

Self-Assembled Multilayer Films Based on Diazo-resins Studied by Atomic Force Microscopy/Friction Force Microscopy

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ABSTRACT: The layer-by-layer self-assembled NDR-PSS (nitro-containing diazo-resin-polysodium *p*-styrenesulfonate) films were fabricated. The crosslinking structure formed from the conversion of ionic bond to covalent bond after UV irradiation, confirmed by small angle X-ray diffraction. The roughness and microtribological properties of NDR-PSS films were investigated by atomic force microscopy/friction force microscopy. The ordered multilayer films after photoreaction are better in microtribological performance than that of the monolayer film. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 631–638, 2000

Key words: self-assembled nitro-containing diazo-resin-polysodium *p*-styrenesulfonate film; UV irradiation; roughness; microtribological property; atomic force microscopy/friction force microscopy

INTRODUCTION

The studies of microtribological properties have been developed into an interdisciplinary field that encompasses organic, polymeric materials. The ordered thin polymer films on solid surfaces have attracted much attention in recent years,^{1,2} because polymer molecules are typically flexible, the soft chains are reasonable to consider antiwear, and the existence of rod segments in these films is expected to be beneficial for bearing the applied load.

Some self-assembled films formed from amphiphilic polymer³ and C60-polystyrene copolymer films⁴ were reported. Their synthesis, structure, and microtribological properties were investigated.

Layer-by-layer self-assembly technique by electrostatic interaction as the driving force is a general approach for the fabrication of oppositely charged polyelectrolytes.⁵ This technique has been proved to be a rapid and experimentally very simple way to prepare layered structure with precise control.⁶

In our previous work, a multilayer thin film based on diazo-resin via self-assembly technique on mica was fabricated.⁷ The crosslinking structure of the multilayer film was formed from the conversion of ionic bond to covalent bond under UV irradiation, so that the films are very stable toward polar solvents.^{6–8}

In present paper, we report that the multilayer film from nitro-containing diazo-resin (NDR) as polycation and poly(sodium *p*-styrenesulfonate) as polyanion were fabricated. Using UV-vis, small angle X-ray diffraction (SAXD), and atomic force microscopy/friction force microscopy (AFM/FFM), the film structure, surface morphology, and microtribological properties before and after photoreaction were characterized.

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EXPERIMENTAL

Fabrication of Films

NDR, prepared in our laboratory as described elsewhere,⁸ $M_n \approx 2500$ g/mol, PSS (ACROS) with $M_w = 100,000$ g/mol, was used as received. The fabrication process was conducted in the dark at room temperature. The freshly cleaved mica, which has a negative surface in water, was used as substrate. The mica was first immersed in NDR aqueous solution (2 mg/mL) for 5 min; after rinsing with deionized water and air drying, the mica was immersed in PSS aqueous solution (2 mg/mL) for 5 min, then rinsed and dried as above. Repeating the procedures, a layer-by-layer self-assembled polyelectrolyte film was obtained. In this paper, the films with 1 bilayer, 4 bilayers, 5 bilayers, 10 bilayers, and 12 bilayers were prepared.

Photoreaction

The films were irradiated with a 80 w medium pressure mercury lamp at a distance of 13 cm for 10 s. The photoreaction was monitored by determining the absorbance of the films on a Shimadzu 2100 UV-vis spectrophotometer at 383 nm, which is the characteristic absorption of the diazodium group of NDR.

Small Angle X-Ray Diffraction

An RINT 2000 instrument was used to investigate the regularity of self-assembled films. As described above, the 12-bilayer NDR-PSS film on mica was prepared, the mica was adhered onto a glass slide, the glass slide was set with the standard sample holder, and the film surface and holder surface was kept to be in same level. The measurements were performed with an X-ray of CuK- α 1/40 kV/100 ma in reflection mode and the scan speed 4.000°/min. The scan angle was from 1° to 10°.

Atomic Force Microscopy/Friction Force Microscopy

The measurements were performed with Nanoscope IIIa (Digital Instruments, Inc.) equipped with a bioscope G scanner (90 μ m) in contact mode and tapping mode, respectively. A commercial Si₃N₄ cantilever with spring constants of $K = 0.32$ and $K = 0.58$ N m⁻¹ were used to obtain the roughness and friction images in air at 25°C

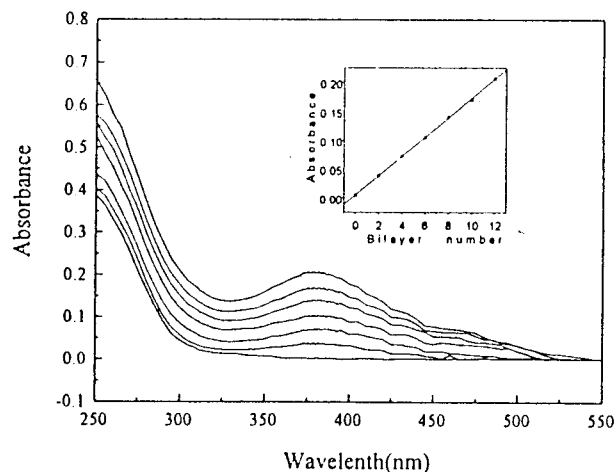


Figure 1 The UV-vis spectra of the multilayer films with different numbers of bilayer. The bilayer numbers (bottom to top): 0, 2, 4, 6, 8, 10, 12. Inset plot shows the relationship of absorbance and bilayer numbers.

and relative humidity 50%. The typical scan rates were 2 Hz.

The frictional images were obtained through frictional channel with the scan angle of 90°. The frictional forces were presented by taking the difference of the frictional signals between the film surface and mica surface (which was created by scraping the film surface with the tip). As the lateral force constant of the V-shape cantilevers and the lateral sensitivity of the optical detector were not measured, we could not obtain the absolute frictional force. In this paper, we used the frictional signals (in volts) to present the relative frictional force.⁹

RESULTS AND DISCUSSION

The UV-vis spectra (Figure 1) show the absorbance of polyelectrolyte films at 383nm increases with the numbers of bilayer (NDR-PSS). This is fair evidence that the film is really fabricated via layer-by-layer self-assembly. The film consists of oppositely charged polyelectrolytes; both cationic and anionic polymer chains exhibit an extremely high tendency to aggregate orderly by electrostatic attractive force, as schematically shown in Figure 2.

Usually, the polyelectrolyte film requires a certain number of ionic bonds with substrate. But the film fabrication on the surface (substrate and newly formed film surface) is mostly dependent on the chosen of polyelectrolytes and adsorption

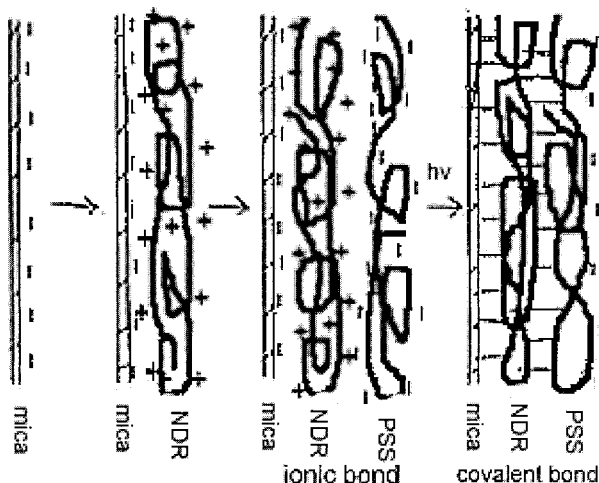
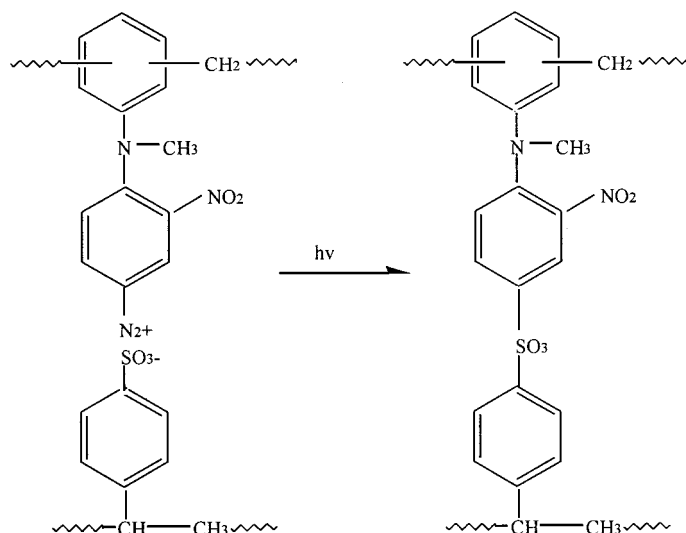


Figure 2 The schematically representation of a bilayer film of NDR-PSS fabrication on mica surface and the conversion of ionic bond to covalent bond under UV irradiation.

conditions rather than the substrate itself, because polymers can simply bridge over underlying defects.¹⁰ So we used the freshly cleaved mica without further treatment; the original hydroxy groups that existed can chemically bond with cationic polyelectrolyte.⁷

After photoreaction, the crosslinking structure of the multilayer films was formed via the conversion of ionic bond to covalent bond, as shown in Scheme 1. It was confirmed by Fourier transform IR studies.⁶



Scheme 1 The structure of NDR-PSS changes from ionic bond to covalent bond under UV irradiation.

SAXD is well suited for the characterization of multilayer films, as it allows the determination of structure regularity.¹¹ As revealed in Figure 3, the diffraction peaks indicate that the 12-bilayer film of NDR-PSS is ordered periodically, whether before (a) and after (b) photoreaction.

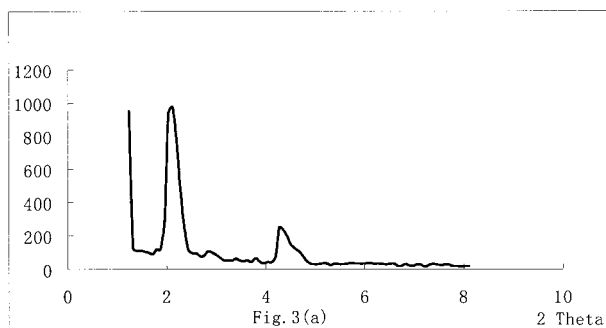
It is more interesting that after photoreaction, the first diffraction peak shifts from $2\theta = 2.04$ to $2\theta = 2.12$, according to the Bragg equation; the d value changes from 4.33 to 4.16 nm. The long period shortened 0.17 nm, so that the more compact combination occurs in the NDR-PSS bilayer film after UV irradiation. This agrees well with the $-\text{N}\equiv\text{N}^+$ group disappearance and covalent bond $-\text{C}-\text{O}-\text{S}-$ formation after photoreaction.

To study surface roughness and friction property of thin film on a micro-nanoscale, AFM/FFM is considered an excellent tool.¹²⁻¹⁴

The surface roughness of 4-bilayer NDR-PSS films on mica were visualized using AFM in tapping mode, shown in Figures 4 and 5. The images revealed the films are rather flat and uniform before and after photoreaction.

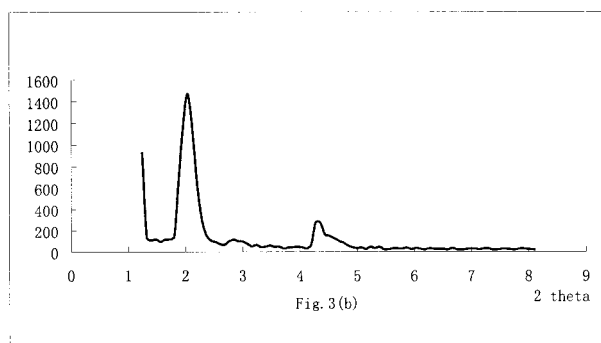
In order to test film stability in the microwear process, AFM with contact mode was used. The AFM images of the 5-bilayer film of NDR-PSS before and after photoreaction were obtained, as shown in Figure 6.

From Figure 6(a), we can see the film material easily removed by the tip under normal condition (scanning only once by contact mode



Peak	2Theta	d-value (Å)	Intensity	I/I ₀
1	2.040	43.2708	2856	48
2	2.840	31.0834	206	3
3	4.300	20.5322	587	10

(a)



Peak	2Theta	d-value(Å)	Intensity	I/I ₀
1	2.120	41.6381	1864	29
2	2.860	30.8660	195	3
3	4.300	20.5322	514	8

(b)

Figure 3 SAXD diagrams of 12-bilayer film of NDR-PSS on mica before (a) and after (b) photoreaction, and the d values calculated from 2θ .

with 5 nN applied load). Comparatively, the film was not damaged in Figure 6(b). It was demonstrated that the photoreacted films are more closely and stably absorbed, and adhered on the mica substrate.

The photoreacted films with 1 bilayer and 10 bilayer were used in AFM/FFM studies. The height and friction images were obtained simultaneously in contact mode, as shown in Figures 7 and 8, respectively. The local variations in the micrometer-scale friction were observed.

Many frictional properties of the self-assembled organic compound monolayer are revealed

in topographic and friction data by AFM and FFM, which demonstrated that frictional force depends on chemical structure, packing density,¹⁵ intrinsic molecular tilt,¹⁶ molecular chain length, functional groups, sliding velocity, and humidity.^{17,18} In our paper, the NDR-PSS films have more long and flexible molecular chains than organic compound films. What are the main effective factors for friction properties of polymer film?

Our experimental results demonstrated the films were in regularity in macroscale, but we believe the intrinsic molecular chains were locally disordered due to long chains tangled in polymers. We attempt to show that the local variation of friction in Figures 7 and 8 has a contribution at least, which is that the intersection for both the NDR layer and PSS layer was presented, and that the packing density of NDR-PSS film was increased with the layer numbers. This has been described in our previous AFM determination elsewhere.⁷ The polymer films have a more flat and closely surface.

The other effects for polymer film need further investigation elsewhere. However, for a fundamental understanding, the friction phenomena of multilayer polymer film is inherently remained elusive.

The investigation of the relation between friction force and load (including adhesive force) could help the interpretation of AFM/FFM images at the molecular level.¹³ The typical approach to characterizing friction is to use the friction signals in trace friction images.⁹ Here we study the frictional properties of NDR-PSS film on mica using frictional signals; the frictional signals could be measured at a different applied load for the same area in FFM trace image. The friction properties of NDR-PSS film were presented by taking the difference of the frictional signals between the film surface and mica surface.

Figure 9 illustrated how we get the frictional signals from the FFM trace image. As shown, we created a clean mica surface as a frictional reference surface by scanning the film surface with high load (~ 100 nN). Therefore, we could obtain the friction signals of both mica and film simultaneously.

We varied the applied load, and the relative friction signals between mica and NDR-PSS film were recorded, as shown in Figures 10 and 11.

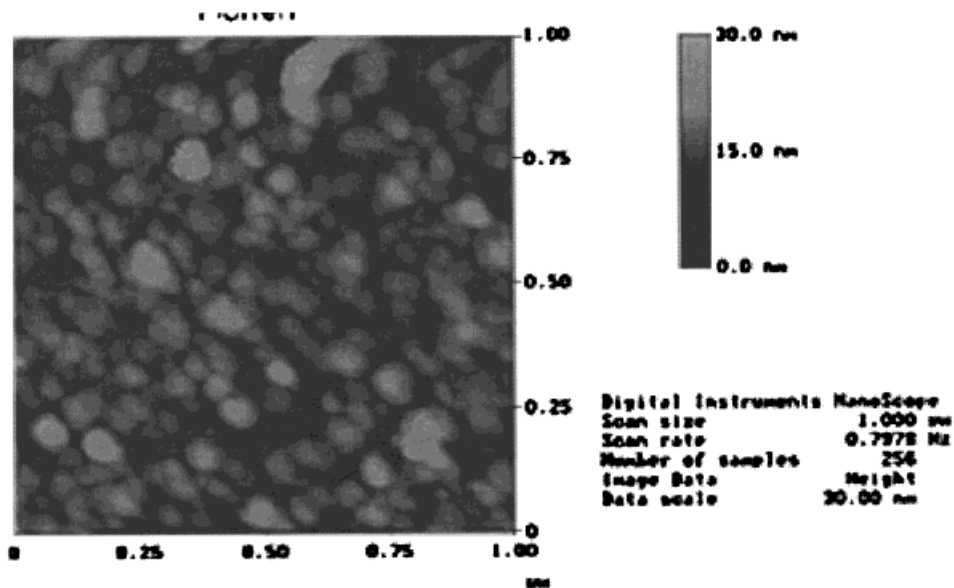


Figure 4 Tapping mode AFM image of the unirradiated 4-layer film of NDR-PSS on mica surface.

In Figures 10 and 11, the friction signals increased with the applied loads, which revealed the nonlinear relation.

As reported by many researchers,^{9,19} the friction force obtained in FFM is mostly proportional to applied load for organic compounds. The nonlinear relation shown in Figures 10 and 11 could be contributed from the nature of

NDR-PSS self-assembled film. The possible interpretation is that since viscoelasticity is a polymer characteristic, it mainly depends on chemical structure, applied load, time, and temperature, which is caused by the intrinsic long chain moving in polymer.²⁰ The relation between friction signals and applied load on the polymer film surface may deflect from pro-

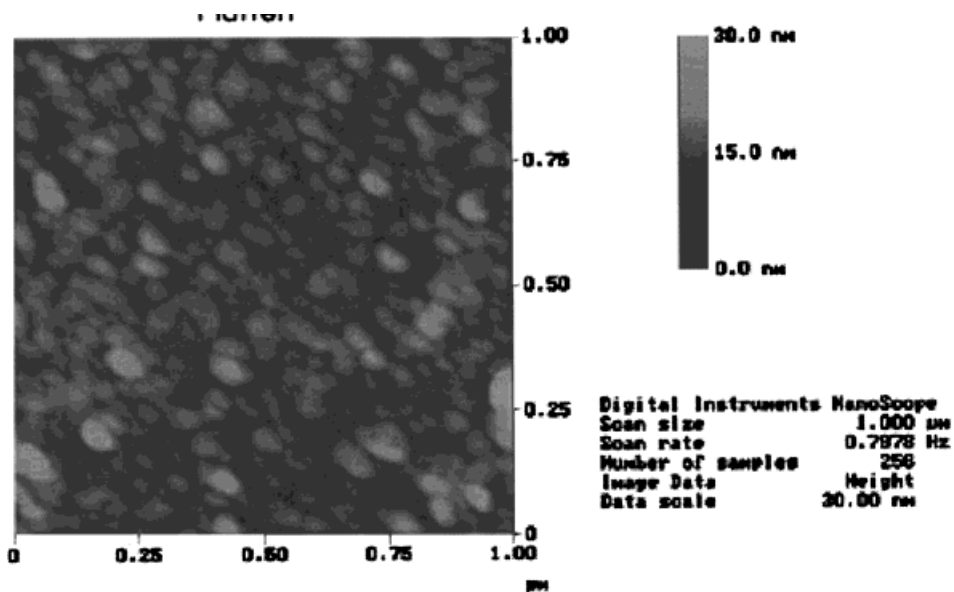


Figure 5 Tapping mode AFM image of the irradiated 4-layer film of NDR-PSS on mica surface.

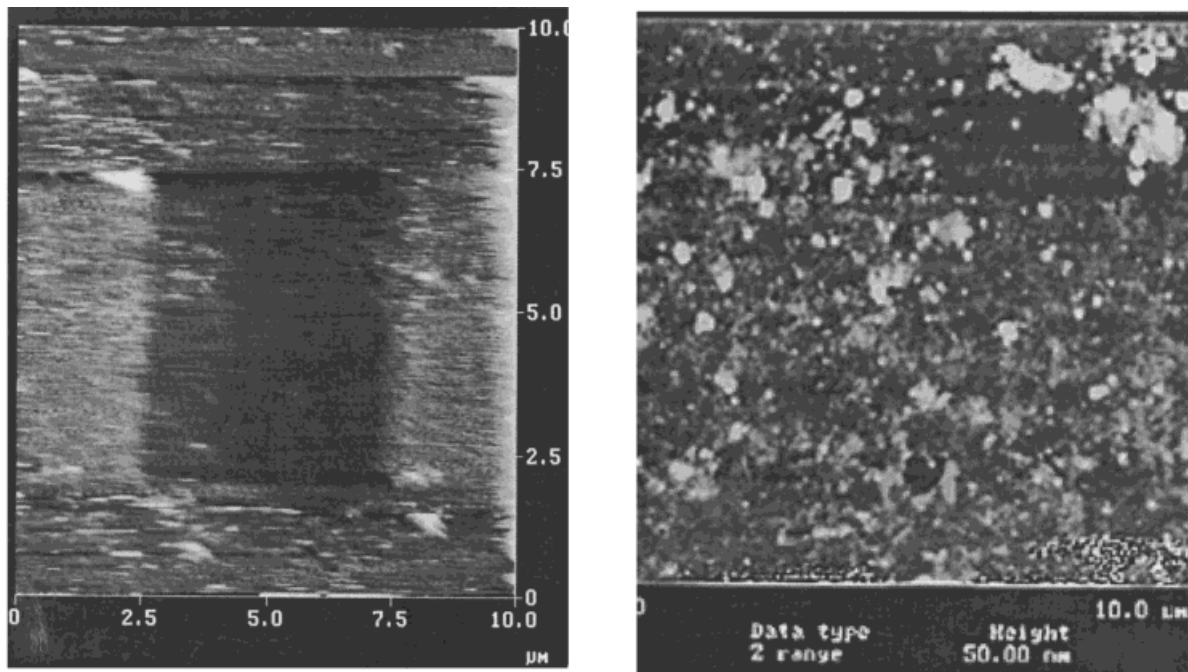


Figure 6 The AFM images of 5-layer film of NDR-PSS before (a) and after (b) photoreaction in contact mode under 5 nN applied load.

portionality with changes in load, temperature, and humidity. Further exploration is necessary.

Meanwhile, it is observed that both 1-bilayer and 10-bilayer films exhibit stable and lower friction force signals below the 50 nN load. Obvi-

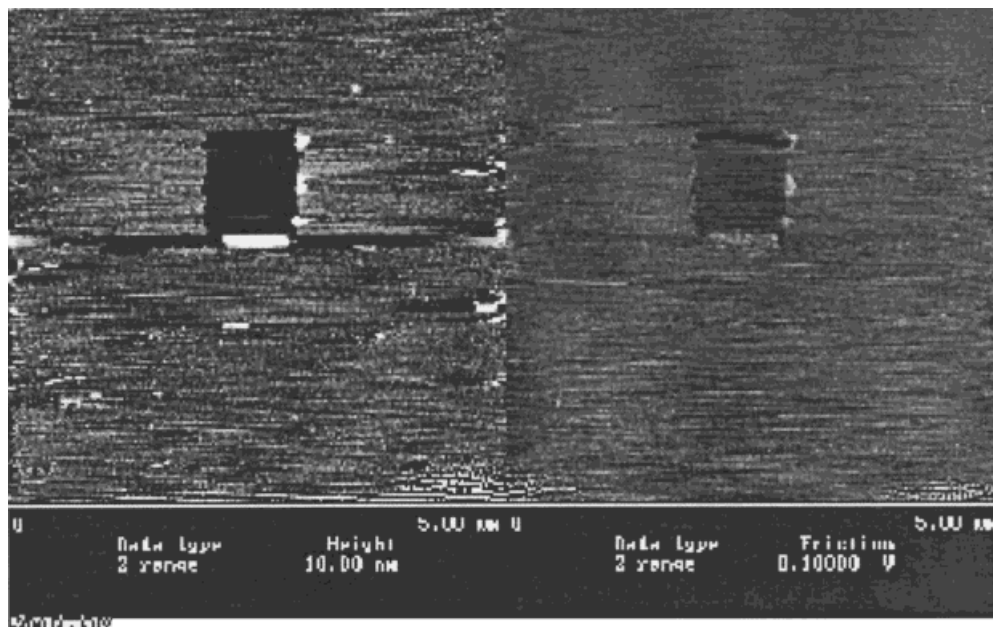


Figure 7 The roughness and friction images of 1-bilayer film of NDR-PSS were obtained simultaneously in contact mode with cantilever spring constant $K = 0.32$ commercial Si_3N_4 tip.

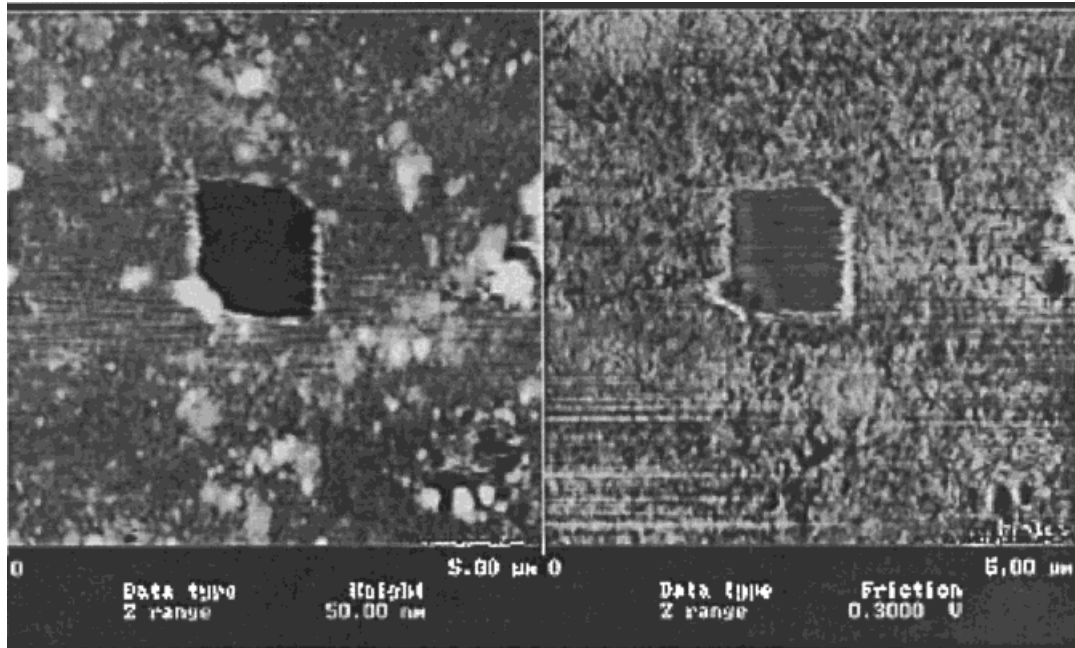


Figure 8 The roughness and friction images of 10-bilayer film of NDR-PSS were obtained simultaneously in contact mode with cantilever spring constant $K = 0.58$ commercial Si_3N_4 tip.

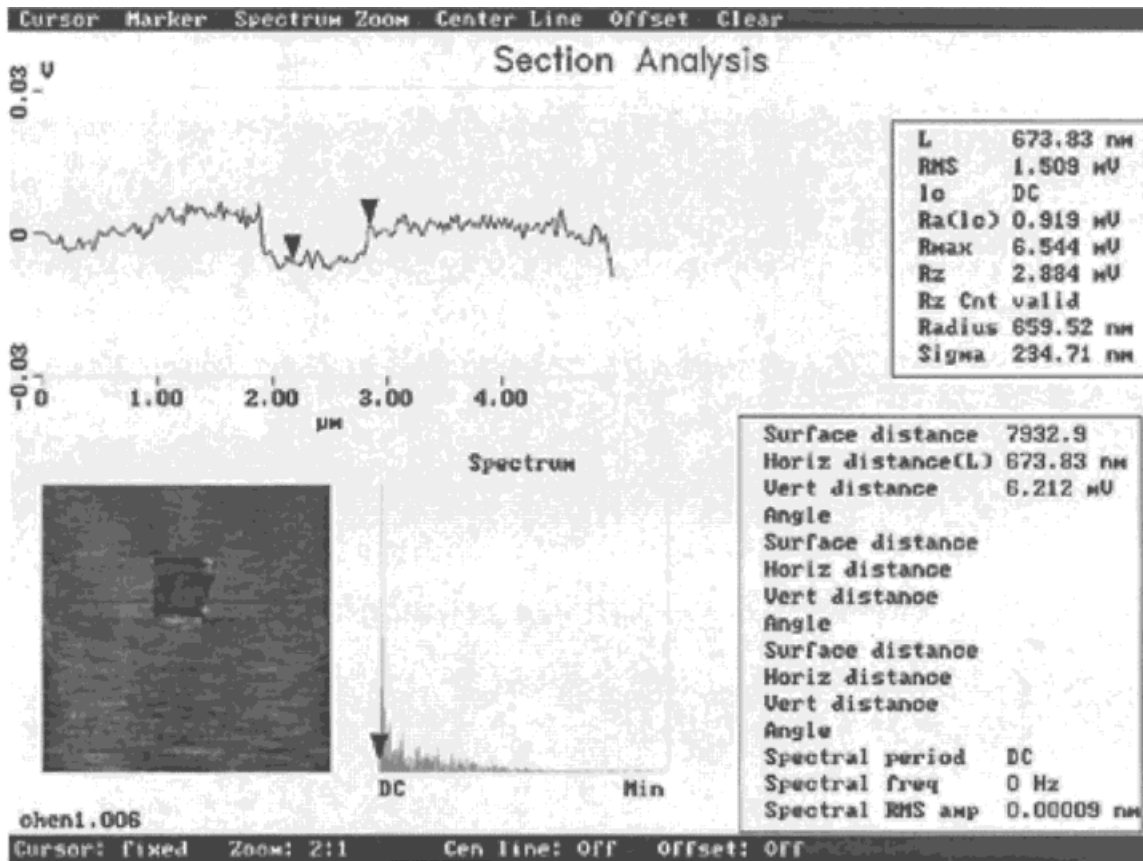


Figure 9 The friction force signal was measured in FFM trace image along with a profile line.

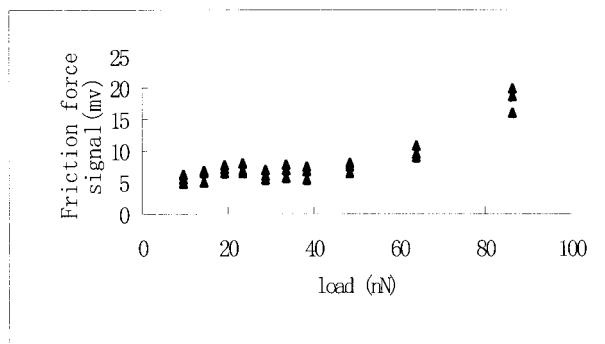


Figure 10 Diagram of friction force signal vs load for 1-bilayer film of NDR-PSS after photoreaction.

ously, the 10-bilayer film is better in bearing load and antiwear than that of 1-bilayer film.

The microtribological properties of NDR-PSS ordered film explored should encourage the idea that polyelectrolyte self-assembled films can be lower in friction and wear at the microscale.

CONCLUSION

The self-assembled thin films of NDR-PSS were studied by SAXD and AFM/FFM. The crosslinking structure formed from the conversion of ionic bond to covalent bond after photoreaction was further confirmed. These films are ordered and stable. AFM/FFM studies provide insights into the friction and wear properties on the microscale; this kind of self-assembled multilayer

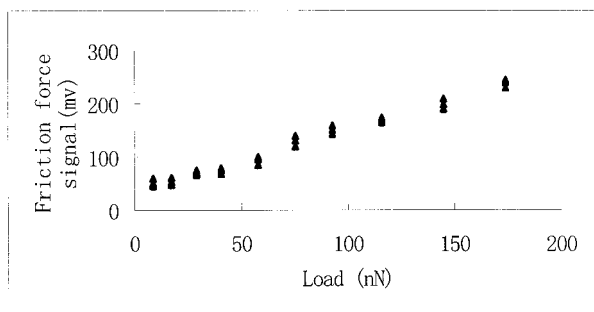


Figure 11 Diagram of friction force signal vs load for 10-bilayer film of NDR-PSS after photoreaction.

film is promising for lubrication materials. The study of microtribological properties of polymer thin film poses novel challenges of its own.

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