Fabrication of Polymer Particle Monolayer onto Alkylated Glass Plates

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Polymer particle monolayer was fabricated onto alkylated glass plates. The concentration of sodium chloride and cetyltrimethylammonium bromide (CTAB) was found to play a key role in control of the morphology and coverage of the monolayer on the alkylated glass plates.

Recently, fabrication of functional polymer latex particles onto solid plates has received much attention, because of the high potential applications to several devices, such as biosensor, multiple electrode and photolithography.[1] In fact, the fabrication of polymer particle monolayers by electrostatic adsorption, self-assembled monolayers (SAMs), and chemical immobilization, have been reported.[2–5]

In the previous paper, we reported the synthesis of novel cationic polymer particles with a high surface density of sulfonium groups and active ester groups by emulsifier-free emulsion copolymerization of styrene (ST) with methacryloyloxyphenyldimethylsulfonium methylsulfate (MAPDS) (Figure 1). The active ester groups at the surface of the particles, which have high reactivity with primary amino compounds, successfully worked for the chemical immobilization onto the aminated glass plates treated with 3-aminopropyltriethoxysilane.[6] Recently, we found a novel immobilization technique for fabrication of polymer particle monolayer. In this communication, we report that the fabrication of the polymer particles can be also made onto alkylated glass plates treated with methyltrimethoxysilane (MS) or *n*-octadecyltriethoxysilane (ODS).

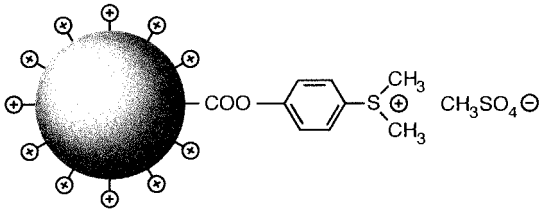
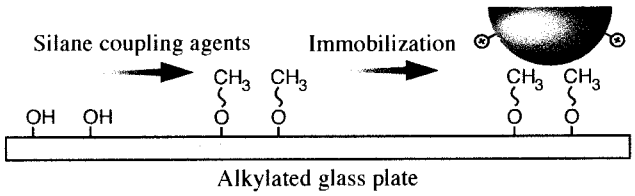


Figure 1. Structure of P(ST-*co*-MAPDS) particles.

Monodispersed P(ST-*co*-MAPDS) particles with ca. 220 nm in diameter were prepared by emulsifier-free emulsion copolymerization of ST (320 mmol) with MAPDS (3.2 mmol) at 60 °C using 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50) (3.2 mmol) as an initiator, as described previously.[7] Glass plates were cleaned with boiling HNO_3 solution for 1 h, washed with water, and dried in vacuum. The plates were reacted with a toluene solution of MS or ODS at 110 °C for 1 h, followed by washing with ethanol and drying in vacuum.[8,9] Characterization of alkylated glass plates treated with the silane coupling agents was carried out by using contact angle measurements. The average contact angles of water for methylated glass plate and octadecylated glass plate were 65.3° and 63.0°, respectively, which are higher than that of original glass plate. Immobilization experiments were conducted as follows: the glass plates were immersed into P(ST-*co*-MAPDS) latex dispersion (0.025 wt%) for 24 h, taken out of the dispersion, and washed in water by ultrasonic cleaning for 5 min to remove weakly and/or physically bound particles (Scheme 1). The morphology of P(ST-*co*-MAPDS) particles immobilized on the plates was observed by a scanning electron microscope (SEM) (JEOL, JSM-5310) and the coverage with particles was calculated.



Scheme 1. Schematic representation of immobilization of P(ST-*co*-MAPDS) particles onto alkylated glass plates.

Figure 2 shows SEM photographs of P(ST-*co*-MAPDS) particles immobilized on alkylated glass plates. It is clearly seen that polymer particle monolayer is fabricated onto the glass plates. When methylated glass plate was immersed into electrolyte-free P(ST-*co*-MAPDS) latex dispersion (0.025 wt%), the coverage was found to be low (ca. 20%), as shown in Figure 2(a), and the polymer particles were immobilized onto the glass plates, partially at regular intervals. This may be due to the strong elec-

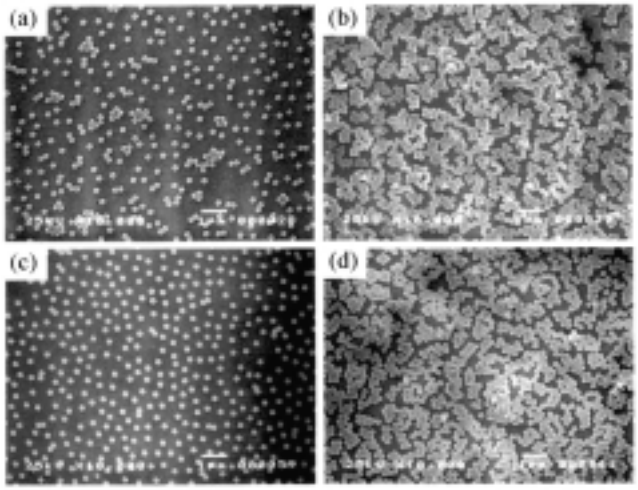


Figure 2. SEM photographs of P(ST-*co*-MAPDS) particles immobilized on alkylated glass plate: methylated glass plate ((a), (b)); octadecylated glass plate ((c), (d)). [Latex], 0.025 wt%; [NaCl], 0 mM ((a), (c)), 25 mM ((b), (d)).

trostatic repulsion between cationic polymer particles. In P(ST-*co*-MAPDS) latex dispersion (0.025 wt%) containing 25 mM NaCl, the coverage dramatically increased up to ca. 80%, as shown in Figure 2(b). The polymer particles, however, were immobilized onto the glass plates as aggregates. This can be ascribed to the decrease in the electrostatic repulsion between the polymer particles. The similar results were obtained for octadecylated glass plates, as shown in Figure 2(c) and (d).

To clarify the reason for the immobilization of the present polymer particles onto alkylated glass plates, we made an additional experiment of adsorption of CTAB on the polymer particles. It was found that one polymer particle adsorbs ca. 1×10^4 CTAB molecules, indicating that the surface of polymer particles is of hydrophobic character. In the presence of CTAB (0.75 mM), no polymer particles were immobilized on the glass plates. This would imply that hydrophobic interaction between polymer particle and alkylated glass plate is responsible for the immobilization.

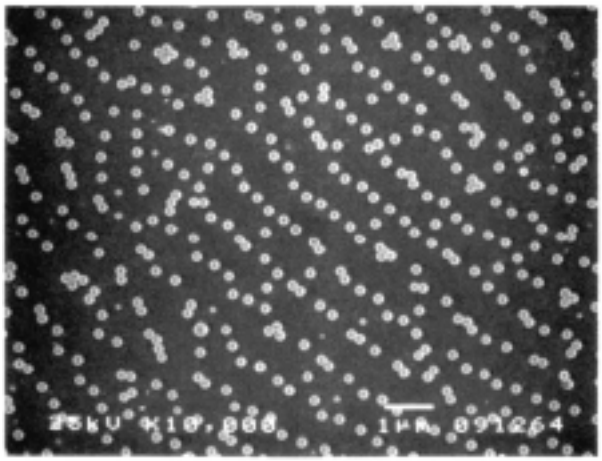


Figure 3. SEM photograph of the ordered particle monolayer of P(ST-*co*-MAPDS) particles immobilized at the surface of methylated glass plate. [Latex], 0.25 wt%; [NaCl], 0.1 μM.

Figure 3 shows SEM photograph of the ordered particle monolayer of P(ST-*co*-MAPDS) particles immobilized at the surface of methylated glass plates. The fabrication of the ordered particle monolayer was achieved only for the alkylated glass plates. The formation of the ordered structure may be attributed to a balance of electrostatic repulsion between the polymer particles controlled by electrolyte (NaCl) at a fairly low concentration (0.1 μM).

Remaining sulfonium groups or active ester groups of particle monolayers at the surface of alkylated glass plates were confirmed to easily react with dansylhydrazine. Thus, primary amino compounds can be introduced to the particle monolayers.

In summary, P(ST-*co*-MAPDS) particles were found to be immobilized onto alkylated glass plates. The hydrophobic interaction between the polymer particle and alkylated glass plates would be a key interaction for the present immobilization. Morphology of the particle monolayer was changed by controlling the electrostatic repulsion between the polymer particles.

References and Notes

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