Multilayer Assemblies of Poly(4-vinylpyridine) and Poly(acrylic acid) Bearing Photoisomeric Spironaphthoxazine via Hydrogen Bonding

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The hydrogen bonding directed formation of a photochromic multilayer film was achieved on the basis of alternating assembly of poly(4-vinylpyridine) and poly(acrylic acid) bearing spironaphthoxazine. The assembling process was followed by UV−vis spectroscopy and X-ray diffraction measurement. Atomic force microscopy was used to investigate the surface morphology of the multilayer film, and the interaction between the two polymers was identified as hydrogen bonding through Fourier transform infrared spectroscopy. The resulting multilayer film presents photochromic properties through photochemical interconversion of spironaphthoxazine between closed-ring and colored open-ring forms. This method of alternately assembling polymers in an organic solvent via hydrogen bonding provides a solution to the problem of incorporating functional polymers with poor water solubility into a layer-by-layer self-assembled film.

Introduction

Ultrathin organic films with thicknesses from a few nanometers to about a tenth of a micrometer have shown considerable technological potential as a novel class of materials.[1] One of the most important and universal techniques to construct ultrathin organic films is the alternating assembly of oppositely charged polyelectrolytes, the so-called "layer-by-layer self-assembly" method. Recently, more and more attention has been paid to this technique in both theoretical and application fields due to its simplicity, versatility, and systematic control of the film structure and thickness.[2−4] Incorporation of photoisomeric molecules provides the layer-by-layer (LBL) self-assembled film with additional interesting properties such as optically induced orientation, nonlinear optical properties, and so forth.[5] Tieke et al. have explored the photoisomerization process of a self-assembled film containing azobenzene groups and indicated that the self-assembled film could be used as an effective medium for reversible photochemical switching and optical information storage.[6] Tripathy et al. have fabricated azo polymer multilayer films by electrostatic self-assembly and layer-
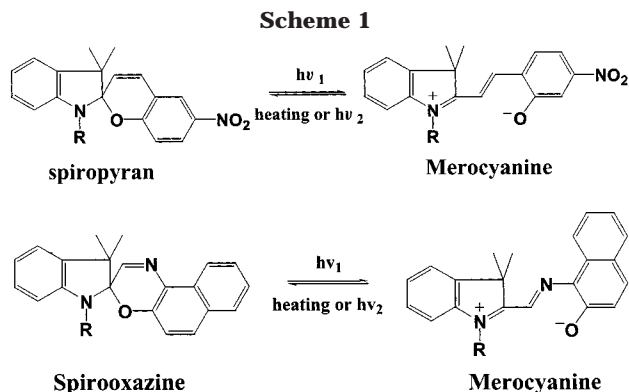
Scheme 1

by-layer post-azo functionalization. Moreover, a second harmonic generation was observed without any polling.[7]

Spiropyran/spirooxazine is a type of well-known photoisomeric molecules. As shown in Scheme 1, they can isomerize from the spiropyran/spirooxazine form to the corresponding intensely colored merocyanine form under ultraviolet irradiation, and this process can be reversed by visible-light irradiation or heating.[8] On the basis of the color and other changes in physical and chemical properties, numerous applications such as optical data storage and switches were examined.[9] Ultrathin films containing spiropyran/spirooxazine constructed by LB (Langmuir−Blodgett)[10] and SAM (self-assembled monolayer)[11] techniques have been reported. However, to the best of our knowledge, there are few reports on spiropyran/spirooxazine-containing LBL self-assembled film. This could be

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Scheme 2
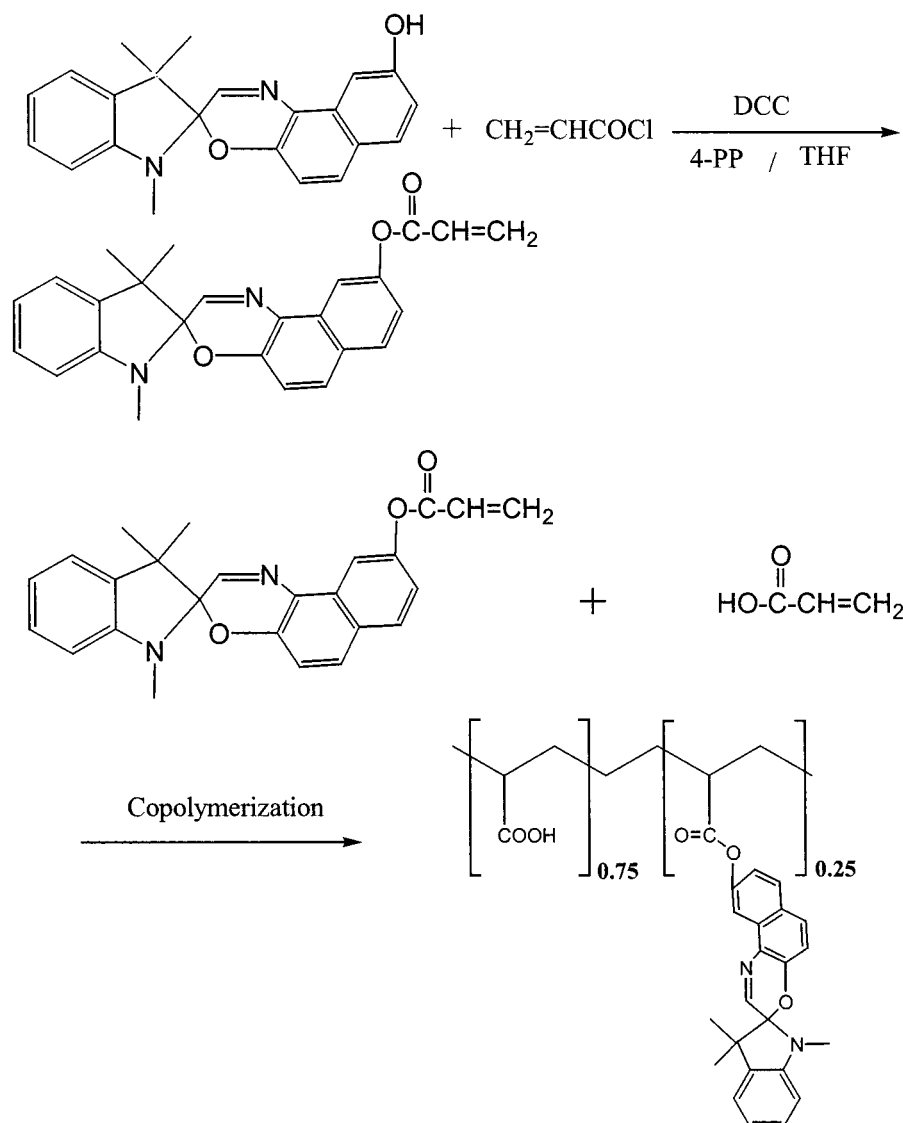
explained by the challenge in the synthesis of water soluble polyelectrolyte bearing spiropyran/spirooxazine and the effect of pH value on the photoisomerism of spiropyran/spirooxazine.[12] One of the solutions to the problem of incorporating spiropyran/spirooxazine into LBL self-assembled films is alternately assembling the polymers in an organic solvent. Recently, a new concept of assembling LBL films via hydrogen bonding was developed by Rubner et al. and Zhang et al.[13] One of the advantages of the hydrogen bonding directed film is allowing the fabrication of the LBL film in an organic solvent. Therefore, we took advantage of this concept to fabricate the LBL self-assembled film with spironaphthoxazine in an organic solvent via hydrogen bonding. The spironaphthoxazine was chosen for its excellent light fatigue resistance and high photostability, which are important to reliable and durable photoisomeric control systems.[14]

Experimental Section

General Methods. ^{1}H NMR spectra were recorded on a Varian 400 (400 MHz) spectrometer using the tetramethylsilane (TMS) proton signal as an internal standard with CDCl3 solution. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker IFS 66V instrument. X-ray diffraction (XRD) was carried out on a Rigaku X-ray diffractometer (D/max 2500V PC, using Cu Kα radiation of a wavelength of 1.542 Å). Ellipsometry was

carried out on an I-Elli2000 imaging ellipsometer (Nanofilm Technologie GmbH, Goettingen, Germany) at a 532 nm laser with a 50° incident angle. The values reported represent an average of at least five separate measurements on each film. UV−vis spectra were carried out on a Shimadzu 3100 UV−vis−near-IR recording spectrometer. UV and visible-light irradiation were carried out by using a 100 W Xe lamp with an excitation wavelength of 340 and 610 nm. Atomic force microscopy (AFM) images were taken with a multimode Nanoscope IIIA (Digital Instruments, Santa Barbara, CA) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Si cantilevers.

Synthesis of Poly(acrylic acid) Bearing Spironaphthoxazine. The poly(acrylic acid) bearing spironaphthoxazine (PAA−SO) was synthesized by copolymerization of the acryloyl ester of spironaphthoxazine with acrylic acid as is shown in Scheme 2, which is similar to the synthesis of polymer bearing spirobenzopyran.[15] The acryloyl ester of spironaphthoxazine was synthesized by adding dropwise and in an ice bath 1.086 g of acryloyl chloride (from Fluka) (30 mL of dry dioxane solution) to a mixture of 3.00 g (0.00872 mol) of 1,3,3-trimethyl-9′-hydroxyspiroindolinenaphthoxazine (SO) and 1.32 mL of triethlyamine in 60 mL of dry dioxane. The mixture was stirred for 2 h at room temperature. The crude product was purified with column chromatography eluting with CHCl3/ether (3:1 v/v). Yield: 28.8%. ^{1}H NMR (CDCl3 TMS): $\delta = 8.284-8.279$ (d, 1H, $J = 2$ Hz), 7.784−7.762 (d, 1H, $J = 8.8$ Hz), 7.716 (s, 1H), 7.672−7.650 (d, 1H, $J = 8.8$ Hz), 7.249−7.208 (m, 1H, $J = 16.4$ Hz), 7.195−7.167 (m,

Chart 1
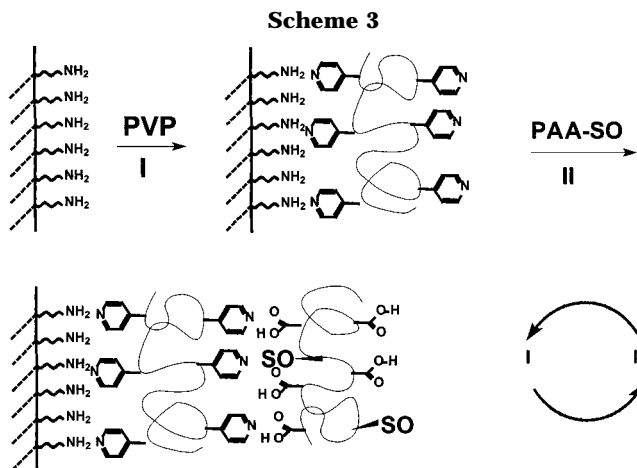

PAA-SO

PVP
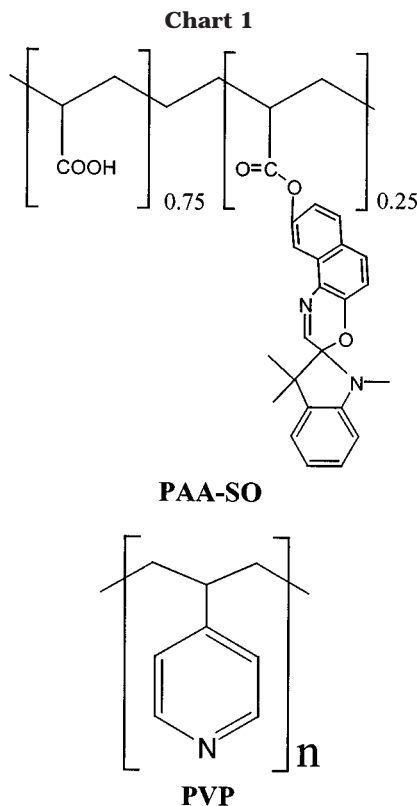
1H, $J = 11.2$ Hz), 7.102−7.085 (d, 1H, $J = 6.8$ Hz), 7.006−6.984 (d, 1H, $J = 8.8$ Hz), 6.926−6.889 (t, 1H, $J = 14.8$ Hz), 6.693−6.647 (m, 1H, $J = 18.4$ Hz), 6.597−6.578 (d, 1H, $J = 7.6$ Hz), 6.428−6.359 (m, 1H, $J = 27.6$ Hz), 6.075−6.046 (m, 1H, $J = 11.6$ Hz), 2.760 (s, 3H), 1.348 (s, 6H).

The purified product (0.5 g) and acrylic acid (0.37 g) were copolymerized with benzoylperoxide (BPO) in 10 mL of dry tetrahydrofuran (THF). The mixture was stirred at 70 °C for 12 h. The product was obtained by depositing its THF solution into ether. The Mw is about 11 000 (GPC, Waters 410, polystyrene as standard). The content of spironaphthoxazine units in the polymer was evaluated as about 25 mol % by comparing the absorption spectrum with that of low molecular spirooxazine[16] ($\lambda_{max} = 343$ nm, $\epsilon_{max} = 7900$ in THF). The content determined by elemental analysis (according to nitrogen content) is 21 mol %, which is in agreement with the above UV result.

Poly(4-vinylpyridine) (PVP) (Chart 1) and SO were prepared according to the literature.[17,18]

Multilayer Fabrication. The LBL films were assembled on substrates of quartz or CaF$_2$ plates. The quartz was ready for

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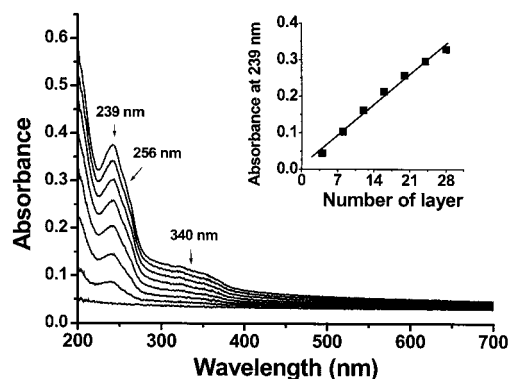
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Scheme 3

UV−vis, X-ray, and AFM measurements, and the CaF$_2$ for FT-IR. The quartz slides and CaF$_2$ plates need to be modified before LBL deposition. In the case of quartz, the surface was modified with (4-aminobutyl)-dimethylmethoxysilane in advance, having a NH$_2$-tailored surface,[19] and the CaF$_2$ surface was modified with a monolayer of poly(ethyleneimine) (PEI). Scheme 3 shows the assembling process on a quartz slide. The NH$_2$-terminated substrate was first immersed in PVP methanol solution (1 mg/mL) for 10 min. In this way, the substrate was covered with a PVP layer, and thus a hydrogen bonding acceptor (pyridine groups) tailored surface was formed. After being rinsed by dipping into three beakers with pure methanol for 1 min each, the resulting substrate was transferred into a PAA−SO THF solution (1 mg/mL) for 10 min, to add a PAA−SO layer with a hydrogen bonding donor (carboxylic acid groups) tailored surface. After being rinsed, the substrate covered with hydrogen bonding donors was again dipped into a PVP solution for 10 min to get another PVP layer. By repetition of the above steps in a cyclic fashion, the LBL self-assembly film was obtained.

Results and Discussion

The assembly process of the LBL film was monitored by UV−vis spectroscopy. Figure 1 shows the UV−vis spectra of the LBL film of PAA−SO and PVP with different numbers of layers. The absorption bands appearing at 239 nm and around 340 nm are separately assigned to indole ring and naphthoxazine ring absorption of SO in PAA−SO.[20] The shoulder around 256 nm is attributed to the pyridine absorption of PVP. As shown in the inserted figure, the absorbance at 239 nm increases linearly with the number of layers, which indicates a uniform assembly process. The colored merocyanine absorption around 610 nm is not observed, which indicates that most of the SO groups in the LBL film are in spirooxazine forms.

To choose an appropriate assembly time in PAA−SO and PVP solution, the absorption dynamic processes of PAA−SO and PVP were monitored separately by UV−vis spectroscopy. The PAA−SO and PVP were absorbed separately onto the 5-layer film and 6-layer film of PAA−SO and PVP in order to exclude the effect of the substrate. Figure 2A shows the growth of the absorbance at 239 nm as a function of the absorption time of PAA−SO. The absorbance increases rapidly at the very beginning, and then after about 60 s it reaches the saturation. A similar dynamic process was found in the case of PVP, as shown in Figure 2B. The saturation time of PVP is about 20 s. For the consideration of equilibrating deposition of the polymer adequately at the film surface, the immersing time of both PAA−SO and PVP was set as 10 min.

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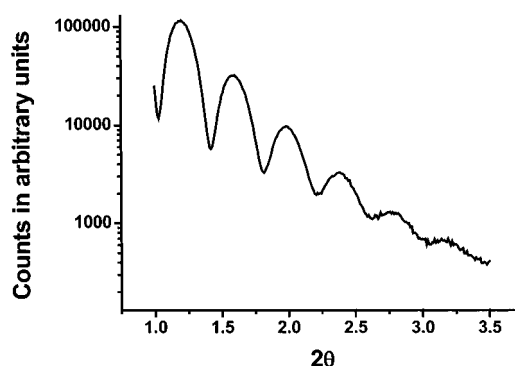
Figure 1. UV−vis absorption spectra of the LBL film of PAA−SO and PVP with different numbers of layers: (from bottom to top) 0, 4, 8, 12, 16, 20, 24, and 28. The inserted figure shows the absorbance at 239 nm vs the number of layers.
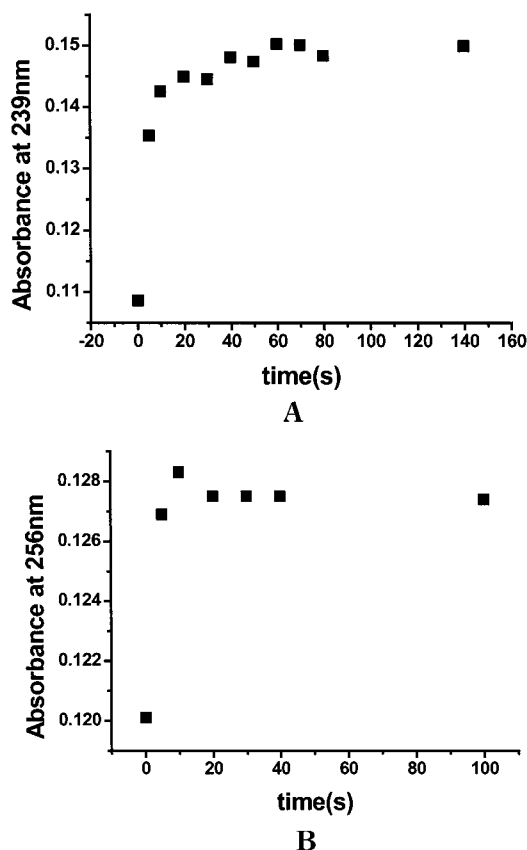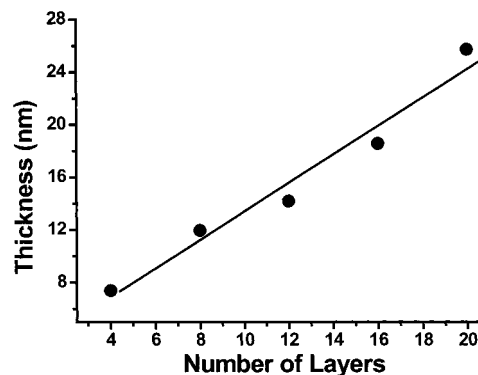

Figure 2. (A) Absorbance at 239 nm of a PAA−SO layer on a 5-layer LBL film vs the adsorption time. (B) Absorbance at 256 nm of PVP on a 6-layer LBL film vs the adsorption time.

X-ray diffraction measurement is an effective and powerful method to detect the structure and follow the assembly process of the LBL film.[21] Figure 3 shows the X-ray diffraction pattern of a 16-layer film of PAA−SO and PVP, in which the Kiessig fringes are found and no Bragg peaks are observed. The X-ray results suggest the formation of a good and smooth film with constant thickness and low surface roughness and without regular electron density modulation across the film. This is in agreement with another investigation which indicates that the neighboring layers in the LBL film are interpenetrated.[22] The thicknesses of the LBL films with different

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Figure 3. X-ray diffraction pattern of a 16-layer LBL film of PAA−SO and PVP.

Figure 4. The total thickness of the LBL film of PAA−SO and PVP vs the number of layers.

numbers of layers could be calculated according to their corresponding X-ray patterns. As shown in Figure 4, the thickness of the LBL film increases linearly with the number of layer pairs and the layer pair thickness is about 2 nm. The similar linear increase of the film thickness is also indicated by ellipsometry, and the ellipsometry thickness of the layer pair is about 3 nm.

AFM was employed to investigate the surface morphology of the LBL film. The AFM height (A) and phase (B) images of the 10-layer film shown in Figure 5 demonstrate remarkably homogeneous coverage of the LBL film, and the mean roughness (Ra) is about 1 nm. The AFM results combined with the above X-ray data suggest that the LBL film of PAA−SO and PVP should be of high quality.

FT-IR was employed to characterize the interaction between two neighboring polymers in the LBL film. To discuss the FT-IR results clearly, FT-IR spectra of PAA and SO are first shown in Figure 6. The bands of PAA appearing at 1708 and 1741 cm^{-1} can be separately assigned to vibrations of the carbonyl of carboxylic acid groups in associated and free states.[25] In the case of SO, there is no characteristic band from 1680 to 1800 cm^{-1}. Figure 7 shows the FT-IR spectra of pure PAA−SO, PVP, and the 16-layer film. The peaks appearing at 1595, 1556, and 1450 cm^{-1} can be ascribed to the ring vibration of pyridine in PVP. The broad band of PAA−SO at about 3200 cm^{-1} and the bands around 1714 cm^{-1} are separately assigned to stretching vibrations of hydroxyl and carbonyl groups. There should be two different types of carbonyl groups in PAA−SO. They are originated from the carboxylic acid groups and the ester groups. However, they are overlapped as shown in Figure 7. To distinguish the two different types of carbonyl groups, the PAA−SO polymer was taken as a second derivative in the region from 1660 to 1770 cm^{-1} as is shown with the solid line in Figure 8. The two peaks occurring at 1714 and 1729 cm^{-1}
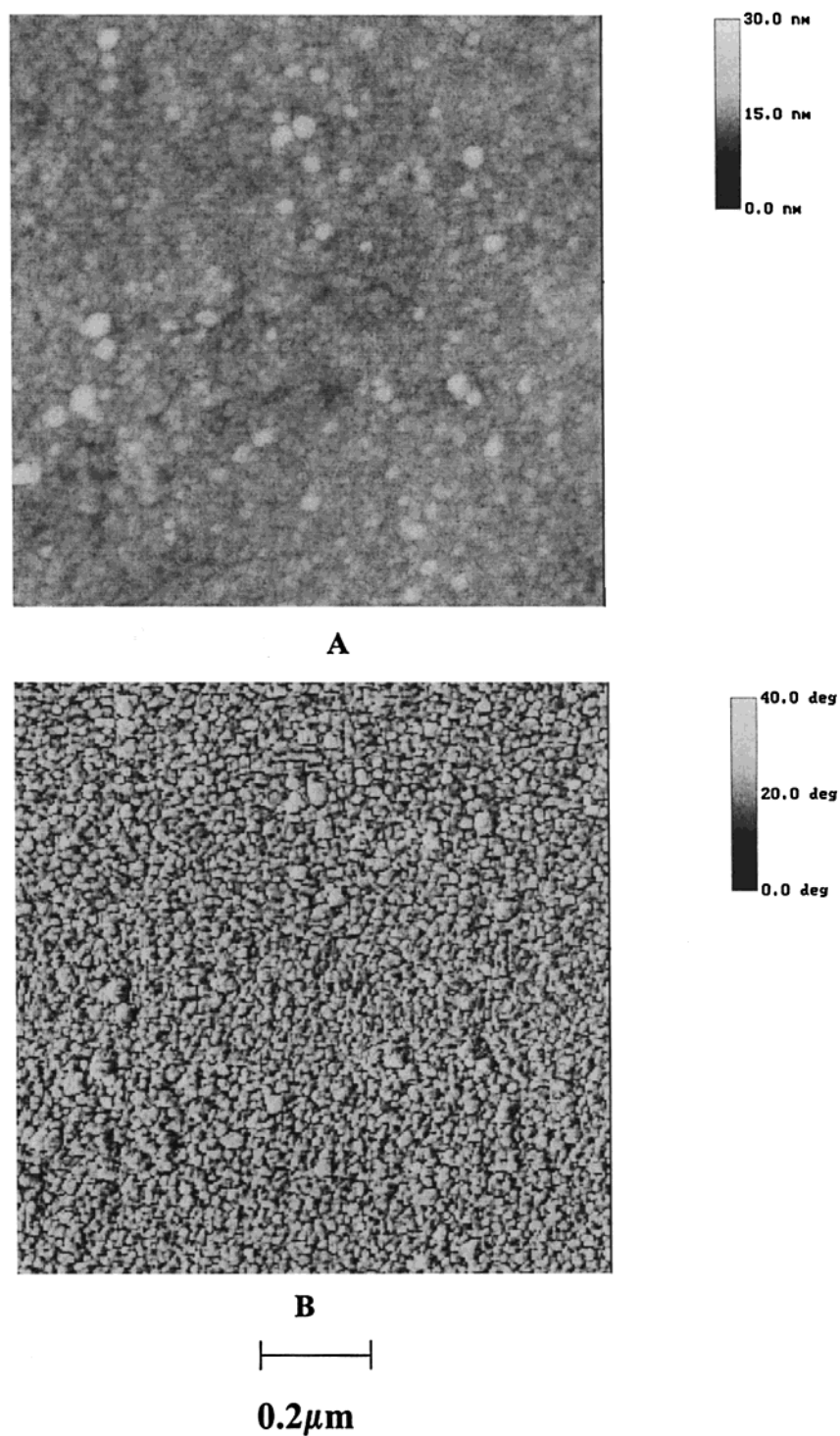
Figure 5. The AFM height (A) and phase (B) images of a 10-layer LBL film of PAA−SO and PVP with the size 1 × 1 μm.

could be assigned separately to the vibration of the carbonyl of carboxylic acid and of the ester groups. The above result indicates that the carboxyl group in pure PAA−SO is not free but is in an associated state. As shown in Figure 6, the vibration of the hydroxyl group in the LBL film appears around 2450 and 1900 cm^{-1}.[23] Concomitantly, only one absorption peak around 1729 cm^{-1} was observed in the second derivative plot of the LBL film as is shown with the dash line in Figure 8. It could be attributed to the shift of the carbonyl absorption peak of

the carboxylic acid group in PAA−SO from 1714 to 1729 cm^{-1}. The hydrogen bonding formation between carboxylic acid and pyridine in the LBL film frees carbonyl groups from the associated form in pure PAA−SO and shifts their stretching vibration absorption to a higher wavelength. As a result, the vibrations of the two different types of carbonyl groups become undistinguished. Both of the above two changes suggest that hydrogen bonds are formed between PAA−SO and PVP in adjacent layers.[24,25] Furthermore, there is almost no change in the positions of the bands from 1300 to 1650 cm^{-1} in the LBL film compared with those in the pure polymers, which implies
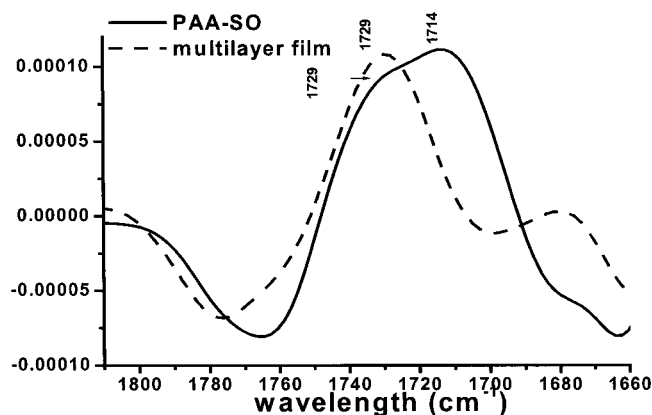
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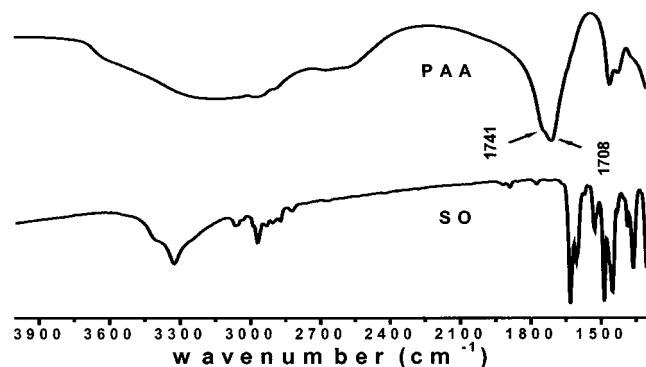
Figure 6. FT-IR spectra of PAA and SO.
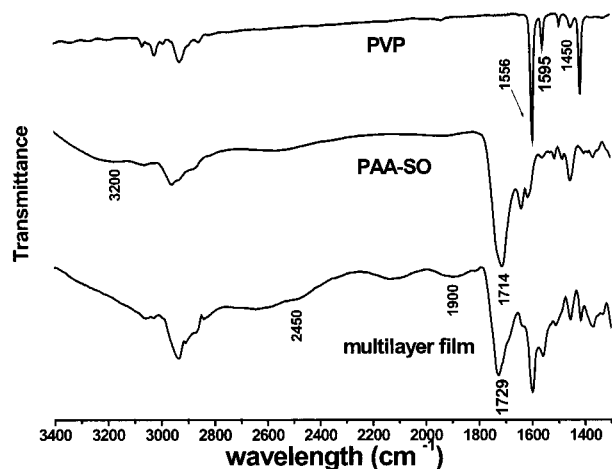
Figure 7. FT-IR spectra of pure PVP, pure PAA−SO, and a 16-layer LBL film of PAA−SO and PVP.
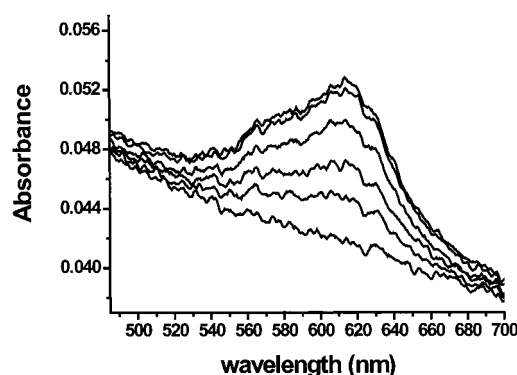

Figure 8. Second derivative plots of the pure PAA−SO polymer (denoted by the solid line) and a 16-layer LBL film of PAA−SO and PVP (denoted by the dashed line) in the region from 1660 to 1770 cm^{-1}.

Figure 9. UV−vis absorption spectra of a 28-layer film of PAA−SO and PVP under UV irradiation at 360 nm at different times: (from bottom to top) 0, 0.5, 1.5, 4, 9, and 16 min.

Figure 10. Absorbance of a 28-layer LBL film of PAA−SO and PVP at 610 nm vs time. The absorbance increases under the irradiation at 360 nm and decreases upon visible-light irradiation at 610 nm.

that the carboxyl group of PAA−SO and the pyridine group of PVP in the LBL film are not ionized.[26] The FT-IR of the bulk blend has also been done for comparison. The stretching bands of hydroxyl and carbonyl groups in the film and the bulk blend are similar except the intensity. Thus, it is reasona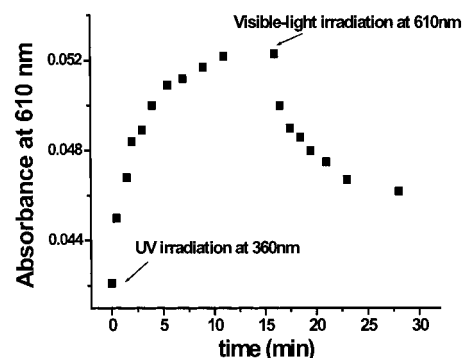ble to draw the conclusion that the fabrication of the LBL film is directed not by electrostatic attraction but by hydrogen bonding.

The photoisomeric property of the LBL film of PAA−SO and PVP was explored. Figure 9 shows the spectra of a 20-layer film of PAA−SO and PVP under UV irradiation at 360 nm at different times. The absorption band occurring at 610 nm is ascribed to the absorption of the colored merocyanine group.[27] Figure 10 shows the change of the absorbance at 610 nm upon UV or visible-light irradiation with time. Under UV irradiation at 360 nm, the spironaphthoxazine in the film isomerizes into its corresponding colored merocyanine and reaches an equilibrium state within about 15 min, whereas under visible-light irradiation at 610 nm the merocyanine can revert to the spironaphthoxazine form. From the above phenomena, it could be suggested that SO could photochemically interconvert between spirooxazine and merocyanine in the LBL self-assembled film medium.

Conclusion

In conclusion, the concept of the hydrogen bonding directed LBL self-assembled film was used to fabricate the LBL film containing photoisomeric spirooxazine by alternately assembling poly(acrylic acid) bearing spironaphthoxazine with poly(4-vinylpyridine) in an organic solvent. The assembling process, the structure, and the interaction between the two polymers of the LBL film were carefully characterized. Furthermore, the spirooxazine groups can photochemically interconvert between their closed-ring and colored open-ring forms in the LBL film. The application of multilayer films containing

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spiropyran/spirooxazine for photo information storage and photoswitches is greatly anticipated.