  at 360 nm). A good linear relationship between  $\ln[(A_0 - A_e)/(A_t - A_e)]$  and  $t$ , where  $t$  represents irradiation time and  $A_t$ ,  $A_0$ , and  $A_e$  represent the absorbance at the beginning, at time  $t$ , and at the end of the reaction, respectively, indicates that the photoreaction is in accord with the first-order reaction kinetics.

The multilayer film of DR and PMS is rather unstable when exposed to polar solvents. When immersed in DMF, the UV absorption of a 16-bilayer film dropped quickly. The film was etched almost completely within 30 min (Figure 5). On the contrary, the UV-irradiated film is very

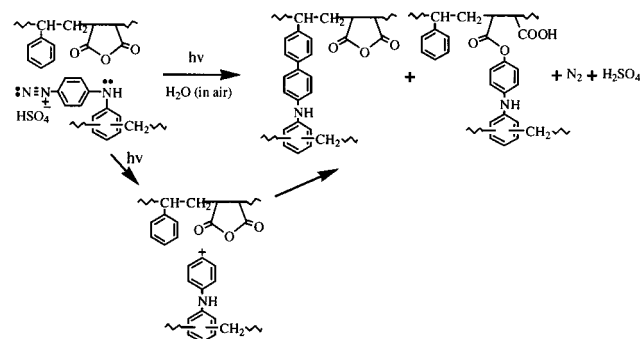


**Figure 5.** UV-vis spectra of a 16-bilayer film after immersing in DMF for 0, 5, 15, 25, and 35 min (from top to bottom).

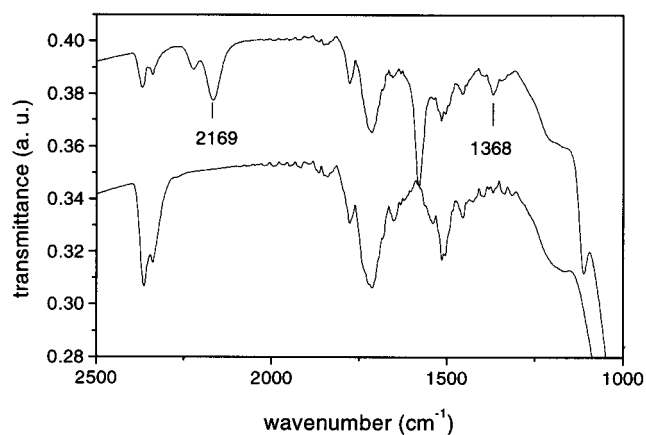


**Figure 6.** UV-vis spectra of an irradiated 16-bilayer film before (solid line) and after etching in DMF for 24 h (dot line).

stable, and no change in the absorption spectra was observed after being immersed in DMF for 24 h (Figure 6). The high stability of the film toward polar solvents should be ascribed to the formation of covalent bonds in the film following the decomposition of the diazonium groups. The mechanism of the covalent bond formation may be rather complex and is not fully clear now. Since usually the cationic intermediate forms following the decomposition of the diazonium group, a possible mechanism is proposed as follows:



FTIR spectra of a 40-bilayer film fabricated on  $\text{CaF}_2$  before and after UV irradiation give some information about the photoreaction (Figure 7). The peak at  $2169 \text{ cm}^{-1}$ , which is assigned to the stretching vibration of the



**Figure 7.** FTIR spectra of a 40-bilayer film fabricated on  $\text{CaF}_2$  before (top) and after (bottom) UV irradiation. Irradiation intensity:  $300 \mu\text{W}/\text{cm}^2$  at 360 nm. Irradiation time: 10 min.

diazonium group, disappears completely after UV irradiation. At the same time, the intensity of the peak at

$1368 \text{ cm}^{-1}$ , which is assigned to the stretching vibration of the  $-\text{C}-\text{O}-\text{C}-$  bond in a cyclic anhydride, almost disappears. The result indicates that most of the cyclic anhydride was opened after UV irradiation.

### Conclusions

Charge transfer interaction occurs between PMS and DR in methanol. On the basis of this interaction, a multilayer film was fabricated successfully in an alternative deposition mode. The resulting film is sensitive to light. After UV irradiation the film becomes very stable toward polar solvents due to the formation of covalent bonds in the film structure.

**Acknowledgment.** The authors greatly appreciate the NSFC for financial support to this work (Contract 29874001).

LA0103214