

# Self-assembly of Carboxyl Functionalized Polystyrene Nanospheres into Close-packed Monolayers via Chemical Adsorption

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The polyacrylic acid functionalized polystyrene nanospheres were synthesized and self-assembled into irregular, densely packed monolayers in non-aqueous media. The polymer nanoparticles were chemically adhered to substrates. The morphologies of the resulting films were investigated. The impact of the volume fraction of alcohol in the mixed solvents on the particle adsorption and fabrication of nanosphere assembled films was examined.

**Keywords** self-assembly, polystyrene/polyacrylic acid, nanosphere

## Introduction

A general definition of self-assembly is the spontaneous organization of materials through noncovalent interactions (H-bonding, Van der Waals forces, electrostatic forces,  $\pi$ - $\pi$  interactions, *etc.*) with no external intervention.<sup>1-3</sup> The self-assembling technology has been extensively used in chemistry and material science as an effective strategy for fabricating a variety of complex structures that are difficult or impossible to generate by traditional approaches.<sup>4</sup> These self-assembled, complex materials are potentially useful in a number of areas such as chemical sensors, corrosion resistance, biomaterial coatings and other molecular electronic devices.<sup>5-10</sup> As a result, there has been considerable interest in self-assembling nanoscale building blocks into thin films using both novel building block compositions and assembling strategies.<sup>11</sup> Examples of these self-assembled structures include self-assembled monolayers (SAM),<sup>12,13</sup> multilayered thin films,<sup>14,15</sup> metal nanoparticle assemblies,<sup>16,17</sup> aggregates (micelles, liposomes) derived from surfactant molecules,<sup>18,19</sup> host-guest inclusion complexes,<sup>20,21</sup> phase-separated block copolymers,<sup>22,23</sup> crystalline arrays of proteins or colloidal particles,<sup>24,25</sup> and aggregated structures of mesoscale objects.<sup>26,27</sup>

Polystyrene (PS) nanospheres have been widely used in many areas, such as photonics, nanotechnology, life science.<sup>28,29</sup> In recent years, much work has been focused on polystyrene nanosphere 2D self-assembled

films with either close-packed ordered arrays or irregular and less densely packed layers or patterned monolayers. Many assembling strategies were explored and the methods for fabricating PS particle monolayers driven by physical interactions were most commonly used.<sup>30</sup> In order to enhance the substrate-particle interaction, control the selectivity and packing density, and apply them into varied environmental conditions, regulating colloidal assembly with chemical interaction has now received much attention.<sup>31,32</sup> But among chemical methods presented so far, they were all applied in aqueous system, while preparing PS particle self-assembled monolayers via chemical interaction in non-aqueous media has not been found. In this paper, we first synthesized carboxyl functionalized polystyrene nanoparticles and then assembled them onto amino terminated glasses in chloroform/alcohol mixed solvent to form a densely-packed monolayers with strong bonding based on acid-base reaction between the amino groups on the surface of glass and the carboxylic acid groups on the surface of polystyrene nanoparticles.

## Experimental

### Reagents

Styrene (ST, A.R.) and acrylic acid (AA, A.R.) were decompressed and distilled to eliminate inhibitor. Divinyl benzene (DVB) was of C.P. grade, and the inhibitor in it was removed by sodium hydroxide solution. Sodium laurylsulfonate (C.P.) and ammonium persulfate

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(APS, A.R.) were recrystallized and dehydrated before use. Distilled water was used.

### Preparation of polystyrene/polyacrylic acid nanospheres

The preparation procedures are as follows: the mixture of 0.4 g of sodium laurylsulfonate, 100 mL of distilled water, 3 mL of ST and 0.3 mL of DVB were put into a 250 mL reaction flask. Under the protection of  $N_2$  gas, the mixture was emulsified by continuous magnetic stirring for 30 min at room temperature. After the system was heated to 80 °C, 10 mL of 0.03 g/mL APS solution was dropped slowly in 30 min and the system continued to react for 2 h at that temperature. After dropping 0.3 mL of AA, and 10 mL of 0.02 g/mL APS solution, the system continued to react for another 3 h at 80 °C. At last, the product was obtained by emulsion breaking, filtration, scrubbing and drying.

### Pretreatment of glasses

Glass was treated with a hot  $H_2SO_4/H_2O_2$  (7 : 3 / V : V) solution for 1 h, then extensively rinsed with distilled water and sonicated alternately in pure water and 2-propanol for 20 min. After being dried with  $N_2$  gas, the cleaned substrates were immersed into a  $5 \times 10^{-3}$  mol/L  $\gamma$ -aminopropyltriethoxysilane benzene solution for 3 h, taken out, washed thoroughly with chloroform, distilled water and acetone in turn, and dried with  $N_2$  gas.

### Apparatus

IR spectra were recorded on an AVATAR 360 FT-IR spectrometer. XRD patterns were acquired with an X'Pert Pro X-ray powder diffraction apparatus. TEM pictures were obtained using a JEM-2010 transmission electron microscope. Morphology measurements of polystyrene nanosphere films were carried out with an SPA-400 atomic force microscope.

## Results and discussion

### IR Characterization of polystyrene/polyacrylic acid nanospheres

Figure 1 shows the IR spectrum of polystyrene/polyacrylic acid nanospheres. The peaks at 1452.29, 1492.81, 1601.29  $cm^{-1}$  are characteristic ones for C—C oscillation frequency of benzene ring and those at 3025.49, 3059.46, 3081.98  $cm^{-1}$  correspond to the peaks of C—H oscillation frequency of benzene ring, which indicates that there is a benzene ring in the samples. Meanwhile, there are three absorption peaks at 697.83, 765.74 and 832.25  $cm^{-1}$  in the range of 690—860  $cm^{-1}$ , which shows that the product contains a substituted benzene ring. So it could be concluded that the samples contain styrene and divinylbenzene groups. The strong peak observed at 1703  $cm^{-1}$  is due to asymmetric stretch of carbonyl group and the peak at 3440  $cm^{-1}$  corresponds to O—H stretching vibration, which proves that acrylic acid exists in the samples. In addition, the

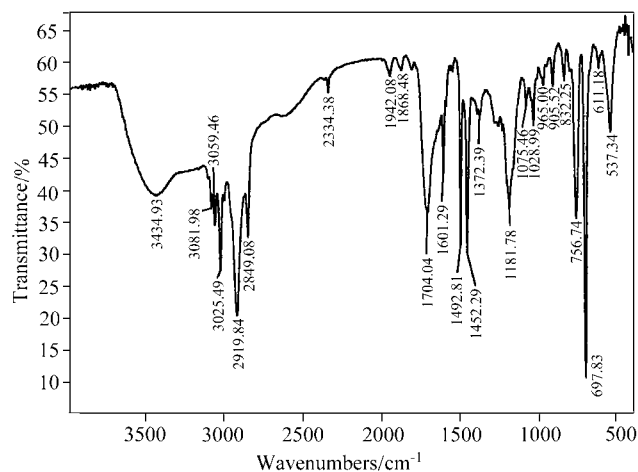


Figure 1 IR picture of PS/PAA nanospheres.

absorption peak of C=C at 1680—1620  $cm^{-1}$  disappears, confirming that both styrene and acrylic acid were polymerized.

Polyacrylic acid is a kind of hydrophilic polymer and can be dissolved in water, while polystyrene is hydrophobic. The peaks of polyacrylic acid would not be observed if the products were just a mixture of polystyrene and polyacrylic acid, which means that monomers of styrene and acrylic acid were polymerized separately, as polyacrylic acid could be scrubbed out. In addition, considering that stepwise polymerization technique was used during the preparation process, it was concluded that polyacrylic acid was grafted on the surface of polystyrene to form a coating.

### Morphology and structure characterization of polystyrene/polyacrylic acid nanospheres

The polymer latex was diluted by distilled water and transferred to copper-net, then dried in the air. Figure 2 shows that PS/PAA nanospheres are spherical and the average diameter of their particles is about 50 nm. The PS/PAA nanospheres are uniform and do not occur to aggregation. In addition, there is a wide diffraction peak

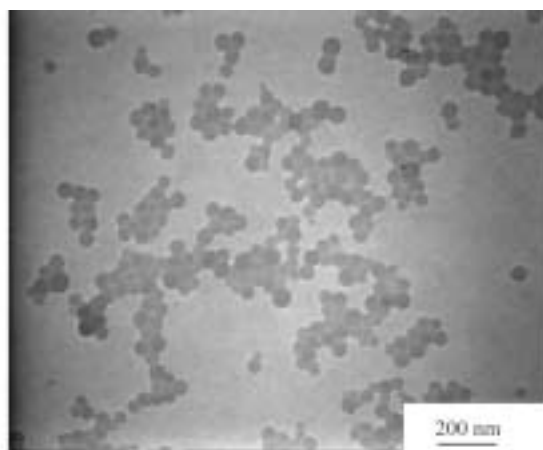


Figure 2 TEM picture of PS/PAA.

at 19 °C in XRD pattern (Figure 3), which shows that PS/PAA nanospheres have amorphous structure.

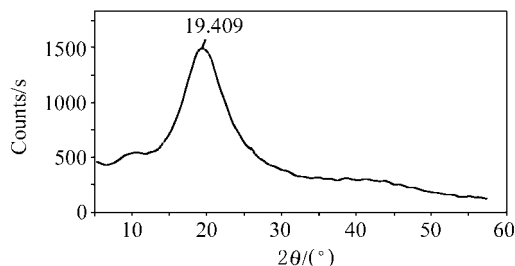


Figure 3 XRD picture of PS/PAA nanospheres.

### Self-assembly of polystyrene/polyacrylic acid nanospheres on glasses

The assembly process involved the following steps. First, dissolve a fixed amount of polystyrene/polyacrylic acid nanospheres into a mixed solvent of alcohol and chloroform in different ratios. Second, put pretreated glasses into the above solution for 10 h at room temperature. At last, the glasses were rinsed off with a large amount of alcohol and chloroform to remove loosely adsorbed materials, and then dried with N<sub>2</sub> gas.

Here we mainly studied how the solvent ratios affect the formation of polystyrene/polyacrylic acid nanosphere assembled films. As stated previously, polyacrylic acid is hydrophilic but polystyrene is hydrophobic, so we selected alcohol and chloroform as solvent components, and examined what was an appropriate proportion of the mixed solvent favoring nanosphere adsorption and film fabrication. During the assembling process, the volume fractions at 0, 20, 30, 40, 50, 60, 70, 100 (%) of alcohol in the mixed solvent were used. As shown in Figure 4, it was found that there was no polymer nanospheres on the glasses both in pure alcohol and in pure chloroform, and at the ratios of 20%, 60%, 70%, nanospheres could be sparsely adsorbed on the surface of the glasses, while nanospheres could be well assembled in 30%—50% mixed solvent, and a ratio of 40% yielded the best results in the sense of the highest uniformity. It was supposed that at the ratio of 40%, polystyrene/polyacrylic acid nanospheres could be well dispersed and not rapidly swollen, furthermore, polyacrylic acid chains on the surface of polystyrene nanospheres could be extended in a certain degree, then a large number of carboxylic acid groups could be exposed to the surface of nanospheres, which would facilitate the nanospheres adsorbed on amino terminated surface of glasses to form a nanoparticle ultra thin film with a certain packing density. This means that the nanoparticle adsorption mechanism is based on the interaction between the carboxylic acid groups on the surface of nanospheres and the amino groups on the surface of glasses. In order to further clarify this, we conducted other two experiments to prepare polystyrene nanospheres with different surface groups. Under the same synthetic conditions, pure polystyrene nanospheres were

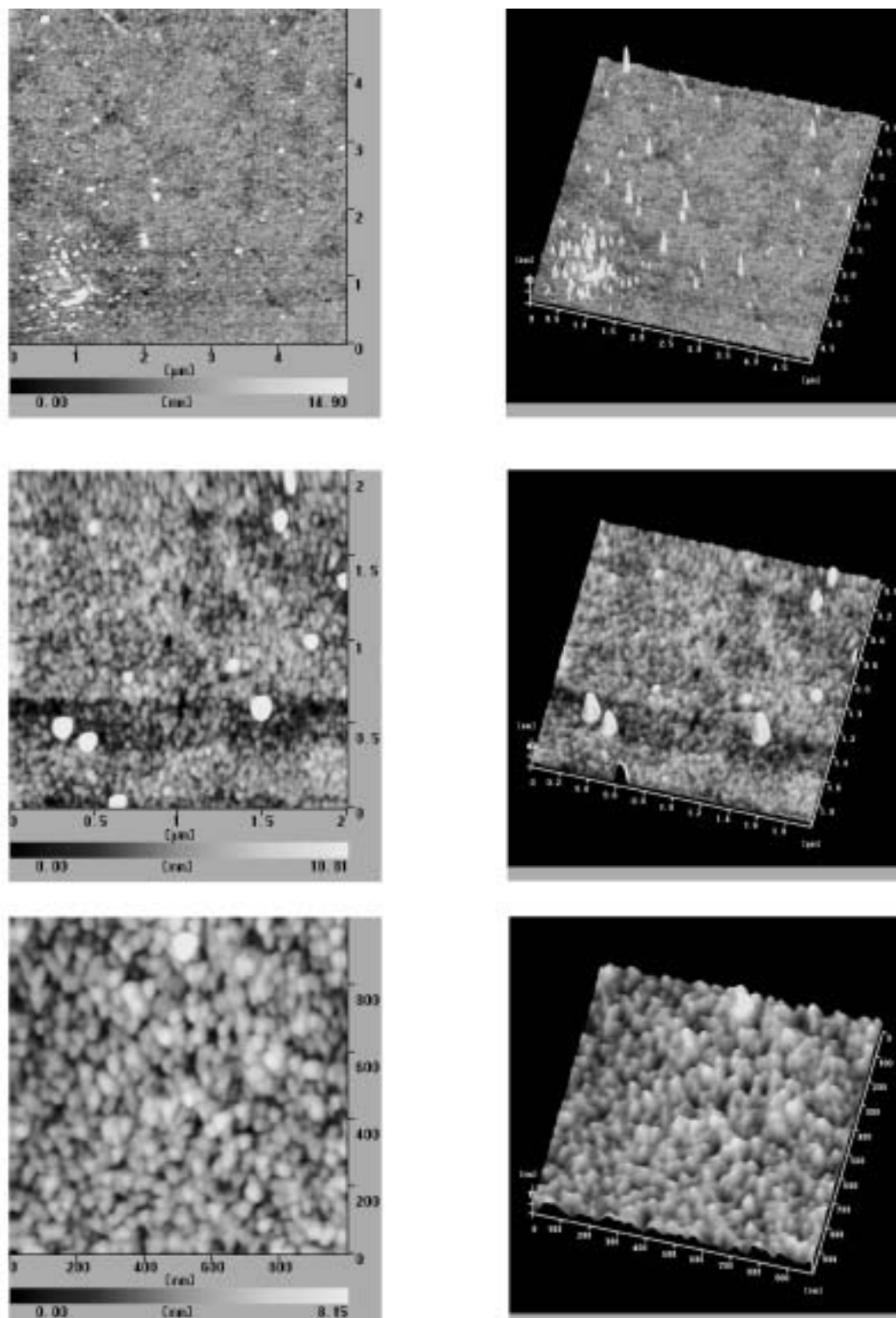
prepared, which means that there are no grafted groups on the surface, and acrylic acid was replaced with methyl acrylic acid and methyl acrylic acid surface grafted polystyrene/polymethyl acrylic acid nanospheres were obtained, which was very similar with polystyrene/polyacrylic acid nanoparticles both in size and morphology. Then they were assembled into films according to the same processes mentioned above. AFM measurement results showed that pure polystyrene nanospheres could not be adsorbed on the surface of modified glasses in the mixed solvent at any ratios used above. For polystyrene/polymethyl acrylic acid nanoparticles, they followed similar adsorption behaviors with polystyrene/polyacrylic acid nanoparticles, but much less nanoparticles were adsorbed and the amount of surface coverage on the glasses was reduced significantly, which tended to decrease the interaction between the carboxyl groups on the nanospheres and the amino groups on the substrates due to steric hindrance of methyl groups. These results imply that the interaction between the particles and the surface has a certain chemical nature.

### AFM measurements of PS/PAA nanospheres assembled monolayer

The topographic AFM images and accompanied three-dimensional pictures of PS/PAA nanosphere film fabricated at the ratio of 40% are shown in Figure 4. It can be seen that an irregular, but flat and densely packed layer with height of 50 nm was formed. The measured height, which is almost the same as that acquired using TEM, confirms that polymer nanospheres are not swollen and a densely-packed PS/PAA nanosphere monolayer was obtained. On the other hand, the nanospheres were not rinsed off the surface of glasses with alcohol and chloroform, which indicates that the interaction is very strong. Therefore, it was assumed that the formation mechanism of nanoparticle assembled monolayer is as follows: firstly, glass wafers are hydroxylated, then  $\gamma$ -aminopropyltriethoxysilane reacts with hydroxyl groups to form Si—O bond and leave amino groups outmost on the surface of the glass to yield amino terminated self-assembled monolayer. Because the polystyrene nanospheres used have carboxylic acid groups on the surface, when the substrate is immersed in the PS/PAA nanosphere suspensions, the carboxylic acid groups of PS/PAA nanoparticles interact with the amino groups, leading to chemical linkage between particles and substrates. Then polymer nanoparticles are adsorbed on the glass to self-assemble into a PS/PAA nanosphere monolayer.

### Conclusion

Polystyrene/polyacrylic acid nanosphere monolayer was fabricated by a self-assembling technique based on an acid-base reaction mechanism. The nanoparticles assembled monolayer was densely packed and chemically adhered to substrates.



**Figure 4** Topographic AFM images and accompanied three-dimensional pictures of PS/PAA nanosphere assembled monolayer ( a:  $5000 \times 5000$  nm; b:  $2000 \times 2000$  nm; c:  $1000 \times 1000$  nm ).

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