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Self-assembly films from diazoresin and carboxy-containing polyelectrolytes

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Multilayer films from diazoresin (**I**) and poly(sodium acrylate) (**II**) or a hydrolyzed maleic anhydride–styrene copolymer (**III**) have been fabricated on mica. During the fabrication process the absorbance of the film at 380 nm, which is the characteristic absorption of the diphenylamine 4-diazonium group of **I**, increases about 0.033 for each fabrication cycle. This means that the thickness of the film increases regularly. Under irradiation with UV light or heating, following the decomposition of the diazonium group, the ionic bond in the film structure converts to a covalent bond; this conversion was preliminarily verified by FTIR spectrum analysis. The stability of the different films (irradiated or unirradiated) was determined by UV-vis spectroscopy and the results show that the resistance of the film to etching by polar solvents increases significantly after bond conversion.

Introduction

Since Iler's pioneering work,[1] the self-assembly technique comprising two oppositely charged components has developed rapidly[2–9] and is used in many fields.[10–16] This method, usually involving the alternate adsorption of two oppositely charged components on a substrate such as mica, silica wafer *etc.* from aqueous solution, is environmentally friendly, easy in processing and does not require specific equipment. Therefore it is interesting both in theory and in practice. A principal defect of the films fabricated in this way from two oppositely charged polyelectrolytes is that the films are not very stable towards polar solvents. An approach to solve this problem has been developed using diazoresin—a polycondensation product from diphenylamine 4-diazonium salts and formaldehyde—as a positively charged component. Self-assembled films made from diazoresin and different negatively charged components have been prepared and it has been confirmed that the films' stability towards polar solvents can be improved significantly by UV irradiation or heating.[17,18] In this article we report self-assembled thin films fabricated from diazoresin and carboxy-containing polyelectrolytes for the first time. The stability of the irradiated (or heated) films towards polar solvents is also reported.

Experimental

Materials

Styrene–maleic anhydride copolymer was obtained by free radical polymerization of maleic anhydride and styrene in toluene at *ca.* 80 °C using 2,2′-azoisobutylonitrile (AIBN) as initiator: $M_n = 6.30 \times 10^4$, $M_w = 1.57 \times 10^5$, $M_w/M_n = 2.50$ (from GPC). The unit ratio of maleic anhydride and styrene (mol : mol) in the copolymer was calculated to be 1 : 1 from titration with 0.05 mol L^{-1} NaOH in ethanol. Hydrolyzed styrene–maleic anhydride copolymer (**III**) was prepared *via* hydrolysis of styrene–maleic anhydride copolymer in 0.35 mol L^{-1} NaOH aqueous solution (NaOH was 2% overload) at reflux temperature, then precipitated by ethanol and dried *in vacuo* at 60 °C. Polyacrylic acid was prepared at 70 °C by free radical polymerization of acrylic acid in water using isopropyl alcohol as a chain transfer agent and potassium persulfate as initiator, and poly(sodium acrylate) (**II**) was prepared by neutralization of polyacrylic acid with 1 mol L^{-1} NaOH solution, then precipitated by ethanol. Diazoresin (**I**) was prepared according to the method described elsewhere.[19]

Preparation of self-assembly films

Self-assembly films were fabricated on mica, which has a negatively charged surface in water, as follows. The newly cleaved mica (6×30 mm^2) was immersed in an aqueous solution of **I** (20 mg **I** in 100 ml H_2O) for 5 min at room temperature in the dark, rinsed thoroughly with water and dried. It was then immersed in aqueous **III** (or **II**) (20 mg **III** or **II** in 100 ml H_2O) for 5 min, rinsed with water and dried, to complete a fabrication cycle. A **I–III** (or **I–II**) bilayer was fabricated on each face of the mica in each cycle. The procedure was repeated as required to obtain the multilayer films.

Characterization of the films

The self-assembly process was monitored after each fabrication cycle by determining the UV-vis spectra of the film (on a Shimadzu-1200 spectrophotometer). The photodecomposition or thermal decomposition of the diazonium group in the film was determined spectrophotometrically. The etching processes of different films (irradiated and unirradiated) were also monitored by measuring their UV-vis spectra. The structural changes in the films after UV irradiation or heating was determined by FTIR (on VECTOR-22).

Results and discussion

Self-assembly fabrication on mica

Diazoresin as a cationic polyelectrolyte deposits on the mica surface easily, then **III** or **II** deposits on the diazoresin layer, to form a **I–III** (or **I–II**) bilayer on both sides of the mica in each fabrication cycle, as shown in Fig. 1.

The absorbance of the **I** film at 380 nm, a characteristic absorption of the diphenylamine 4-diazonium group, increases regularly with the increasing number of bilayers, as shown in

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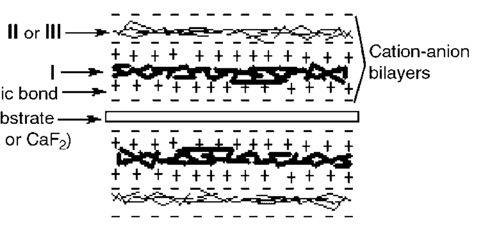


Fig. 1 Schematic diagram of a **I–III** or **I–II** bilayer on both sides of the mica (or CaF_2 wafer) in one fabrication cycle.

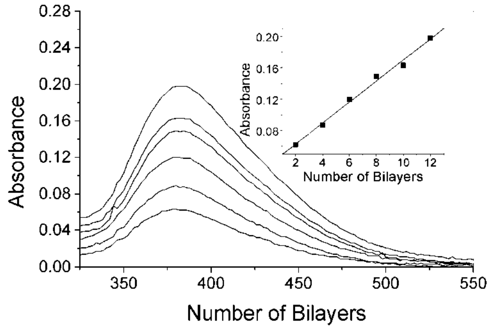


Fig. 2 UV-vis absorbance of the **I–III** film increases with the increasing of bilayer number. Bilayer number (bottom to top): 2, 4, 6, 8, 10, 12. The insert plot shows how the absorbance of the film increases linearly with bilayer number.

Fig. 2. The increase of absorbance is about 0.033 for each fabrication cycle.

Reactions taking place in film under exposure to UV light or heating

The diazonium group of the **I–III** (or **I–II**) film decomposes easily under irradiation with UV light or heating because it is sensitive towards UV light and heat. The UV-vis spectra of the **I–III** films after different irradiation times and the decomposition of the diazonium groups of the film with heating time are shown in Fig. 3 and Fig. 4 respectively.

Following the decomposition of the diazonium group, the ionic bonds of **I–III** (or **I–II**) convert partially to ester bonds; the bond conversion can be schematically represented as shown in Schemes 1 and 2).

In order to obtain evidence of the bond conversion, a film with forty bilayers of **I–III** (or **I–II**) was fabricated on a CaF_2 wafer. The FTIR spectra of the films were recorded before and after irradiation (or heating). The spectra are shown in Figs. 5 and 6.

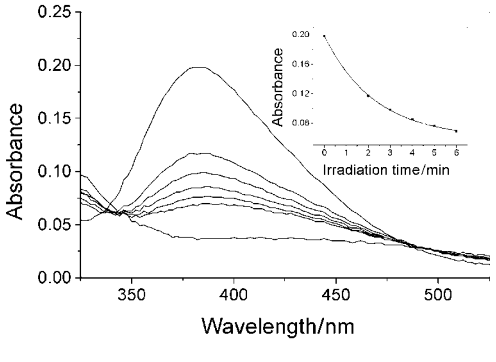


Fig. 3 UV-vis spectra of **I–III** film (12 bilayers) after different irradiation times. Irradiation times (top to bottom): 0, 2, 3, 4, 5, 6, 30 min. Irradiation intensity: 230 μW cm^{-2}. The insert plot shows how the absorbance of the film decreases with irradiation time.

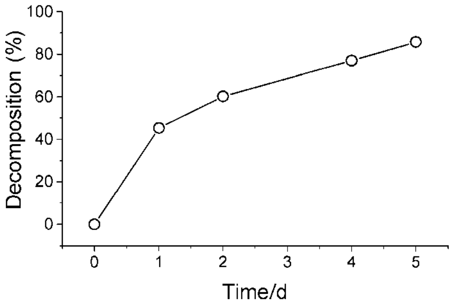
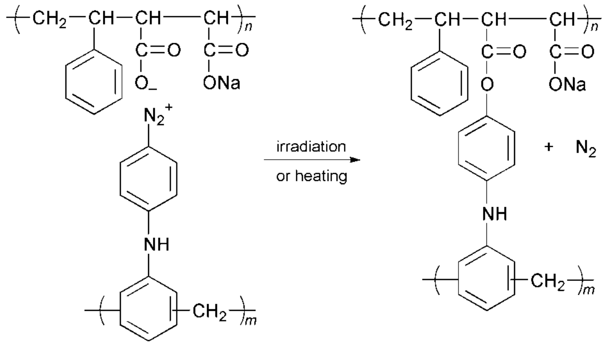


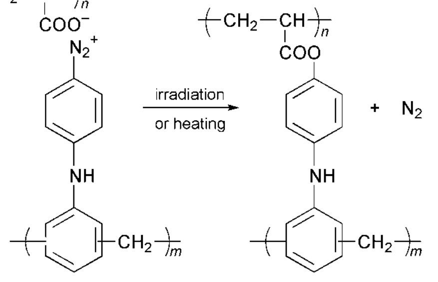
Fig. 4 Decomposition (N_2^+ mol%) of **I–III** film (12 bilayers) *vs.* heating time at 70 °C.

From Figs. 5 and 6 we can see that the peak at 2165 cm^{-1} (stretching vibration of the diazonium group) disappears after irradiation or heating, indicating that the diazonium groups of **I–III** or (**I–II**) decompose. The absorption at 1590 cm^{-1}, which is assigned to the carboxylic anion, decreases due to the conversion of the ionic bonds to ester bonds ($-CO_2C-$). Meanwhile the absorption at 1740 cm^{-1}, characteristic of carboxylic ester groups, increases. From the increasing carboxylic ester group absorption it is clear that the degree of conversion of ionic bonds to ester bonds is low as compared with the decomposition of the diazonium groups, which decompose completely. Except for the formation of ester groups the formation of other covalent bonds is not clear as yet, but we believe that bond conversion does occur following diazonium decomposition. The conversion of ionic bonds to covalent bonds in the multilayer thin film is schematically represented in Fig. 7.

Owing to bond conversion after UV irradiation, the film's stability changes greatly. Fig. 8 shows the changes in the absorbances of irradiated and unirradiated films (eight bilayers of **I–III** on quartz wafer) during DMF etching. The benzene ring absorbance of the unirradiated film at 204 nm dropped quickly, which means that the unirradiated film (ionic structure) is unstable towards DMF etching, while under the



Scheme 1 Schematic representation of bond conversion from ionic bond to ester bond in **I–III** film under irradiation with UV light or heating.



Scheme 2 Schematic representation of bond conversion from ionic bond to ester bond in **I–II** film under irradiation with UV light or heating.

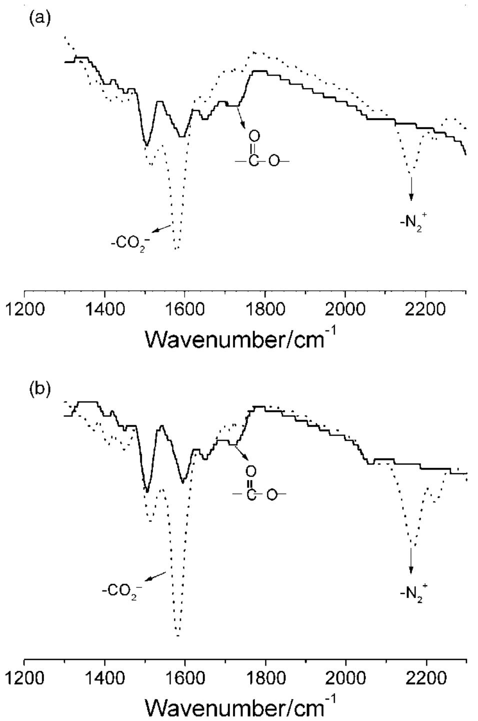


Fig. 5 IR spectra of **I–III** and **I–II** films (40 bilayers) before and after irradiation of UV light. Irradiation conditions: 230 μW cm^{-2}. Irradiation time: 1 h. ··· before irradiation; — after irradiation. a: **I–III** film; b: **I–II** film.

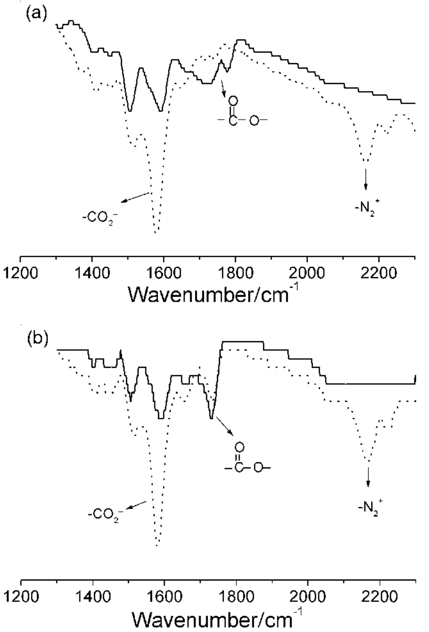


Fig. 6 IR spectra of **I–III** and **I–II** films (40 bilayers) before and after heating (70 °C/7days). ··· before heating; — after heating. a: **I–III** film; b: **I–II** film.

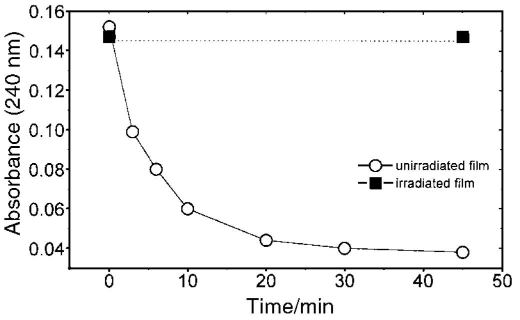


Fig. 8 The relationship between the UV-vis absorbance of the diazonium group and the etching time in unirradiated and irradiated films (8 bilayers on quartz wafer) in DMF at 20 °C.

same conditions the benzene absorbance of the irradiated film (covalent structure) was only reduced by a factor of 0.002 (from 0.147 to 0.145) after etching by DMF for 24 h. This result provides clear evidence that the stability of the film towards polar solvents is improved significantly after bond conversion.

The photosensitive behavior of **I–III** or **I–II** films towards UV light may be valuable in photoimaging. The solubility of the film changes dramatically after irradiation. The irradiated area does not dissolve in any solvent or solvent system, because of the formation of the covalently crosslinked structure, while the unirradiated area keeps the original ionic structure and is much more unstable in polar solvents such as DMF, ternary solvents composed of H_2O–DMF–NaCl,[18] or in sodium dodecyl sulfate (SDS, 0.1 mol L^{-1}) aqueous solution,[20] and can be washed away. However, the quality of the imaging is not too good because the first layer combines strongly with the substrate surface and is difficult to remove completely. In 0.5% NaOH aqueous solution, the remaining first layer can be dissolved, and a clear image can be obtained.

Conclusion

Multilayer thin films have been fabricated on mica from diazoresin (**I**) as a cationic polyelectrolyte and carboxy-containing polyelectrolytes such as poly(sodium acrylate) (**II**) or hydrolyzed maleic anhydride–styrene copolymer (**III**) as anionic polyelectrolyte *via* the self-assembly technique in dilute aqueous solution. UV-vis spectroscopy shows that film fabrication progresses smoothly with an absorbance increase of about 0.033 for each fabrication cycle. Under irradiation with UV light or heating the diazonium groups decompose, and the ionic bonds between the two types of layers convert to covalent bonds, especially ester bonds. As a result, the stability of the film towards polar solvents was improved significantly. The conversion of ionic bonds to ester bonds has been verified preliminarily by FTIR for a 40 bilayer multilayer film on a CaF_2 wafer.

Acknowledgement

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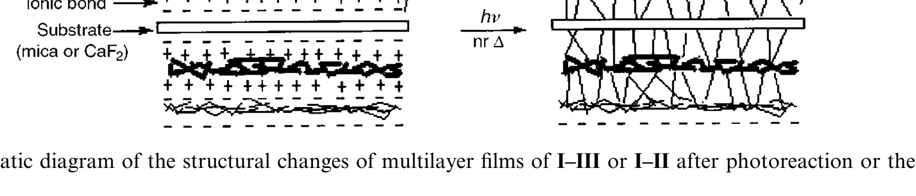

Fig. 7 Schematic diagram of the structural changes of multilayer films of **I–III** or **I–II** after photoreaction or thermal reaction.

References

1 R. K. Iler, *J. Colloid Interface Sci.*, 1966, **21**, 589.

2 G. Decher and J. D. Hong, *Makromol. Chem., Macromol. Symp.*, 1991, **46**, 321.

3 D. Decher and J. D. Hong, *Ber. Bunsen-Ges. Phys. Chem.*, 1991, **95**, 1430.

4 D. Decher, J. D. Hong and J. Schmidt, *Thin Solid Films*, 1992, **210**, 831.

5 S. Watanabe and S. L. Regen, *J. Am. Chem. Soc.*, 1994, **116**, 8855.

6 G. Mao, Y. Tsao, M. Tirrell, H. T. Davis, V. Hessel and H. Ringsdorf, *Langmuir*, 1995, **11**, 942.

7 S. L. Clark, M. F. Montague and P. T. Hammond, *Macromolecules*, 1997, **30**, 7237.

8 M. Losche, J. Schmitt, G. Decher, W. G. Bouwman and K. Kristian, *Macromolecules*, 1998, **31**, 8893.

9 M. Tarabia, H. Hong, D. Davidov, S. Kirstein, R. Neumann and Y. Avny, *J. Appl. Phys.*, 1998, **83**, 725.

10 Y. Lvov, K. Ariga and T. Kunitake, *Chem. Lett.*, 1994, 2323.

11 A. K. Kakkar, S. Yitzchaik, S. B. Roscoe, F. Kubota, D. S. Allan, T. J. Marks, W. Lin and G. K. Wong, *Langmuir*, 1993, **9**, 388.

12 S. Watanabe and S. L. Regen, *J. Am. Chem. Soc.*, 1994, **116**, 8855.

13 V. V. Tsukruk, V. N. Bliznyuk and F. Rinderspacher, *Polm. Prepr.*, 1996, **37**(2), 571.

14 V. V. Tsukruk, F. Rinderspacher and V. N. Bliznyuk, *Langmuir*, 1997, **13**, 2171.

15 T. W. Cooper, A. L. Campbell and R. L. Crane, *Langmuir*, 1995, **11**, 2713.

16 J. H. Fendler and F. C. Meldrum, *Adv. Mater.*, 1995, **7**, 607.

17 J. Sun, T. Wu, Y. Sun, Z. Wang, X. Zhang, J. Shen and W. Cao, *Chem Commun.*, 1998, 1853.

18 W. Cao, S. Ye, S. Cao and C. Zhao, *Makromol. Rapid Commun.*, 1997, **18**, 983.

19 S. Cao, C. Zhao and W. Cao, *Polym. Int.*, 1998, **45**, 142.

20 W. Cao, Y. Lei and H. Luo, *J. Appl. Polym. Sci.*, 1998, **70**, 1817.