Ordered Monolayer Structures of Electrostatically Adsorbed Polystyrene Nanospheres on an Ultrathin Polymer Film Surface

Takeshi Serizawa, Hiroko Takeshita, and Mitsuru Akashi*
Faculty of Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890

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The electrostatically adsorbed polystyrene nanospheres showed an ordered monolayer structure on an ultrathin polymer film surface.

The two-dimensional formation of ordered monolayer assemblies that are composed of organic or inorganic nanoparticles have received a great deal of attention from researchers in regard to not only producing their specific characteristics but also producing functionally modified substrate surfaces. Several research groups have studied regulated monolayer structures by using external forces against particles on substrates.[1-7] However, there must be other techniques that can more easily control a specific monolayer structure on a substrate. In our previous study, we found that anionic polystyrene nanospheres were favorably and electrostatically adsorbed onto the surface of a cationic ultrathin polymer film, which was prepared by the alternative adsorption technique.[8] As the adsorption procedure (which is simply the immersion of a substrate into nanosphere dispersion in one hour) was easy, we expected that it would be a simple technique that could regulate the monolayer structures. In this study, we showed an ordered monolayer structure that was spontaneously formed by an electrostatically adsorbed polystyrene nanosphere on the surface of an ultrathin polymer without any external forces. Both the quartz crystal microbalance (QCM) technique and a scanning electron microscopic (SEM) observation were used to monitor the adsorption behavior quantitatively and directly, respectively. QCM could detect a mass increase (Δm) on an electrode as its frequency decrease (ΔF) with a nano-gram level when the nanospheres were adsorbed onto it. A 9 MHz QCM that was 9 mm in diameter (that was used in this study) followed Sauerbrey' equation[9], which is expressed as $-\Delta F = 0.87 \times \Delta m$. We also combined this technique with SEM observation in order to directly analyze the adsorption state.

The fabrication process of the polystyrene nanosphere adsorption onto the surface of an ultrathin polymer film is shown in Figure 1. We prepared the charged ultrathin polymer film on the QCM (USI, Japan) substrate as the precursor film for nanosphere adsorption using an alternative adsorption technique, which was developed by other researchers,[10-13] with both cationic poly(allylamine hydrochloride) (PAH) (Aldrich Co., USA) (Mw 8500-11000) and anionic poly(sodium 4-styrenesulfonate) (PSS) (Aldrich Co., USA) (Mw 70000) and has been used in previous particle adsorption studies.[8,14-17] First, in order to clean their surfaces, both of the QCM electrodes were treated with a piranha solution (H_2SO_4:H_2O_2=3:1) for 3 minutes, followed by rinsing with pure water and drying with N_2 gas. The QCM obtained was immersed into a PAH aqueous solution (0.02 unit M containing 2M NaCl) for 20 min, taken out, washed with pure water for several tens of seconds, and dried with N_2 gas; then its frequency decrease was measured in order to analyze the adsorption amount of the polymer. Subsequently, QCM was immersed into a PSS aqueous solution again, followed by the same procedure. This alternative cycle was repeated for the polymer film deposition. Here, we adjusted the polymer aqueous solutions for the precursor film formation so that they contained 2M NaCl. As a consequence, the nanospheres could be adsorbed electrostatically onto the film, as was discussed in our previous study.[8] After the above preparation of the precursor film, we immersed QCM into an aqueous dispersion of the polystyrene nanosphere (dispersed in distilled water without salt) at a concentration of 1.0×10^{12} ml^{-1} at 10 °C with a diameter of 209±7 nm (with a ζ-potential of -40.7±3.7 mV, indicating the presence of an anionically charged surface), followed by rinsing with pure water and drying with N_2 gas. Next, we also measured the frequency decrease in air as the adsorption amount. We obtained the SEM images with a HITACHI S-4100H (Hitachi, Japan).

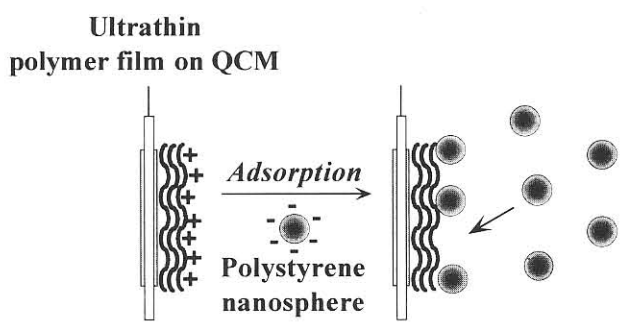

Figure 1. Schematic illustration of the electrostatic adsorption of polystyrene nanospheres onto the surface of an ultrathin polymer film.

Figure 2 shows the time courses of the frequency decrease when QCM was immersed into a nanosphere dispersion. We observed a larger adsorption amount of the anionic polystyrene nanospheres onto the surface of a $(PAH\text{-}PSS)_3$-PAH film than that onto a $(PAH\text{-}PSS)_3$ one (obviously indicating its electrostatic adsorption), as we noted in a previous study.[8] The adsorption process was saturated after 20 min and reached 1601 ± 154 ng (-1393±134 Hz). The saturated surface coverage by the nanosphere at the concentration was estimated as 40±4% from its size when we assumed monolayer adsorption; the density of the polystyrene was assumed to be 1.0.

Next, we directly observed the adsorbed structure of the nanospheres on a $(PAH\text{-}PSS)_3$-PAH film surface by using a SEM image that had an accelerated voltage of 5 kV after sputtering gold on the QCM at a thickness of approximately 20 nm, as is shown in Figure 3a. The adsorbed nanosphere on the surface of a $(PAH\text{-}PSS)_3$-PAH film surprisingly showed a well ordered monolayer structure without any multi-layering. The surface coverage that was calculated from an area analysis of the SEM image was around 37%, which was consistent with the value

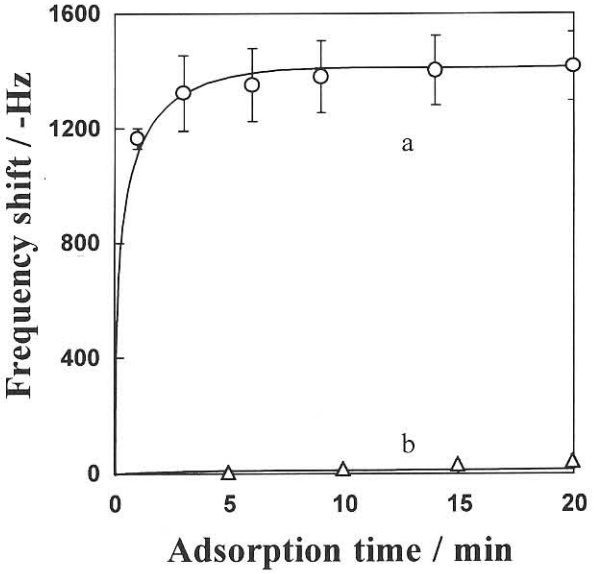

Figure 2. Time courses of polystyrene nanosphere adsorption onto $(PAH\text{-}PSS)_3$-PAH (a) and $(PAH\text{-}PSS)_3$ (b) film surfaces at a concentration of 1.0×10^{12} ml^{-1} at 10°C (The measurements were repeated three times, indicating error bars.).

from the above QCM measurement, thereby confirming the reliability of the two measurements. As many nanospheres on the SEM image seem to be adsorbed independently, we analyzed the average distance between the edges of the independently adsorbed nanosphere and the percentage of the independent nanosphere against the total number. The values analyzed were 180 ± 80 nm and 87%, respectively. Significantly, for a polystyrene nanosphere with a diameter of 548 nm (whose adsorption we have already studied[8] but not the detail of its structure), the values for almost same surface coverage were 510 ± 190 nm and 38%, respectively (in this case, it was adsorbed at 3.8×10^{10} ml^{-1}), as is shown in Figure 3b (for details see reference 8). In both cases, the average distances were slightly smaller than their sizes. The percentage became smaller when the nanosphere size became larger. They seem to be dependent on their sizes. Consequently, smaller nanospheres showed a more ordered monolayer structure. It is difficult to completely explain the formation mechanism. However, one possibility is that repulsive or adhesive forces between the nanospheres during their electrostatic adsorption processes onto a substrate cause the formation of the ordered structure. In fact, the larger nanosphere in its aqueous dispersion aggregate and precipitate more easily at room temperature than the smaller one. Such a different aggregation behavior might affect the ordered structure. Further research on the formation mechanism is needed. We found that the electrostatically adsorbed polystyrene nanospheres showed a well ordered monolayer structure on the surface of an ultrathin polymer film. In the future, direct observation of the formation process by using SEM, the charge effects of the nanospheres on the adsorption behavior, and the possible use of ordered monolayer structures as functional coating materials will be studied.

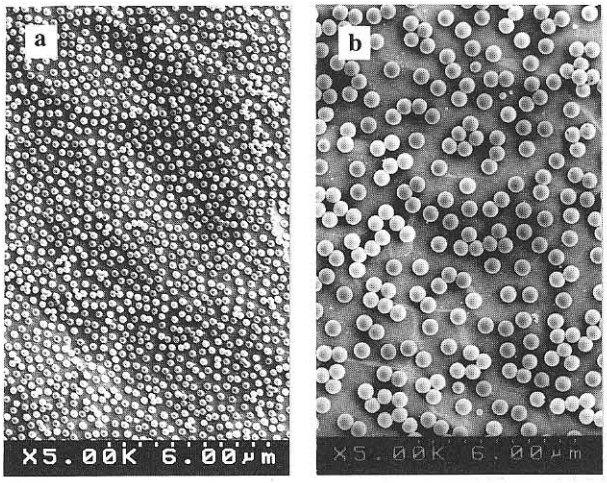

Figure 3. SEM images of the adsorbed polystyrene nanospheres with a diameter of (a) 209 nm (b) 548 nm onto $(PAH\text{-}PSS)_3$-PAH.

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