

Monolayer Formation of Cationic Polymer Particles on Hydrophobic Solid Substrates in Aqueous System

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Monodispersed cationic polymer particles bearing quaternary ammonium groups on their surfaces were well self-organized through hydrophobic interaction on hydrophobically modified glass plates in aqueous system. We could fabricate the particle monolayer of close-packed structure with a relatively regular interval by tuning hydrophilic–hydrophobic balance of particles and temperature.

Recently, fabrication of particle monolayers on solid substrates has received much attention. Regularly arranged particle monolayers have many potential applications such as lithographic mask, microlens array, biochips, and biochemical sensors.^{1,2} It has been proposed to utilize intrinsic interactions between particle and substrate surfaces for self-organization of particles. Electrostatic interaction³ and chemical bond formation⁴ have been used as intrinsic driving forces to form particle monolayers on a substrate surface.

In the previous paper, we reported the self-organization of cationic polymer particles with sulfonium groups on hydrophobic solid substrates through hydrophobic interaction.^{5–8} In this letter, we demonstrate that cationic polymer particles bearing quaternary ammonium groups on their surfaces are also effectively self-organized on alkylated glass plates treated with methyltriethoxysilane (MES) or *n*-octadecyltriethoxysilane (ODES). Schematic representation of this study was shown in Figure 1, indicating self-organization of the cationic polymer particles on alkylated glass plates through hydrophobic interaction. We investigated the effect of tuning hydrophilic–hydrophobic bal-

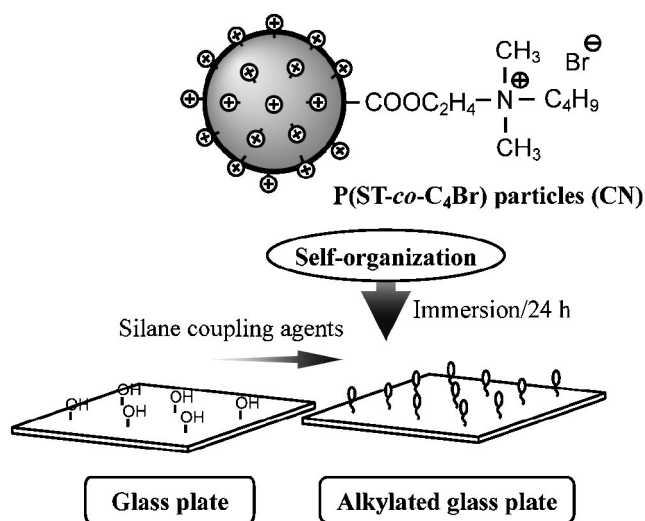


Figure 1. Schematic representation of self-organization of cationic polymer particles on alkylated glass plates.

ance of particles on orderly surface self-organization.

Monodispersed P(ST-*co*-C₄Br) particles bearing quaternary ammonium groups (Latex Code; CN-0.1, CN-0.5, CN-1.0, CN-2.0) were prepared by emulsifier-free emulsion copolymerization of styrene (ST) (320 mmol) with methacryloyloxyethylbutyldimethylammonium bromide (C₄Br) at 60 °C using 2,2'-azobis(2-amidinopropane) dihydrochloride (V-50) (3.2 mmol) as initiator. Water was distilled and deionized by a Millipore system before use. Characteristics of the resulting cationic polymer particles were summarized in Table 1. With an increase of the amount of C₄Br (mol %) to ST, the particle diameter decreased and the particle surface charge density increased. This implies that the particle having a higher charge density and a smaller diameter is of less hydrophobicity. Glass plates were cleaned with boiling HNO₃ solution for 1 h, washed with water and dried in vacuum. The plates were immersed in a toluene solution of MES or ODES for 24 h, followed by washing with methanol and drying in vacuum. Surface hydrophobicity of alkylated glass plates treated with silane coupling agents was characterized by contact angle measurements. The average contact angles of MES and ODES plates for water were 82.1° and 96.4°, respectively. Self-organization of the CN particles was carried out as

Table 1. Characteristics of CN particles produced by emulsifier-free emulsion copolymerization^a

Latex Code	C ₄ Br/mol % to ST	Particle Size ^b		Surface Charge Density ^c µeq/m ²
		<i>d_n</i> /nm	<i>C_v</i> /%	
CN-0.1	0.1	373	3.1	1.33
CN-0.5	0.5	212	2.6	1.46
CN-1.0	1.0	203	2.4	1.62
CN-2.0	2.0	138	19.1	1.94

^aStyrene, 320 mmol; V-50, 3.2 mmol; water, 160 g; temp., 60 °C, stirring rate, 200 rpm; time, 12 h.

^bDetermined by SEM. *d_n*, number-average diameter; *C_v*, coefficient of variation of particle size distribution.

^cDetermined by colloid titration.

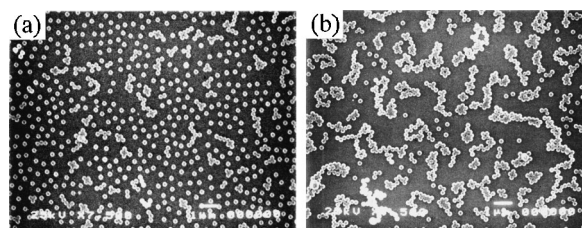


Figure 2. SEM photographs of CN-1.0 particles self-organized on (a) methylated glass plate and (b) an octadecylated glass plate at 25 °C. [Latex], 0.025 wt %.

follows: the glass plates were immersed in each latex dispersion (0.025 wt %) for 24 h, and washed in water by ultrasonic cleaning for 5 min. The self-organized morphology of CN particles on the alkylated glass plates was observed by a scanning electron microscope (SEM) (JEOL, JSM-5310), to investigate surface coverage and the average aggregate size (N_a).⁹

Figure 2 shows SEM photographs of CN-1.0 particles self-organized on MES and ODES plates. The CN-1.0 particles were self-organized on a MES plate in a dispersed type, whereas they were self-organized on an ODES plate in an aggregated type. This would be ascribed to an increase of hydrophobic interaction between particles and alkylated glass plate surfaces.

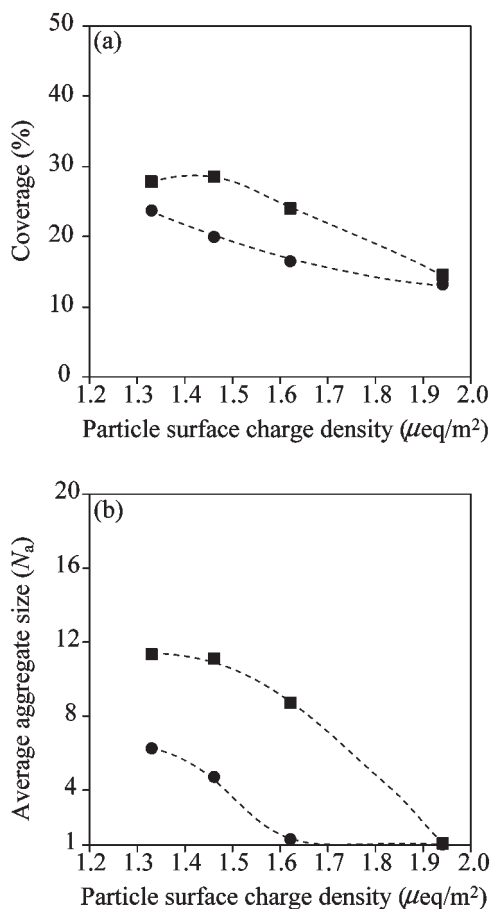


Figure 3. (a) Surface coverage and (b) average aggregate size (N_a) of CN particles on a glass plate treated with (●) MES and (■) ODES against particle surface charge density. [Latex], 0.025 wt %; temp., 25 °C.

Figure 3 shows (a) the surface coverage and (b) the average aggregate size (N_a) of CN particles on two alkylated glass plates against particle surface charge density. The surface coverage gradually decreased with an increase of the particle surface charge density. The surface coverage on an ODES plate was higher than that on a MES plate. These results strongly suggested that CN particles were self-organized on the substrate surfaces through hydrophobic interaction. The average aggregate size (N_a) also decreased with an increase of the particle surface charge density. The N_a on an ODES plate was higher than that on

a MES plate. Thus, the CN particles exhibiting a higher surface charge density were self-organized in a dispersed type on both methylated and octadecylated glass plates.

The CN particles were self-organized at 60 °C, to investigate the effect of temperatures on morphology types of the particle monolayer. Figure 4 shows the SEM photograph of CN particles self-organized on an ODES plate at 60 °C. The morphology changed from an aggregated type at 25 °C to a closely packed dispersed type at 60 °C. This would arise from enhanced electrostatic repulsion between particles and hydrophobic interactions, concomitantly with broadening an electric bilayer of a particle.¹⁰

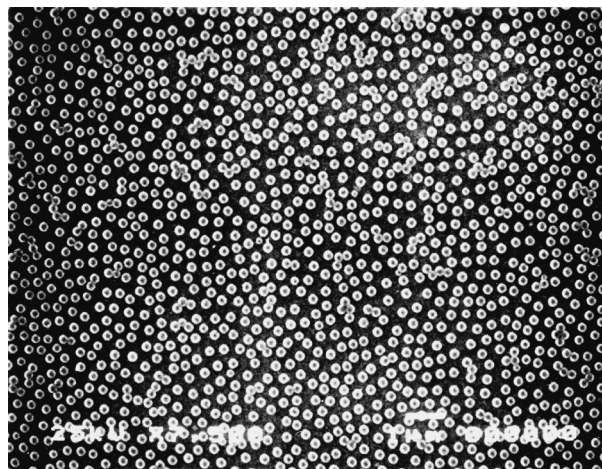


Figure 4. SEM photograph of CN-1.0 particles self-organized on octadecylated glass at 60 °C. [Latex], 0.025 wt %.

In summary, the formation of an ordered particle monolayer at a regular interval could be accomplished by tuning hydrophilic–hydrophobic balance of particles and substrates. The hydrophilic–hydrophobic balance of particles would be an important factor to determine the organized morphology of particle. Using this method, new areas will be explored to fabricate particle monolayers based on interactions between particles and substrates.

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