Reversible conformational behavior of poly(acrylic acid) LB film with changes in pH, ionic strength and time

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Received 7 April 2005; received in revised form 3 August 2005; accepted 9 August 2005

Abstract

Poly(acrylic acid) brushes were prepared on polystyrene-coated glass substrates via physisorption, and a number of techniques (Langmuir–Blodgett technique, X-ray photoelectron spectroscopy, water contact angle measurement, atomic force microscopy) were used to prepare and characterize the brushes. Contact angle measurements showed the polystyrene-coated glass surface to become more hydrophilic after poly(acrylic acid) grafting on it. XPS results confirmed the presence of PAA on the topmost surface of the substrate. From the results of AFM topographic imaging of the surface of PAA brush on PS-coated glass substrate, PAA brushes was found to form bigger and less densely distributed aggregates on the surface with a decrease in the grafting density. Also, PAA brush aggregates were found to undergo marked reversible conformational changes from coiled to stretched and vice versa with changes in pH, ionic strength and contact time.

Keywords: Polymer; LB film; Dynamic; Reversible conformation

1. Introduction

Polymers can be modified in a variety of ways to make them sensitive to different kinds of stimuli. The stimuli that can induce changes in physical properties are diverse, and include temperature, pH, solvent and composition. A thin layer of polymer chains attached by one end to a solid substrate (polymer brushes) [1–3] can affect the surface properties of the substrate markedly. The end-grafted polymer brushes have thus important applications in the stabilization of colloidal suspensions [4] and in controlling interfacial mechanical properties like adhesion [5,6] and friction [7,8]. They are also useful in other applications such as lubrication [9], chemical gating [10–12] which are sensitive to pH, photo, oxidoreduction, etc. A knowledge of the dynamics of the conformational changes and the stimuli that can lead to changes in the nanostructure of the polymer brushes would allow tailoring of the properties of the polymers brushes for desired changes to external perturbations.
2. Experimental

2.1. Materials

2.1.1. Solid substrates
Polystyrene-coated glass slides were prepared by first cleaning the slides with chromic acid to remove organic impurities and drying in oven at 100 °C for 24 h. Spin coating of a polystyrene layer of 7 nm was then done from a 1 g/l solution of polystyrene (MW: 5000) in toluene at 3000 rpm followed by drying at 120 °C. The result was a glass slide hydrophobized with polystyrene as determined by contact angle measurements.

2.1.2. Polymers
The polystyrene–poly(acrylic acid) block copolymers were purchased from Polymer Source Inc., Quebec. The polystyrene blocks consisted of 34 monomers and the poly(acrylic acid) blocks consisted of 368 monomers. The reported polydispersity is 1.08. The block copolymers were dissolved in dioxane at 60 °C for 2 days.

2.1.3. Reagents
Toluene and dioxane were used to dissolve PS and PS–PAA separately. Sodium chloride, purchased from Fisher Scientific Co., was used for ionic strength control. Standard solutions of hydrochloric acid and sodium hydroxide, also purchased from Fisher Scientific Co., were used for pH adjustment.

2.2. Experiments

2.2.1. Preparation of PAA brush via Langmuir–Blodgett technique [19]
Langmuir–Blodgett “pull-down” technique was used to prepare poly(acrylic acid) brushes on solid substrate. The solution of PS–PAA was spread on an air/water interface via a 100 μl syringe. After 30 min (for evaporating all the organic solvent from the surface), the surface pressure isotherms were measured and polymer brushes with different grafting densities (the reciprocal of surface area per molecule) were prepared on solid substrates by choosing appropriate surface pressure based on the isotherm.

2.2.2. Contact angle measurement
Sessile drop water contact angle measurement was carried out at room temperature with a Rame-Hart Inc. model 100-00 contact angle goniometer. The contact angles were recorded immediately after dispensing 1 μl water droplets with a pipette onto the surface. The reported values were average values of measurements of more than three different samples at more than three different positions for each sample.

2.2.3. X-ray photoelectron spectroscopy (XPS)
XPS spectra were recorded with PHI 5500 model spectrometer equipped with a Al Kα monochromator X-ray source run at 15 kV and 23.3 mA, a hemispherical electron energy analyzer and a multichannel detector. The test chamber pressure was maintained below 2 × 10⁻⁹ Torr during the spectrum acquisition. Low energy electron flood gun was used to neutralize possible surface charging. The XPS binding energy
Fig. 4. High-resolution O 1s XPS spectra of pure PAA and PAA brush on PS-coated glass substrate.

(BE) was internally referenced to aliphatic main C 1s peak (BE = 284.6 eV). Survey spectrum was acquired at an analyzer pass energy of 93.9 eV and BE resolution of 0.8 eV, while the high-resolution spectrum was acquired with a pass energy of 23.5 eV and BE resolution 0.05 eV. Angle-dependent XPS was performed by rotating the sample holder to the desired take-off angle (the angle between the surface normal and the detector) through a motor. Spectrum was fitted by a Gaussian–Lorentz function after subtracting a striped background using the PHI data processing software package under the constraint of setting reasonable BE shift and characteristic full width at high maximum (FWHM) range. Atomic concentration was calculated by normalization of the peak area to the elemental sensitivity factor data provided by PHI database.

2.2.4. Atomic force microscopy (AFM)

The atomic force microscopy (AFM) system used in this study was a commercially available Nanoscope III (Digital instruments, Santa Barbara, CA). The measurements were performed in the tapping mode. Two types of tips (MESP-10: etched Si probes and NP-20: SiN probes) were used in air and underwater, respectively. All images were collected in the height mode, keeping the force constant.

3. Results and discussion

3.1. Preparation of PAA brush via Langmuir–Blodgett (LB) technique

PS–PAA monolayer was prepared on clean water subphase in a Langmuir trough. Subsequently, the PS–PAA block copoly-
mers were transferred from the air/water interface to the coated PS layers by Langmuir-Blodgett technique. The surface pressure of PS(33)-PAA(368) is plotted in Fig. 1, as a function of surface area per molecule. This isotherm shows a low density regime with a small increase in the surface pressure, a crossover to a second regime at higher densities with a larger increase in the surface pressure, and a third regime at very high densities, again with a slow increase in the surface pressure because the film cannot be stable any more at such high pressure and collapses quickly in this region [20].
3.2. Contact angle

The average value of contact angle on PS-coated glass surface was $85^\circ$, which was obtained from sessile drop water contact angle measurements. With PAA brush tethers on PS-coated glass surface, the average value of water contact angle decreased to $57^\circ$. It is clear that the PS-coated glass surface became less hydrophobic after PAA brushes were grafted on it.

3.3. X-ray photoelectron spectroscopy study

Surface composition of PAA brush on PS-coated glass was analyzed via angle-dependent XPS. As expected, the XPS survey spectrum shows typical C and O peaks (Fig. 2). The elemental composition of C and O is listed in Table 1 at three different take-off angles. Since the signal of O should only come from PAA theoretically, the higher the ratio of O/C, the higher the surface molar fraction of PAA within PS and PAA.

Fig. 3 shows the high-resolution C 1s spectra with deconvoluted C subpeaks, corresponding to C with different chemical environments. The peaks centered at around 288.5 eV were from carbonyl C (C\(\equiv\)O\(^\bullet\)), and those centered at around 285 eV were from the Cs neighboring to the carbonyl group. The peak positions and binding energy (BE) shifts (4.0 eV) agree well with those of pure PAA film. Compared to the peaks of pure PAA, the peak area of carbonyl C becomes less and less for PAA brush on PS-coated glass substrate at take-off angle of $15^\circ$ and $45^\circ$, which means that the penetration depth is deeper (penetration depth \(d = 3\lambda \sin \theta\), \(\lambda\): inelastic mean free path of emitted photoelectrons; \(\theta\): take-off angle).

Fig. 4 shows high-resolution spectra of O 1s for pure PAA and PAA brush on solid substrate. It is clear that the typical wide
peaks centered at around 532 eV correspond to two sub peaks of O from carbonyl O and that from ester O with peak area ratio close to 1:1.

The above results confirmed the presence of PAA tethers on the surface of PS-coated glass substrate.

3.4. AFM studies

3.4.1. Topographical observation at solid–air interface

AFM was used to analyze the topography of PAA aggregates on PS-coated glass substrate at the solid–air interface. Fig. 5a shows an AFM image of bare glass surface with RMS of 0.870 nm. From the results of section analysis, the maximum height difference was 3.262 nm. The RMS decreased to 0.383 after PS was spin coated on the glass surface (Fig. 5b) with the maximum height difference also reduced to 0.965 nm. For the surface grafting density of 0.067 chain/nm² (Fig. 5c), the RMS of the surface was 3.017 nm. From the average of section analysis, the maximum vertical height of each global aggregate was around 5.562 nm. With reduction in the grafting density to 0.05 chain/nm² (Fig. 5d), the RMS of the surface of PAA aggregates was found to change significantly. The chains became less densely distributed on the surface compared with that of 0.067 chain/nm². More surfaces were devoid of PAA aggregates with the RMS of it was 3.690 nm with the maximum vertical height of each aggregate increased to 15.323 nm.

3.4.2. Topographical observation at solid–liquid interface

Dynamic conformational behavior

(1) Effect of pH change

AFM was used to monitor the dynamic conformational behavior of PAA aggregates with grafting density of 0.067 chain/nm² on PS-coated glass substrate at the solid–water interface as a function of pH. Effect of pH on the surface topology was observed via AFM to be marked (Fig. 6). A significant decrease in the height was observed when pH was decreased from 10 to 2, with the height decreasing further at pH 2 with time.

(2) Effect of ionic strength

When the pH was changed from 2 to 10, the PAA aggregates with grafting density of 0.05 chain/nm² showed an increase in size because of the intra- and intermolecular electrostatic repulsion among neighbor negatively charged polyelectrolyte (polyacrylic acid) groups (Fig. 8). When the ionic strength of the solution was increased from 0 to 0.5, the size of these aggregates decreased. This can be accounted for by the screening of the electrostatic repulsion by counterions and the resultant polymer chains collapse to a more coiled conformation when the ionic strength is increased.

4. Summary

(1) PAA nanobrushes were prepared in this work via Langmuir–Blodgett technique.

(2) With PAA brushes physisorbed on PS-coated glass, the contact angle changed from 85° to 57°, yielding a less hydrophilic surface.

(3) XPS survey spectrum of the surface of PAA brush grafted PS-coated glass substrate showed typical C and O peaks of PAA. Further experiments on high-resolution C 1s and O 1s XPS spectra confirmed the presence of PAA brush on the surface. The elemental composition analysis of the surface at three different take-off angles showed that lower the penetration depth, higher is the surface molar fraction of PAA within PS and PAA, suggesting that PAA prefers to stay on the outermost surface.

(4) From the AFM topographical imaging of the surface of PAA brush on PS-coated glass substrate, PAA brushes were found to form bigger but less densely distributed aggregate islands on surface with the decrease of grafting density.

(5) Coiled to stretch conformational changes of PAA brush aggregates on PS-coated glass surface were observed upon increasing the pH. The process was found to be reversible with the change in pH.

(6) AFM topographical observation showed an increase in ionic strength to cause a decrease in the size of PAA brush aggregates (stretch ↔ coil) [21].

(7) The results revealed the reversible morphological changes of PAA brush aggregates with different environmental perturbations. Poly(acrylic acid) brushes were found to collapse upon decreasing the pH or increasing the ionic strength. When the pH was increased again, the coiled brushes stretched out. The collapse took several minutes to be completed.

Acknowledgements

The authors acknowledge the support of the National Science Foundation (Grant# CTS-01-03246 and EEC-03-28614).

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