

Studies on the Electrostatic Self-Assembly of Polyelectrolytes and Organic Dyes with Atomic Force Microscopy

Anyong Zhong, Xianjun Lin, Deben Chen, Zonghua Zhou

Department of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China

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ABSTRACT: An ultrathin film was formed by the electrostatic self-assembly of polyelectrolyte poly-*N*-ethyl-*N,N*-dimethylaminoethyl methacrylate (PDMAEB) and the organic dye metanil yellow (MY) on a smooth glass sheet. An atomic force microscope was used to study the topography and the phase of the two samples and the ultrathin film (PDMAEB-MY). The dynamic course of the surface structure was researched by atomic force microscopy also. It is

illustrated that the existence of electrostatic interactions between PDMAEB and MY made MY arrange in order on the polyelectrolyte surface. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1029–1033, 2003

Key words: polyelectrolytes; atomic force microscopy (AFM); self-assembly

INTRODUCTION

The key role of the surface for many material properties and for many biological processes has been recognized before now. Therefore, new strategies have aimed at the tailoring of only the surface of materials or of a thin-surface layer while preserving the bulk properties of the underlying support. Particular emphasis has been given to the surface modification by polymers in an attempt to extend the known versatility of polymer bulk materials to ultrathin films and coatings and to prepare bulk-surface composite materials. The self-organization of polymers has been increasingly explored for the preparation of well-defined surfaces and interfaces in recent years, extending the use of the established methods of low-molar-mass compounds.^{1–3} With such techniques, polymer films are formed spontaneously on substrates due to balanced interactions between substrate, polymer, and medium. Typically, very thin, often monomolecular, layers are produced.

Ultrathin films and multilayered structures are important for many applications, including X-ray optics,⁴ nonlinear optics,⁵ and microelectronics^{6,7} and are under investigation for use as chemical sensors.⁸

The most recent of the self-organization techniques is the alternating physisorption of oppositely charged polyions, a practical method for electrostatic self-as-

sembly (ESA) was developed only in the early 1990s by Decher's group. Its striking simplicity makes it very interesting.^{9–14}

In this study, the polyelectrolyte poly-*N*-ethyl-*N,N*-dimethylaminoethyl methacrylate (PDMAEB) and organic dye metanil yellow (MY) were used to form ultrathin films by ESA. The dynamic course of the surface structure was investigated by atomic force microscopy (AFM). By comparing the appearance and phase of the MY and PDMAEB with the self-assembly film, we induced that the electrostatic interaction between PDMAEB and MY made MY arrange in order on the surface of PDMAEB.

EXPERIMENTAL

Materials

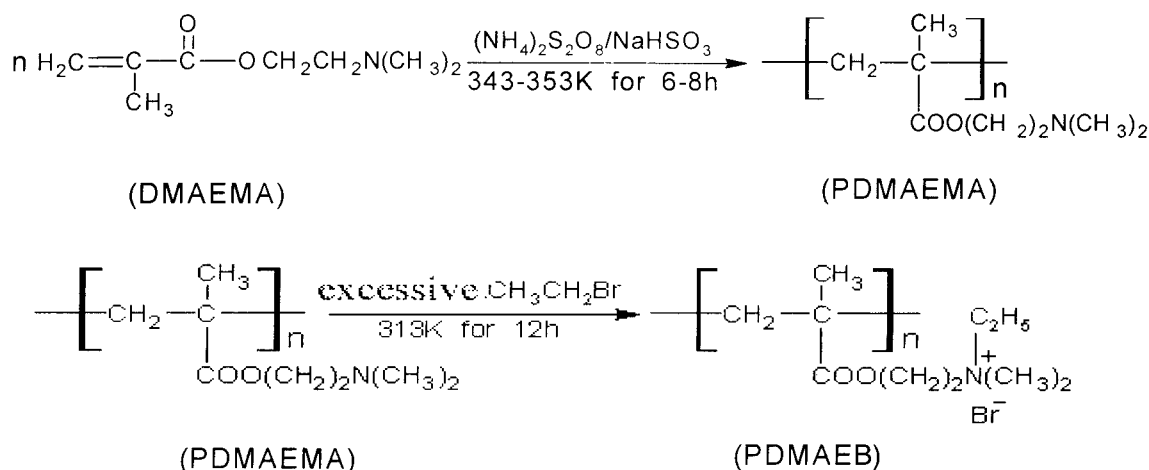
The monomer *N,N*-dimethylaminoethyl methacrylate (DMAEMA, Chenguon Chemistry and Engineering Research Institute, Chengdu, China) was used to prepare the polyelectrolyte. The organic dye was MY. The solvents used in this experiments were NaOH, tetrahydrofuran (THF), bromoethane, alcohol, nitrobenzene, ammonium peroxydisulfate [(NH₄)₂S₂O₈], and sodium hydrogen sulfite (NaHSO₃). The dyes and solvents were analytical pure grade (Beijing Chemical Co., Beijing, China).

Instruments

A scanning probe microscope system SPI3800N Series SPA-400 atomic force microscope (Seiko Instruments Inc., Japan) was used.

Correspondence to: A. Zhong.

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Scheme 1

Sample preparation

1. In a three-necked reaction vessel (250 mL), DMAEMA (20 mL), which had to be purified through distillation before being used; $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (0.84 g); NaHSO_3 (1.68 g); and H_2O (100 mL) were added and then heated to $70\text{--}90^\circ\text{C}$ for 7 h with the protection of N_2 and agitation. After that, a white suspension could be seen. Then, the product was cooled to room temperature until it became a transparent solution. Then, it was poured into a beaker, and aqueous NaOH (25% w/w) was added drop by drop. The white precipitation emerged as soon as the aqueous NaOH was added. The reaction ended when the precipitate did not increase any more. Then, the precipitate was washed several times with highly purified water and put in a vacuum for 48 h. The product was poly-N,N-dimethaminoethyl methacrylate (PDMAEME).
2. A 5 wt % solution of PDMAEMA was first prepared in THF; then, an excess of bromoethane was added into a three-necked reaction vessel (250 mL) and allowed to react at 40°C for 12 h with the protection of N_2 . The final product was recovered by the complete removal of the solvent

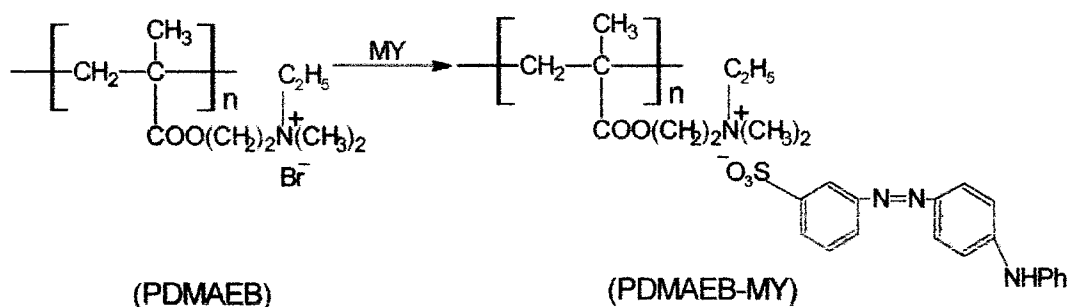
and alkyl halide in excess, and it was put in a vacuum for 2 days. The product was PDMAEB (poly-N-ethyl-N,N-dimethaminoethyl methacrylate). The inherent viscosity was 590.5 (mL/g) in water, measured with an Ubbelohde viscometer (Glass Instruments Factory, Shanghai, China) at a temperature $25 \pm 0.1^\circ\text{C}$.¹⁵ The synthetic routes of PDMAEB are shown in Scheme 1.

3. Smooth glass sheets were used as substrates after being marinated and rinsed in a series of solvents such as acetone, THF, alcohol, and highly purified water. A consistency (<1 wt %) of PDMAEB and MY solution in alcohol were first prepared. Then, the substrate was dipped into the PDMAEB solution for 25–30 min. After airing, it was dipped into the MY solution for 25–30 min. The ultrathin film was prepared. Two more clean sheets were prepared for comparison; one was only dipped into PDMAEB solution, and another was only dipped into MY solution.

RESULTS AND DISCUSSION

Synthesis

The synthetic routes of ultrathin film are shown in Scheme 2. It should be noted that the preparation of



Scheme 2

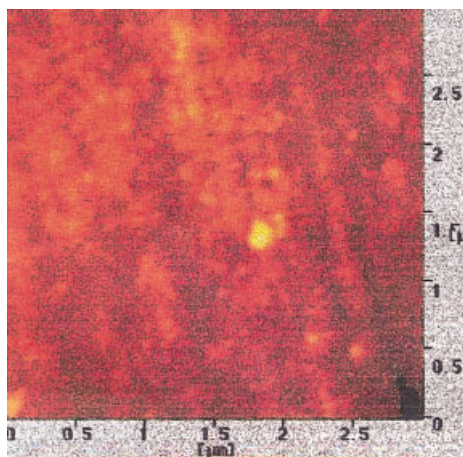


Figure 1 Topography of MY.

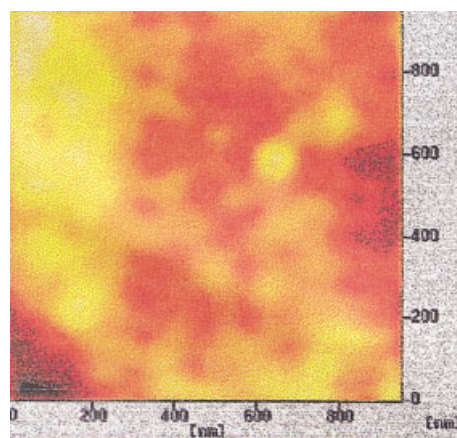


Figure 4 Topography of PDMAEB.

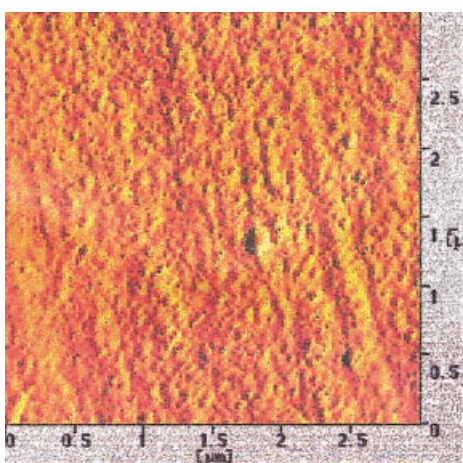


Figure 2 Phase of MY.

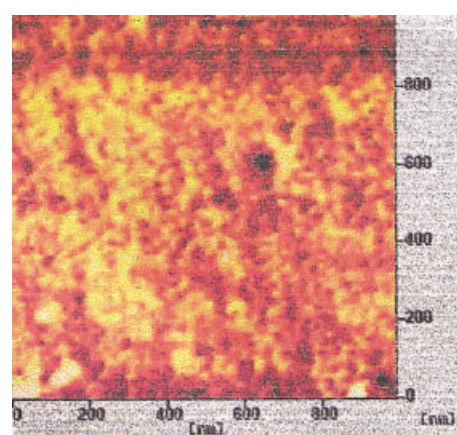


Figure 5 Phase of PDMAEB.

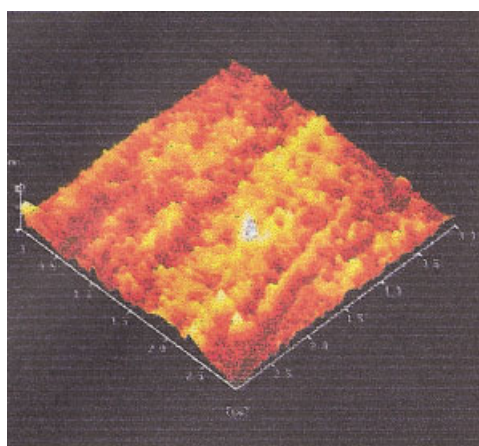


Figure 3 3D topography of MY.

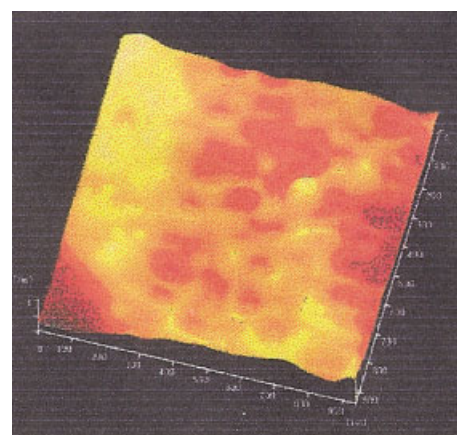


Figure 6 3D topography of PDMAEB.

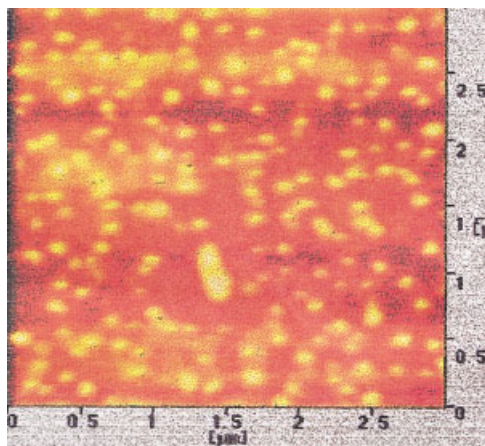


Figure 7 Topography of PDMAEB-MY.

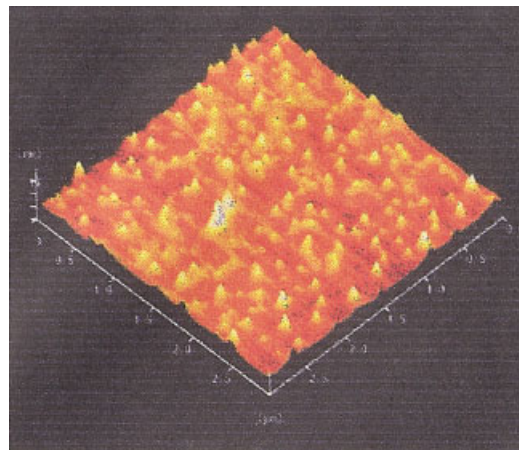


Figure 9 3D topography of PDMAEB-MY.

quaternary ammonium salts made it possible to react with MY without adding other cations into the system.

Results of AFM

AFM is a new, useful way to examine the surface topography of the multilayered samples. The main theory is to use an acute probe scanning of the surface of the samples, through analyzing and controlling the interaction between the probe and the surface of the samples, to gain the messages of the surface topography of the samples. AFM was also used to research the nanostructure and surface performance of polymers and the dynamic course of the surface structure of the samples.

In the topography images of the samples, the brighter the partial samples were, the higher place were they located at. In the phase images of the samples, the thicker the color of the partial samples was, the harder these samples were.

In this article, we use an image of a $3 \times 3 \mu\text{m}$ area on a sample that had been treated with one PDMAEB-MY

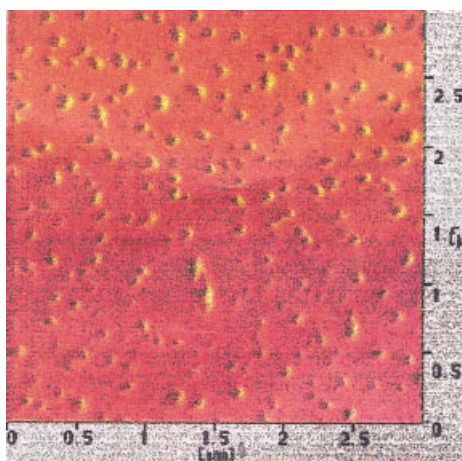


Figure 8 Phase of PDMAEB-MY.

adsorption cycle (Fig. 7, shown later), obtained in dynamic force mode (including noncontact and intermittent contact). Figures 8 and 9 (shown later) give the phase and three-dimensional (3D) topography pictures of the ultrathin film. A sample that had been treated only with MY alcohol solution gave a similar AFM image (Fig. 1); the phase and 3D topography images of the sample are shown in Figures 2 and 3, and another sample that was treated only with a PDMAEB preparation of quaternary ammonium salts made it possible to react with MY without adding any other alcohol solution and gave a similar image, too, as shown in Figures 4–6.

MY could self-congregate, as shown in Figure 1, but it was clear that the congregation was random, especially as seen in Figure 3. From Figure 2, it could be seen that the solidity of the sample was the same. So, it could be deduced that this sample was made up of one sort of substance.

The polyelectrolyte PDMAEB showed a different case, as shown in Figures 4–6. The topography of PDMAEB displayed many tiny holes, not self-congregation, but these holes were distributed asymmetrically.

When the sample had been treated with one PDMAEB-MY adsorption cycle, it revealed absolute differences in topography, phase, and 3D topography images. First, many proportioned bright spots could be seen in the topography image (Fig. 7). It could be inferred that these spots were located at a higher place than that the dull substrate was located at. Second, the color of the spots were thicker than the color of the substrate, as shown in Figure 8. It could be deduced that the rigidity of these spots was larger than that of the substrate. Third, these spots were distributed in order, as shown in Figure 9.

We summarize that these bright spots were MY molecules and the substrate was PDMAEB because of the solidity difference between the MY molecule and the PDMAEB molecule.

CONCLUSIONS

An ultrathin film was prepared, and the dynamic course of the surface topography and phase were researched by AFM. We certified that the electrostatic interaction between MY and PDMAEB made MY form random aggregations to arrange in order on the PDMAEB substrate.

Our next work will detect the functional properties of the ultrathin film. It will be reported in a future article.

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