Photoimaging Technique on Printing Al Plate via Self-Assembly Multilayer Films Based on Diazoresin

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ABSTRACT: A photoimaging technique on a printing aluminum plate (anodized oxidation Al plate) via self-assembly multilayer thin film from nitro-containing diazoresin (NDR) as cationic polyelectrolyte and various anionic polyelectrolytes has been developed. It was confirmed that, under UV-irradiation, the linkage nature of the films changes from ionic to covalent and the solubility of the films converts dramatically, that is, the exposed area of the film becomes insoluble in H_2O–DMF–LiCl (2 : 4 : 1 wt %) ternary solvent, but mainly the unexposed area will be dissolved. After developing in ternary solvent, an image that accepts ink easily appears on the printing Al plate. To resolve the ink-stain problem, originating from a trace remainder of the NDR on the unexposed area of the Al plate, a surface modification technique by polyphosphoric acid, which reacts with NDR to form a hydrophilic surface, was developed. The thickness, homogeneity, and surface morphology of the multilayer film (on mica) determined by atomic force microscopy and UV-vis spectra were also reported. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1983–1987, 2001

Key words: polyelectrolyte; self-assembly technique; surface modification

INTRODUCTION

The self-assembly technique, based on oppositely charged polyelectrolytes to fabricate multilayer ultrathin films, has attracted increasing attention[1–5] since Iler's pioneering work.[6] This technique is characteristically easy in process, friendly to the environment, and cheaper in price than that of the LB membrane method. Diazoresin (DR), a kind of photosensitive polymer from polycondensation of diphenylamine-4-diazonium salt and formaldehyde,[7] used as cationic polyelectrolyte (CPE), reacts with various anionic polyelectrolytes (APE) to form photosensitive polyelectrolyte complexes[8] and a multilayer film from DR and poly(sodium styrene sulfonate) (PSS) has been reported.[9] In this study we present an approach to form an ultrathin film image on printing aluminum plate from nitro-containing diazoresin (NDR) and APE. The image properties and the latent use in printing technique have been preliminarily evaluated.

EXPERIMENTAL

Materials

PSS (MW = 7000 g/mol); poly(sodium ethylene sulfonate) (PES, 25% aqueous solution); polyphosphoric acid (PPA, 98%); 3-sulfopropyl methacrylate, potassium salt (SMS); and tetramethyl ethylenediamine (TMED) were purchased from Aldrich (Milwaukee, WI) and used as received. NDR was prepared by polycondensation of *N*-methyl-2-

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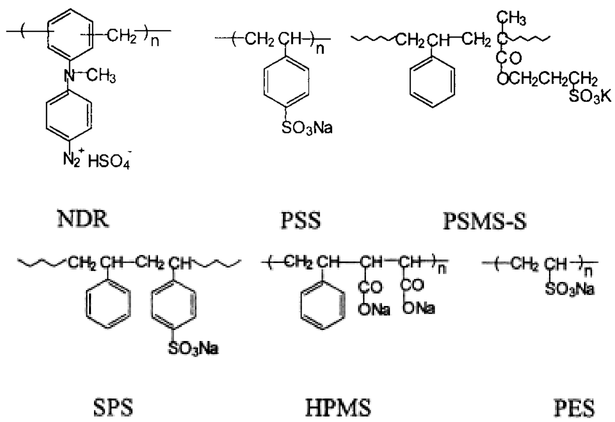
nitro-diphenylamine-4-diazonium salt and paraformaldehyde in concentrated sulfuric acid as described elsewhere.[10] The hydrolyzed copolymer of maleic anhydride and styrene (HPM-S)[11] was used as a carboxy-containing anionic polyelectrolyte. The copolymer of SMS and styrene (PSMS-S)[12] or sulfonated polystyrene (SPS)[13] was used as sulfo-containing anionic polyelectrolytes. The structural formulas of NDR, PSS, PES, PSMS-S, HPM-S, and SPS are illustrated as follows:



Film Fabrication

As an example, a NDR (η_{sp}/c = 0.15 g^{-1}dL, M_n ~ 2600 g/mol) solution (20 mg in 10 mL H_2O) and a PSS (M_n ~ 7000 g/mol) solution (20 mg in 10 mL H_2O) or other anionic polyelectrolyte solutions were prepared. A printing aluminum plate (anodized oxidation Al plate, 10 × 15 cm^2), which has a hydrophilic surface and repels ink, was immersed in an NDR aqueous solution for 5 min, rinsed with water thoroughly, and dried, after which it was immersed in a PSS solution for 5 min, rinsed, and dried to perform a fabrication cycle. A diazoresin-PSS bilayer was to be fabricated on the Al plate surface in each cycle. The process was repeated as required several times to prepare the multilayer thin films on the Al plate.

For determination of UV-vis spectra and atomic force microscopy (AFM), a freshly cleaved mica wafer, which has a negatively charged surface in water,[14] was used as substrate instead of the Al plate.

Characterization

Determination of UV-Vis Spectrum

To monitor the fabrication process, the absorbance of mica wafer at 380 nm, which is the characteristic absorption of the $-N_2^+$ group of NDR, was determined after each cycle deposition of NDR-PSS (or other APE) on a Shimadzu 2100 UV-vis spectrophotometer (Shimadzu, Japan). Every measurement was repeated twice. The scan range selected was from 250 to 550 nm.

Determination of Surface Morphology

Atomic force microscopy (AFM) was used to visualize the surface morphology of the films. The mica on which the ultrathin film was fabricated was adhered to a glass slide for measurement. AFM measurements were performed with the Nanoscopy (Digital Instruments, Inc.) in the tapping mode in air at ambient temperature. Commercial silicon probes (Model TESP-100), with a typical resonant frequency of about 300 kHz, were used to obtain the image.

Photoimaging

A four-bilayer film of NDR-PSS (or other APE) with NDR as cover layer was fabricated on a printing Al plate, after which the plate was exposed under UV light with an intensity of 8 mW/cm^2 (360 nm) from a medium Hg lamp for 10 to 20 s and developed in an H_2O–dimethylformamide (DMF)–LiCl (wt % ratio 2 : 4 : 1) ternary solvent as developer for 5 min at room temperature. The unexposed area, which is ionically crosslinked, dissolved in ternary solvent and was mostly washed away, but the exposed area did not dissolve because of the covalent crosslinking conversion from ionic bond under UV-irradiation. After developing, an image that accepts ink formed on the surface of the printing Al plate.

RESULTS AND DISCUSSION

The Multilayer Film on Mica as a Model Film

The multilayer films on mica were fabricated as a mimic and the thickness of the one bilayer was determined by AFM. Figure 1 is the AFM image of a one-bilayer film; from the defect of the image, the thickness of one bilayer was determined to be about 3.5 nm and the four-bilayer multilayer film is about 15 nm (Fig. 2). The film surface is rather flat and the mean roughness of the one-bilayer film is about 1 nm over a 2 × 2 μm^2 scan area. The absorbance of the film at 380 nm increases with the number of bilayers, as shown in Figure 3. The

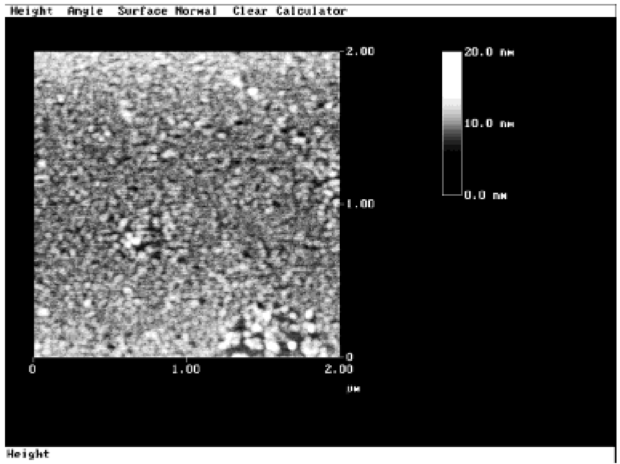
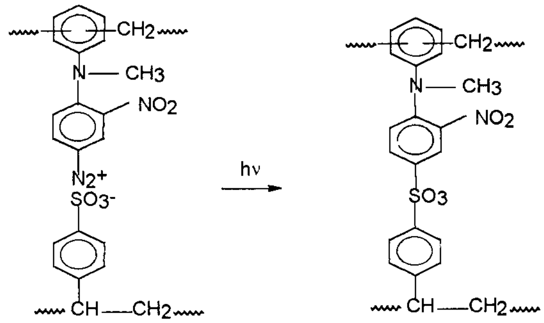


Figure 1 AFM image of an NDR-PSS bilayer film. Scan region: 2 × 2 μm.

linear relation shows that the fabrication is really step by step and the homogeneity of the film is excellent. The multilayer film on the printing Al plate is considered to be similar to that on mica because the driving force of the fabrication is electrostatic interaction both on mica and on the Al plate.

The Photoreaction in Multilayer Film

The force between the layer and layer of NDR-PSS (or other APE) multilayer films is an electrostatic interaction; thus the stability of the film is severely downgraded in the presence of polar solvents, a common problem for most self-assembly films via electrostatic interaction.[13,14] But NDR-PSS (or other APE) multilayer films have important characteristics: the film becomes very stable and does not dissolve in H_2O–DMT–LiCl ternary solvent as it undergoes UV-irradiation. The photoreaction taking place in film can be represented as follows:



In the photoreaction, following the decomposition of the diazonium group, the ionic bond converts to a covalent bond and the ability of the multilayer film to resist etching from polar solvents increases dramatically and it no longer dissolves in any solvents including H_2O–DMF–LiCl ternary solvent.

Surface Modification for Printing Purposes

The image prepared on the printing Al plate, as described earlier, remains a problem if it was designed for use as a printing plate. A trace of NDR remaining on the unexposed area of Al plate is difficult to clear away completely in the developing process because the multilayer film combines compactly with the Al surface. A trace remainder of NDR will stain the Al plate with ink and is thus unsatisfactory for use in the printing technique. To resolve this problem we developed a surface modification, using polyphosphoric acid, which combines easily with the $-N_2^+$ group of NDR remaining on the Al plate to form a stable hydrophilic surface (see Fig. 4), which repels ink completely. Table I lists the results of different images toward ink stain before and after surface modification.

From Table I we can see that the ink stain can be resolved satisfactorily with surface modification by polyphosphoric acid.

CONCLUSIONS

The multilayer thin films from diazoresin, as cationic polyelectrolyte, and various anionic poly-

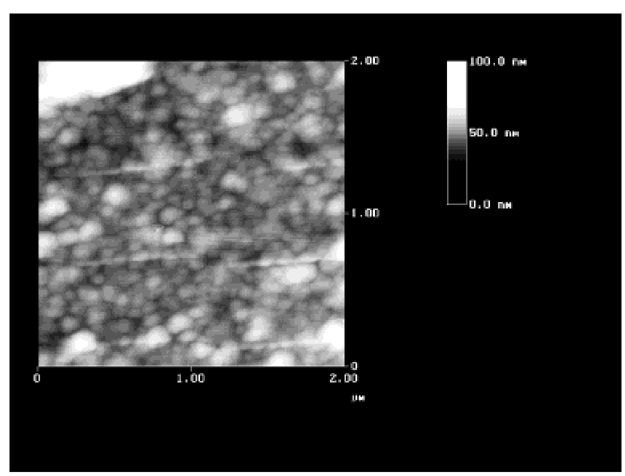


Figure 2 AFM image of an NDR-PSS four-bilayer film. Scan region: 2 × 2 μm.

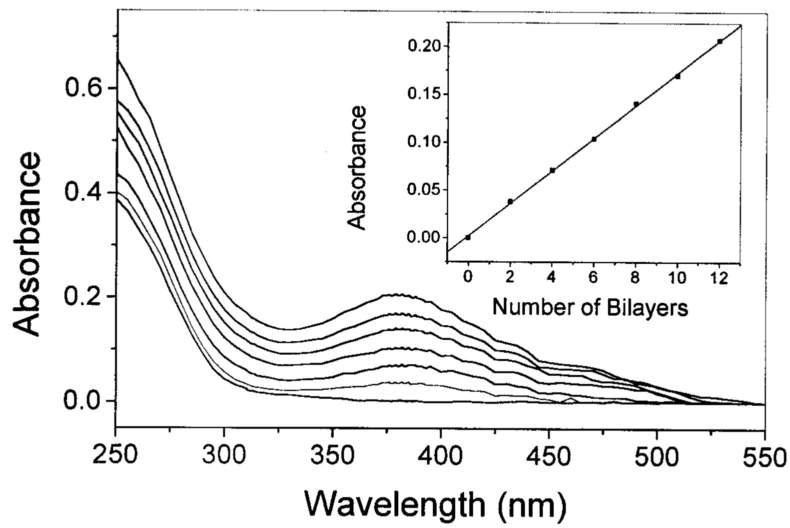


Figure 3 The absorbance at 383 nm of the multilayer film with different numbers of bilayer. The bilayer numbers (bottom to top): 0, 2, 4, 6, 8, 10, 12. Inset plot shows the relationship of absorbance and bilayer numbers.

electrolytes were fabricated on a printing Al plate by the self-assembly technique. Similarly, multilayer film on mica was fabricated as a mimic and its thickness, homogeneity, and surface morphology were determined by AFM and UV-vis spectra. The ink-accepting image formed on a hydrophilic surface of printing Al plate by the self-assembly method may be of great interest in the field of

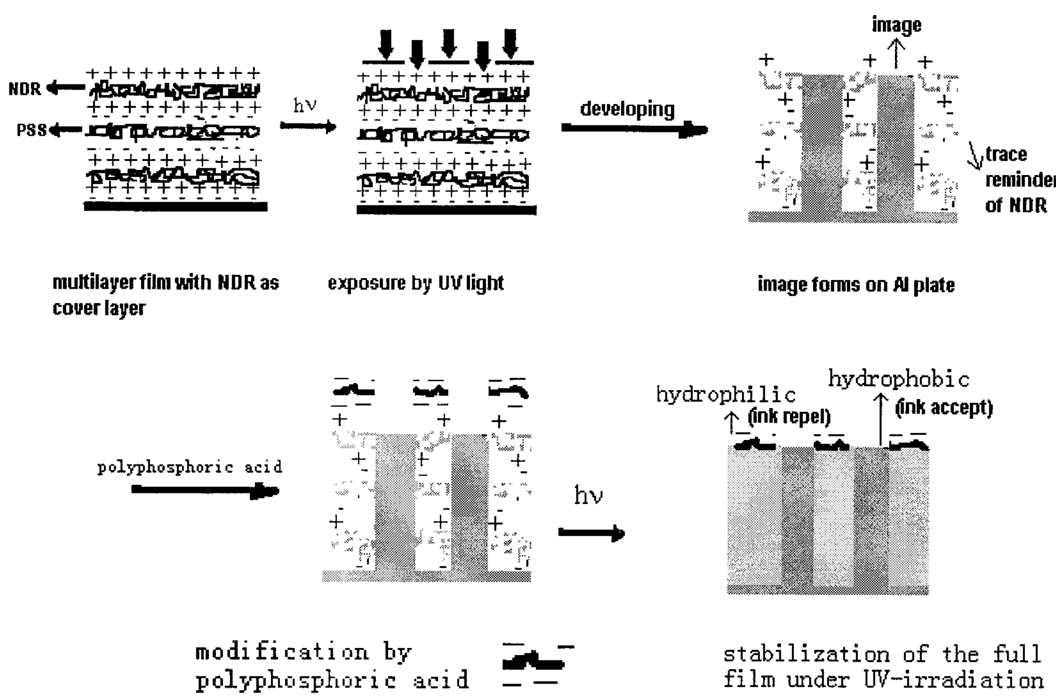


Figure 4 The schematic diagram of imaging on NDR-PSS multilayer film by UV light and modification with polyphosphoric acid.

Table I Different Images Modified by Polyphosphoric Acid Toward Ink Stain

Different Image[a]	Image A[b]	Image B[b]
PSS/diazoresin	Ink stain	Clear image, no stain
SPS/diazoresin	Ink stain	Clear image, no stain
PES/diazoresin	Ink stain	Clear image, no stain
PSMS-S/diazoresin	Ink stain	Clear image, no stain
HPM-S/diazoresin	Ink stain	Clear image, no stain

[a] PSS, poly(sodium styrene sulfonate); SPS, sulfonated polystyrene; PES, polyethylene sulfonate; PSMS-S, copolymer of sulfopropyl methacrylate, potassium salt, and styrene; HPM-S, hydrolyzed copolymer of maleic anhydride and styrene.

[b] Image A, treatment with ink before surface modification; Image B, treatment with ink after surface modification.

printing. A surface modification by polyphosphoric acid, to resolve the ink stain of the printing plate, has been developed.

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REFERENCES

1. Decher, G.; Hong, J. D. Macromol Chem Macromol Symp 1991, 46, 321.
2. Tsukruk, V. V.; Bliznyuk, V. N.; Visser, D. W.; Campel, A. L.; Bunning, T. J.; Adams, W. W. Macromolecules 1997, 30, 6615.
3. Decher, G.; Hong, J. D.; Schmidt, J. Thin Solid Films 1992, 210, 831.
4. Watanabe, S.; Rogen, S. L. J Am Chem Soc 1994, 116, 8855.
5. Tsukruk, V. V.; Rinderpacher, F.; Bliznyuk, V. N. Langmuir 1997, 13, 2713.
6. Iler, R. K. J Colloid Interface Sci 1966, 21, 569.
7. Cao, S.; Zhao, C.; Cao, W. Polym Int 1998, 45, 142.
8. Cao, W.; Ye, S.; Cao, S.; Zhao, C. Macromol Rapid Commun 1997, 18, 983.
9. Sun, J.; Wu, T.; Sun, Y.; Wang, Z.; Zhang, X.; Shen, J.; Cao, W. Chem Commun 1998, 1853.
10. Henry, F. P.; Seshgipt, R. N.; Vinayak, V. Y.; Keith, H. G.; Spencer, P. K. Eur. Pat. 0329899 A2, 1988.
11. Wang, C.; Cao, W. Polym Int 1996, 41, 449.
12. Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Pat. 3,870,841, 1975.
13. Klark, S. L.; Montague, M. F.; Hammond, P. T. Macromolecules 1997, 30, 7237.
14. Mao, G.; Tsao, Y.; Tirrell, M.; Davis, H. T.; Hessel, V.; Ringsdorf, H. Langmuir 1995, 11, 942.