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ORIGINAL CONTRIBUTION

Self-organization of polymer particles on hydrophobic solid substrates in aqueous media. I. Self-organization of cationic polymer particles on alkylated glass plates

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Abstract Monodisperse, cationic polymer particles bearing quaternary ammonium groups effectively self-organized on hydrophobic solid substrates such as alkylated glass plates and polymer films to form particle monolayers. With an increase of the particle surface charge density, the surface coverage decreased and the morphology of particle monolayers changed from aggregated type to dispersed type. The dispersed type of particle monolayers having a relatively regular particle distance was formed at higher temperature. The self-organization behaviors on alkylated glass plates were different from those on unmodified glass plates through electrostatic interaction. The formation of particle monolayers on alkylated glass plates occurred only over a certain latex concentration range in contrast with that on unmodified glass plate. The adhesive strength of particle monolayers was enhanced by annealing at temperatures above the glass transition temperature (T_g) of the particles. Lens-shaped particle monolayers were fabricated by annealing the dispersed type of particle monolayers.

Keywords Polymer particle · Alkylated glass plate · Particle monolayer · Hydrophobic interaction · Self-organization

Introduction

Recently, the development of nanosized process technique was hoped to make smaller and high-performance devices. The conventional lithography method of patterning is difficult in technical and cost respects for the nanoscale process because it needs to use light such as ultraviolet and X-rays. On the other hand, monodisperse and functionalized polymer particles can be prepared over a wide range of particle diameter. Colloidal assemblies in two and three dimensions have attracted much attention in the field of chemistry and optics. Especially, particle assemblies in two dimensions can be applied to lithographic masks [1], anti-reflection surfaces [2], sensors [3], microlens arrays [4, 5] and surface modification of solid substrates [6, 7]. Particle monolayers have been fabricated by solvent evaporation method [8], Langmuir–Blodgett method [9], electrophoretic deposition method [10], and methods through chemical reaction and interaction between particle and substrate [11, 12]. Electrostatic interactions have been widely employed in the assembly of particles ranging from microscale to nanoscale dimensions. Hammond and colleagues have demonstrated a technique for the selective self-organization of latex colloids onto patterned polyelectrolyte substrates through electrostatic interaction [13–16].

Polymer particles are amphiphilic materials, which resemble surfactants in many respects such as surface tension reduction of water by adsorption at air/water interface, stabilization of emulsions by adsorption at oil–water interface, and adsorption at charged surfaces [17–20]. The amphiphilicity of particles can be controlled by tuning the polarity, functional groups, kind of charges, and surface charge densities of the particles. It is known that surfactants adsorb on hydrophobic solid substrates through hydrophobic interaction. However, to our knowledge, only a little was known about the self-organization of polymer particles on hydrophobic solid surfaces.

In our previous papers, we reported the self-organization of cationic polymer particles bearing sulfonium and

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quaternary ammonium groups on hydrophobic solid substrates through hydrophobic interaction, and fabricated aggregated and dispersed types of particle monolayers by changing the hydrophobicity of substrates and the hydrophilic–hydrophobic balance of particles [21–25]. In this work, cationic polymer particles having different surface charge densities were synthesized and self-organized on alkylated glass plates by changing the conditions of self-organization time, latex concentration, and temperature to control the morphology of particle monolayers. The physical stabilization of the resulting particle monolayers was also investigated. Furthermore, we compared the self-organization behaviors on unmodified glass plates through electrostatic interaction with those on alkylated glass plates. A schematic representation of the system studied in this work is shown in Fig. 1, indicating the self-organization of cationic polymer particles on alkylated glass plates through hydrophobic interaction.

Experimental

Materials and methods Styrene (ST) was purified by distillation under reduced pressure in a nitrogen atmosphere. Water-soluble, cationic monomer, methacryloyloxyethylbutyldimethylammonium bromide (C_4Br), was prepared by the reaction of 2-(dimethylamino)ethyl methacrylate with *n*-bromobutane in acetone and purified by recrystallization from a mixture of acetone and acetonitrile (3:1 by volume). 2,2′-azobis(2-amidinopropane) dihydrochloride (V-50) was used as radical initiator for the emulsifier-free emulsion copolymerization. Glass plates (10×26×1.0 mm) used in this study were cleaned with boiling HNO_3 solution for 1 h, washed with water, and dried in vacuum at 100 °C. *n*-Octadecyltriethoxysilane (ODES) and methyltriethoxysilane (MES) were received from Tokyo Kasei Kogyo and Shin-Etsu Chemical, respectively. N/400 Potassium poly(vinyl sulfate) (N/400 PVSK) solution was used with a dilution to N/20,000. Water was distilled and deionized by a Millipore system before use. All reagents were purchased from Wako Pure Chemical Industries unless otherwise noted.

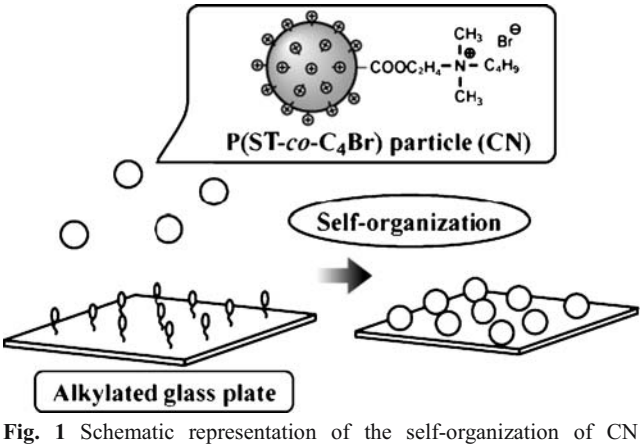

Fig. 1 Schematic representation of the self-organization of CN particles on alkylated glass plates

Synthesis and characterization of cationic polymer particles Monodisperse P(ST-*co*-C_4Br) 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 ST with a water-soluble, cationic monomer, C_4Br in 500 ml three necked, round-bottomed flask equipped with reflux condenser, nitrogen inlet, and mechanical stirrer. The flask was initially charged with ST (320 mmol), C_4Br (0.32–6.4 mmol) and deionized water (140 g). The contents of the flask were stirred at 200 rpm and flushed with nitrogen for about 45 min. Radical initiator, V-50 (3.2 mmol), dissolved in deionized water (20 g) was added into the flask and then the flask was immersed in a water bath thermostated at 60 °C for 12 h. The resulting latex was purified by centrifugation at 12,000 rpm for 30 min and washing with deionized water several times. The number average-diameter, D_n, and the coefficient of variation, C_v, of the resulting particles were determined using a scanning electron microscopy (SEM) (JEOL, JSM-5310). A colloid titration method was employed to determine the surface charge density of the polymer particles [26]. The purified latex dispersion of cationic polymer particles was titrated with N/20,000 PVSK solution using toluidine blue as indicator. The charge density on the particle surface was expressed in the equivalent mole of charge groups per unit area. The degree of flocculation in CN latex dispersions was examined using the turbidity method [27]. CN latex dispersions containing NaCl at a given concentration was subjected to stand at 25 °C for 24 h. The degree of flocculation in the latex dispersion was evaluated from *n* values, which can be determined from the variation of absorbance from 400 to 600 nm by UV–Vis spectroscopy, according to the following Eq. (1):

$$n\,\text{value} = -\frac{d\log(\text{absorbance})}{d\log(\text{wavelength})} \quad (1)$$

The *n* value is constant for the particles without flocculation, and decreases upon the formation of secondary particles. As the electrolyte concentration is increased, the *n* value begins to decrease above a certain concentration, which is defined as the critical flocculation concentration (cfc). Characteristics of the resulting cationic polymer particles are summarized in Table 1.

Preparation of alkylated glass plates Freshly prepared glass plates were reacted with silane coupling agents (4.0 g) in purified toluene solution (200 ml) at 110 °C for 24 h, followed by washing with methanol and drying in vacuum. Surface characterization of alkylated glass plates

Table 1 Characteristics of cationic polymer particles produced by emulsifier-free emulsion copolymerization

Latex code	C_4Br (mol% to ST)	Particle size[b]		Surface charge density[c] (μeq/m^2)	A_p[d] (Å^2)	cfc[e] (mM)
		D_n (nm)	C_v (%)			
CN-0.1	0.1	336	3.1	1.30	125	50
CN-0.5	0.5	212	2.6	1.46	114	150
CN-1.0	1.0	203	2.4	1.62	103	250
CN-2.0	2.0	138	19.1	1.94	86	500

[a] Styrene, 320 mmol; V-50, 3.2 mmol; water, 160 g; temperature, 60 °C; stirring rate, 200 rpm; 12 h
[b] Determined by SEM. D_n, number-average diameter; C_v, coeffecient of variation of particle size distribution
[c] Determined by colloid titration
[d] Occupied area by a charged group
[e] Critical flocculation concentration (cfc) determined in NaCl solution 25 °C

was carried out by contact angle measurements (ERMA, goniometer type, model G-I) of deionized water.

Self-organization of polymer particles on alkylated glass plates Self-organization experiments were conducted as follows: alkylated glass plates were immersed into latex dispersion at a given concentration for 24 h, taken out of the dispersion, and washed in water by ultrasonic irradiation of 18 W at 42 kHz oscillation frequency for 5 min to remove weakly and/or physically adsorbed particles. The morphology of particle monolayers was observed by SEM and the coverage and average aggregate size (N_a) were determined using SEM photographs. The coverage was calculated using Eq. (2):

$$\text{Coverage}\,(\%) = \frac{N}{N_{\max}} \times 100 \tag{2}$$

where N and N_{max} are the number of particles per unit area and the maximum number of particles with hexagonally closed packing, respectively. N_a is defined as

$$N_a = \frac{\sum n_i N_{a,i}}{\sum n_i} \tag{3}$$

where $N_{a,i}$ and n_i are number of particles per aggregate and number of aggregates of i particles, respectively [28].

Physical stabilization of CN particle monolayers CN particle monolayers on alkylated glass plates were annealed at temperatures above T_g of the particles. The strength of the particle monolayer against peeling before and after annealing was examined using adhesive tape.

Results and discussion

Synthesis and characterization of cationic polymer particles

The cationic polymer particles having quaternary ammonium groups on their surfaces were prepared by emulsifier-free emulsion copolymerization at different amounts of C_4Br to ST in feed. The resulting cationic polymer particles having different surface charge densities were used to get an insight into the effect of hydrophilic–hydrophobic balance of particles on the self-organization.

The characteristics of the cationic polymer particles are listed in Table 1, and Fig. 2 shows the number-average diameter and surface charge density of CN particles against the amount of C_4Br to ST in feed. Four kinds of cationic particles having different diameters and surface charge densities were obtained by varying the amount of C_4Br (mol% to ST) in feed. With an increase of the amount of C_4Br (mol% to ST), the particle diameter decreased and the particle surface charge density increased. With an increase of a water-soluble comonomer in emulsifier-free emulsion copolymerization, the number of particles nucleated increases and hence, the amount of ST supplied to the particle nuclei decreases, resulting in the decrease of particle diameter [29]. The cationic charges on CN particle surfaces would stem from initiator (V-50) fragments and water-soluble comonomer (C_4Br) units. The cationic charge density from V-50 can be calculated by extrapolation of the particle surface charge density line shown in Fig. 2 to 0 mol% of C_4Br to ST in feed, and it is 1.28 μeq/m^2, indicating that the cationic charges from V-50 are greater than those from C_4Br. Furthermore, four kinds of particles in Table 1 were prepared at the same initiator concentration in feed and hence, the higher surface charge density of CN particle is brought about from the higher feed concentration of C_4Br. Thus, the surface charge density can be controlled within a certain range by varying the molar ratio of water-soluble comonomer to water-insoluble monomer as a main component for emulsifier-free emulsion polymerization, though the particle size changes concurrently. Because cationic charges at particle surfaces are hydrophilic groups, CN particles having higher surface charge density should be more hydrophilic. Critical flocculation concentration (cfc) was determined by adding NaCl as electrolyte to each CN latex dispersion and refers to the concentration that the

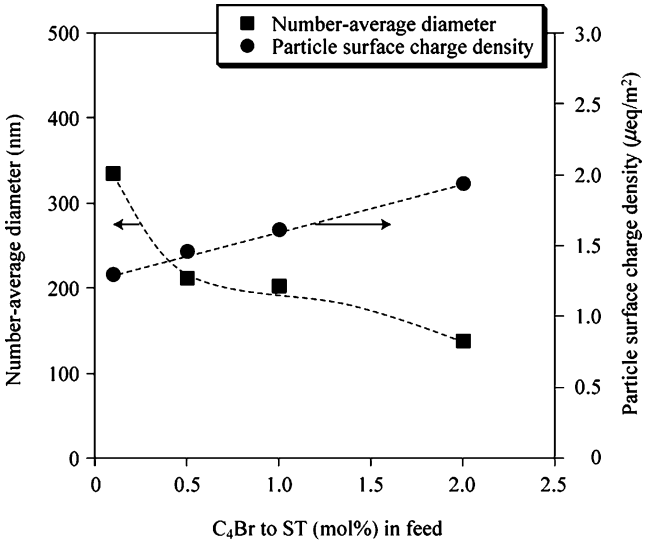

Fig. 2 Number-average diameter and surface charge density of CN particles against the amount of C_4Br to ST in feed

colloids begin to flocculate. It becomes higher for the particle having higher charge density and hence, the hydrophobicity of particles can be compared using the cfc values. Thus, CN-0.1 particle is the most hydrophobic and CN-2.0 particle is the most hydrophilic among these CN particles because cfc increases with the increase of particle surface charge density.

Self-organization of cationic polymer particles on alkyalted glass plates

Yamaguchi et al. found that the cationic polymer particles bearing sulfonium groups on their surfaces self-organized on hydrophobic solid substrates to form dispersed or aggregated type of particle monolayers dependent on the hydrophobicity of the substrates [23, 24].

The average contact angles of water on alkylated glass plates modified with methyltriethoxysilane (MES) and *n*-octadecyltriethoxysilane (ODES) were 82.1° and 96.4°, respectively, indicating that the hydrophobicity of the ODES plate is higher than that of the MES plate. Figure 3 shows the SEM photographs of CN particle monolayers formed, when MES plates were immersed into CN latex dispersions of 0.025 wt% for 24 h. CN-0.1 particle monolayers are mostly composed of a lot of large aggregates. CN-0.5 particle monolayers also consist of many aggregates with smaller sizes and considerable numbers of isolated particles are observed. The number of isolated particles further increases for CN-1.0 particle monolayers, and CN-2.0 particle monolayers are predominantly made up of many isolated particles. Thus, there is a clear change of morphology of particle monolayers from aggregated type to dispersed type with an increase in the particle surface charge density.

Figure 4 shows the coverage and the average aggregate size (N_a) of CN particle monolayers on two alkylated glass plates against particle surface charge density. Average

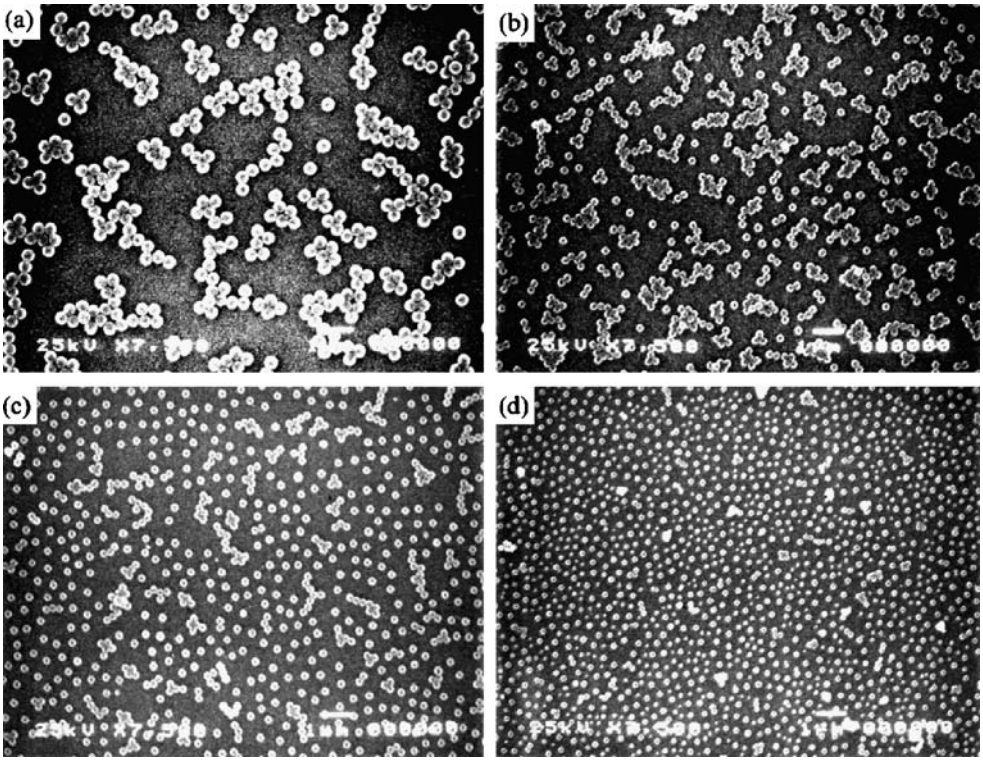

Fig. 3 SEM photographs of CN particles self-organized on MES plates. [Latex], 0.025 wt %; temperature, 25 °C; time 24 h. Particles: **(a)** CN-0.1, **(b)** CN-0.5, **(c)** CN-1.0, and **(d)** CN-2.0. Magnification: **(a)**–**(d)**, ×7,500

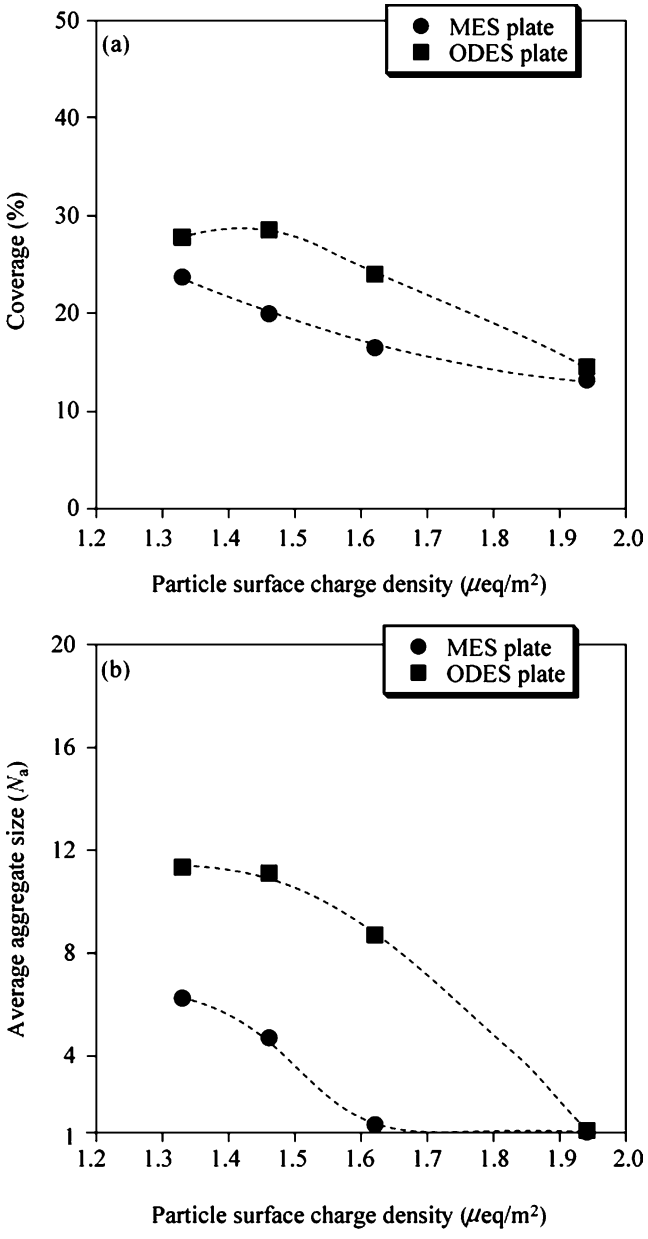

Fig. 4 **(a)** Coverage and **(b)** average aggregate size (N_a) of CN particle monolayers on alkylated glass plates against particle surface charge density. [Latex], 0.025 wt%; temperature, 25 °C; time, 24 h

aggregate size (N_a) is related to the morphology of particle monolayers and indicates that with an increase of the N_a value the larger aggregates form and the morphology of particle monolayer is of aggregated type, while with the approach of the N_a value to one, the each particle self-organizes on the surfaces separately and the morphology is of dispersed type. The coverage gradually decreases with increasing particle surface charge density. Furthermore, the coverage on an ODES plate is higher than that on a MES plate. These results strongly suggest that the particles self-organize on the substrate surfaces through hydrophobic interaction. N_a also decreases with an increase of the particle surface charge density. The N_a on an ODES plate is higher than that on a MES plate. N_a values of CN-1.0 particle monolayers on MES and ODES plates show that the CN-1.0 particle self-organize in aggregated type on ODES plate and in dispersed type on MES plate.

We also synthesized the CNS particles that have comparable surface charge density to that of CN-0.5 particles and larger diameter (354 nm) by shot-growth method. The self-organization behaviors of CNS particles on alkylated glass plates were compared with those of CN-0.5 particles to investigate the effect of particle size. The coverage of CNS particle monolayers was close to that of CN-0.5 particle monolayers but there was a difference in the morphology of particle monolayers. The CN-0.5 particle monolayers on MES plates shown in Fig. 3c consist of many aggregates and considerable number of isolated particles, while only aggregates were observed for CNS particle monolayers on MES plates. This may indicate that the self-organization on hydrophobic solid substrates is also effected to some extent by the particle size.

Thus, the coverage and the morphology of particle monolayers can be controlled by changing factors such as hydrophilic–hydrohobic balance of particles and hydrophobicity of substrates.

The self-organization process of CN particles was followed as a function of self-organization time. Figure 5 shows the self-organization time dependencies of the coverage and N_a for more hydrophobic CN-0.1 particles on alkylated and unmodified glass plates. For both alkylated glass plates, the coverage gradually increases with an increase of self-organization time. On the other hand, for unmodified glass plates, the coverage rapidly increases at the early stage of self-organization and becomes constant. Furthermore, for the MES plate, N_a suddenly increases at the early stage of self-organization and becomes constant, while it steadily increases for the ODES plates. On the other hand, there is no increase of N_a for unmodified glass plates and the time dependence is definitely different from that of alkylated glass plates. Such a difference would be associated with the difference in the interaction of the particles with the substrates.

Figure 6 shows the self-organization time dependence of the coverage and N_a for less hydrophobic CN-1.0 particles on alkylated glass plates. For both alkylated glass plates, the coverage increases with self-organization time like CN-0.1 particles. N_a increases with the self-organization time for more hydrophobic ODES plates, whereas N_a increases at the early stage of self-organization and then gradually approaches to one for less hydrophobic MES plates, indicating that pre-aggregates are formed at the early stage of self-organization and then the morphology of particle monolayers changes to dispersed type. Such behaviors can be considered as follows. At the first stage of self-

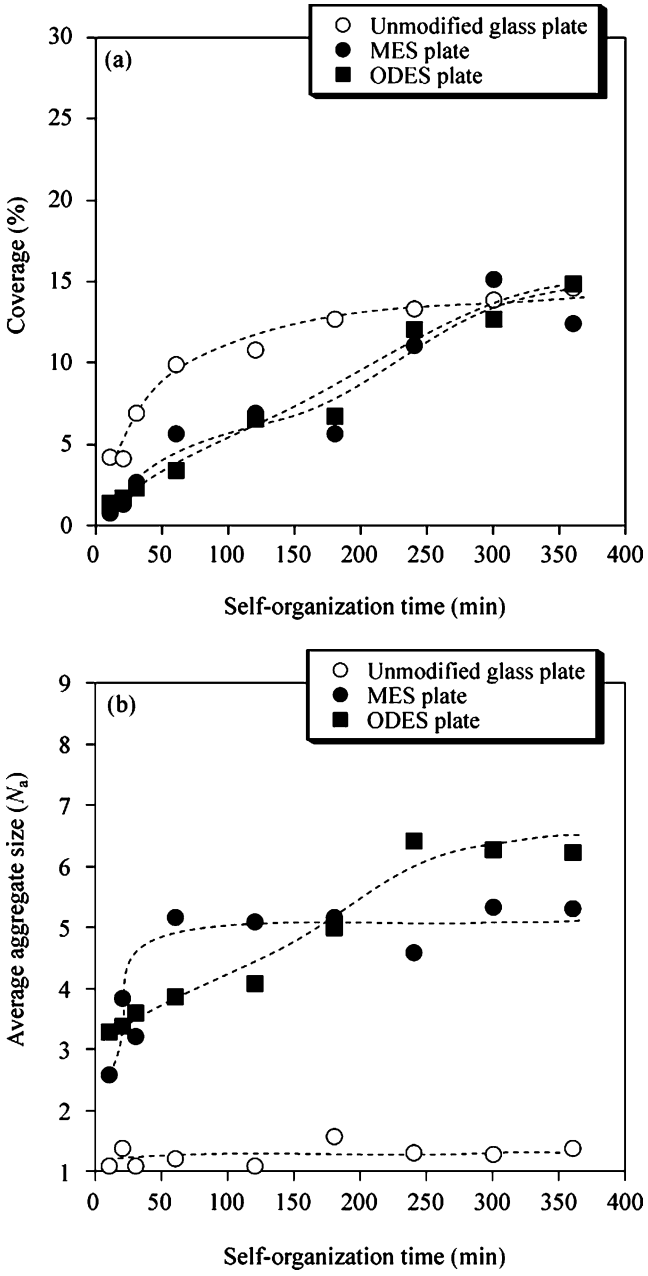

Fig. 5 **(a)** Coverage and **(b)** average aggregate size (N_a) of CN-0.1 particle monolayers on alkylated and unmodified glass plates against self-organization time. [Latex], 0.025 wt%; temperature, 25 °C

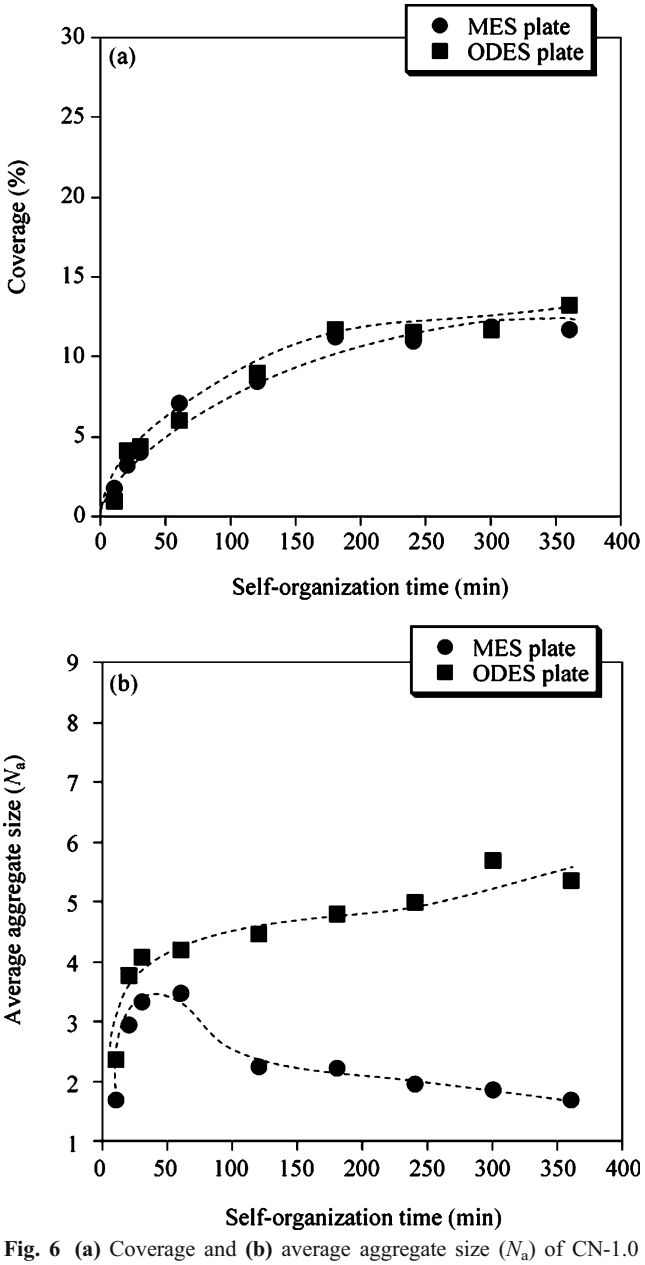

Fig. 6 **(a)** Coverage and **(b)** average aggregate size (N_a) of CN-1.0 particle monolayers on alkylated glass plates against self-organization time. [Latex], 0.025 wt%; temperature, 25 °C

organization, particles randomly adsorb on the substrates. The subsequent adsorption exclusively occurs at the positions adjacent to the particles already adsorbed on the substrates. For the systems that the hydrophobic interaction between particle and substrate works strong, aggregates continue to grow and the aggregated type of particle monolayers is formed. On the other hand, for the systems that the interaction is weak, pre-aggregates rearrange by the action of electrostatic repulsion between the particles to give dispersed type of particle monolayers.

CN particles were self-organized at various latex concentrations to investigate the difference between self-organization behaviors through hydrophobic interaction and electrostatic interaction. Figure 7 shows the coverage or N_a of CN-0.1 particles on alkylated and unmodified glass plates against latex concentration. As the latex concentration is increased, the coverage exhibits maxima for the alkylated glass plates at about 0.025 wt% and decreases at higher latex concentrations. On the other hand, for unmodified glass plates, it still increases at higher latex concentrations, the adsorption isotherm being of Langmuir type. With an increase of the latex concentration, N_a also

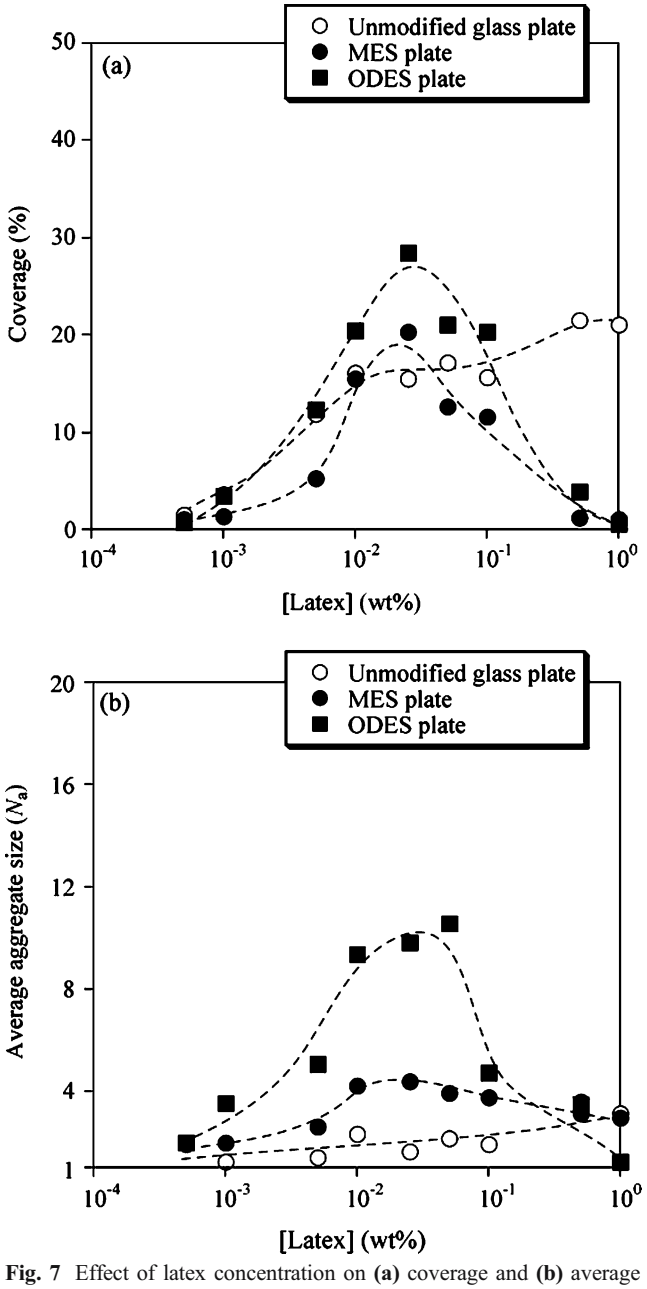

Fig. 7 Effect of latex concentration on **(a)** coverage and **(b)** average aggregate size (N_a) of CN-0.1 particle monolayers on alkylated and unmodified glass plates. Temperature, 25 °C; time 24 h

exhibits maxima for the alkylated glass plates and decreases at higher concentrations. On the other hand, there is no maximum in N_a for unmodified glass plates, and the morphology of particle monolayers remains unchanged. Such a difference in the coverages between the alkylated glass plates and unmodified glass plates, especially at higher latex concentrations, suggests that the interaction between the particle and the alkylated glass plate is different from electrostatic interaction, which is predominant for the self-organization of CN particles on the unmodified glass plate. Surfactants and amphiphilic polymers are known to form various ordered structures such as lamellar, hexagonal, and cubic phases. Furthermore, it was reported that the particles also form network-structured state, granular state, and micelle structure by the self-organization in bulk phases [30, 31]. At higher latex concentrations, polymer particles might prefer the formation of such structures, resulting in the decrease of the self-organization character of the particles on substrates. Such concentration dependencies would be a characteristic feature of self-organization through hydrophobic interaction

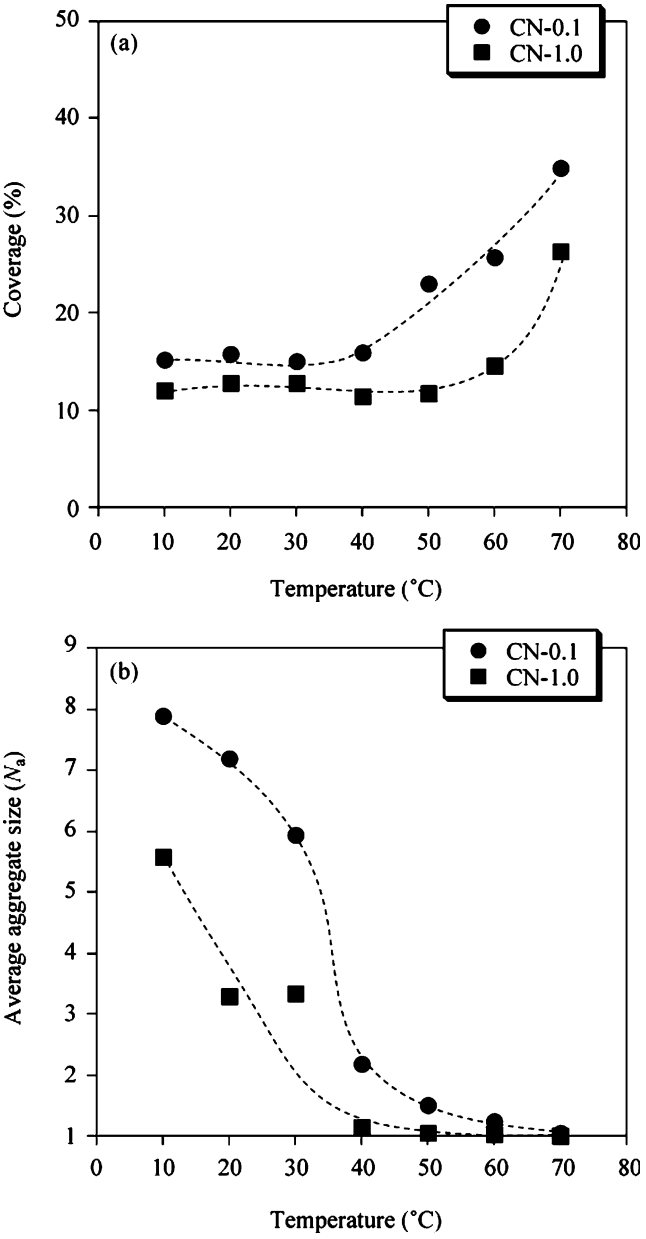

Fig. 8 Effect of temperature on **(a)** coverage and **(b)** average aggregate size (N_a) of CN-0.1 and CN-1.0 particle monolayers on ODES plate. [Latex], 0.025 wt%; time, 24 h

and might be a reason that the self-organization on hydrophobic substrates is not found yet.

The effect of temperature on the self-organization of CN particles was investigated, and Fig. 8 shows the temperature effect of the coverage of CN-0.1 and CN-1.0 particle monolayers on ODES plates. As the temperature is raised, the coverage begins to increase above about 40 °C. The coverages of CN-0.1 particle monolayers are higher than those of CN-1.0 particle monolayers over a whole range of temperatures. At lower temperatures, N_a values are high for ODES plates, as described above and the particles self-organizes in aggregated type. However, N_a decreases and approaches to one with increasing temperature. It means that the morphology of particle monolayers can be changed from aggregated type to dispersed type by tuning temperature. Debye length of particles would increase at higher temperatures resulting in increased electrostatic repulsion between particles, which leads to the formation of dispersed type of particle monolayers [32]. The increase in the coverage at higher temperature might be ascribed to the increase in the particle collision frequency towards substrates caused by more active Brownian motion. Figure 9 shows the SEM photographs of CN-0.1 and CN-1.0 particle monolayers formed on ODES plates at 60 °C. The self-organization at higher temperature yields dispersed type of particle monolayers having a relatively regular particle distance. Thus, the morphology of particle monolayers greatly varies not only with hydrophilic–hydrophobic balance of particles but also with the self-organization temperature.

The adhesive strength of the particle monolayers was evaluated by peeling off the particle monolayers with adhesive tapes. Figure 10 shows the SEM photographs of CN-1.0 particle monolayers formed in NaCl solution (10 mM) (Fig. 10a) and annealed at 120 °C for 3 h (Fig. 10b). In latex dispersions containing electrolytes, the

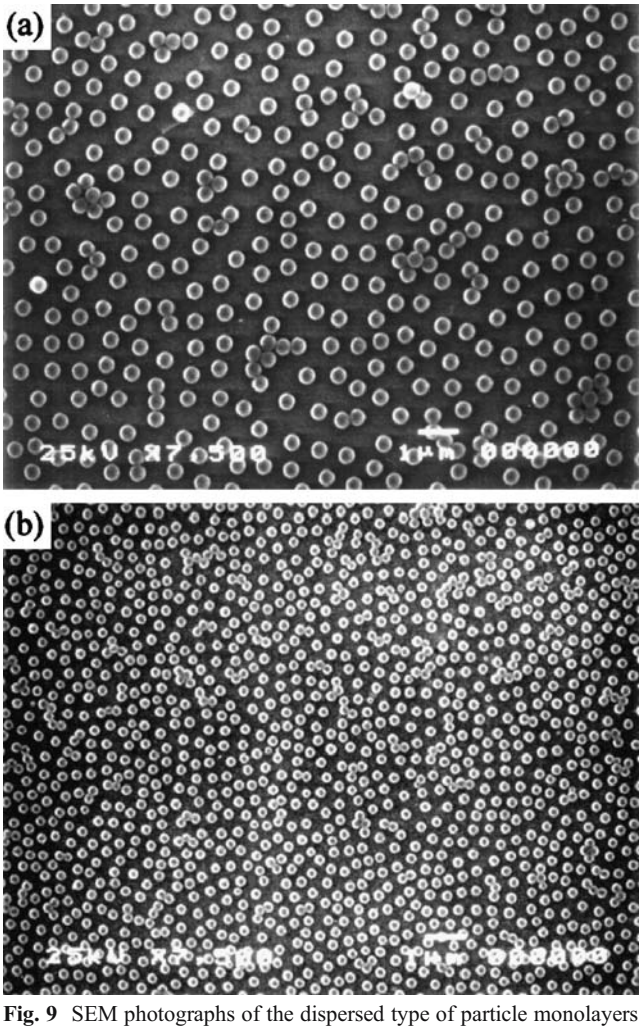

Fig. 9 SEM photographs of the dispersed type of particle monolayers on ODES plates. [Latex], 0.025 wt%; temperature, 60 °C; time, 24 h. **(a)** CN-0.1 and **(b)** CN-1.0 particle. Magnification: **(a)** and **(b)**, ×7,500

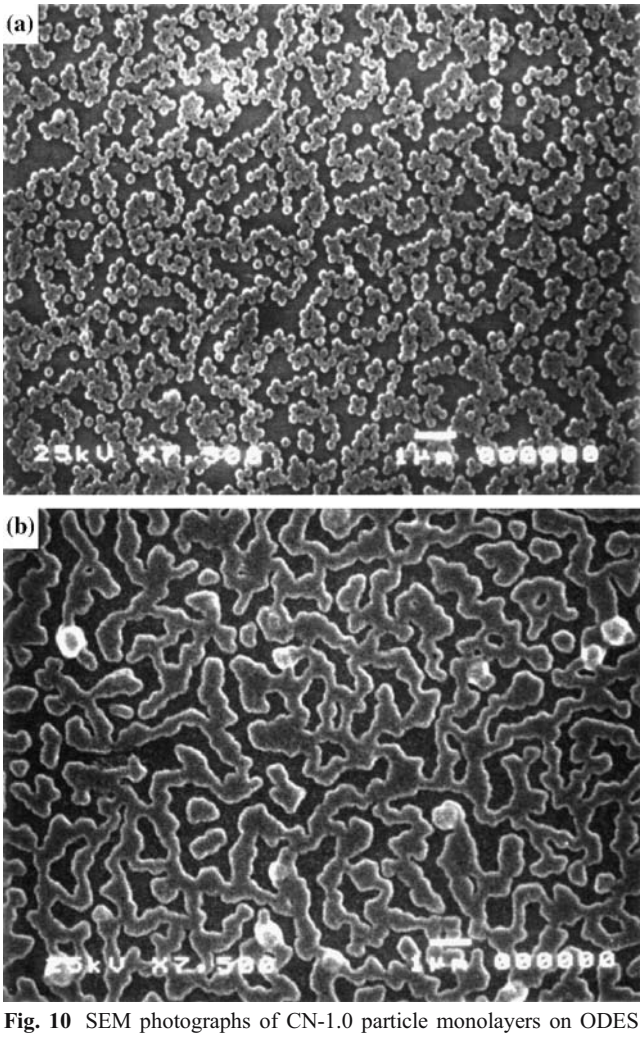

Fig. 10 SEM photographs of CN-1.0 particle monolayers on ODES plates **(a)** before and **(b)** after annealing at 120 °C for 3 h. Self-organization: [latex], 0.025 wt%; temperature, 25 °C; time, 24 h; [NaCl], 10 mM. Magnification: **(a)** and **(b)**, ×7,500

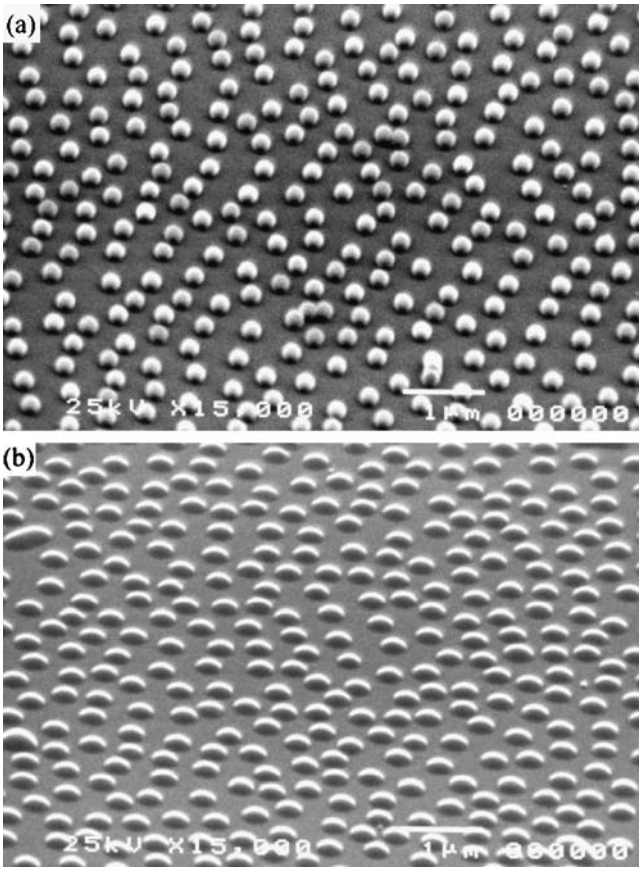

Fig. 11 SEM photographs of CN-1.0 particle monolayers on ODES plates **(a)** before and **(b)** after annealing at 140 °C for 1 h. Self-organization: [latex], 0.025 wt%; temperature, 60 °C; time, 24 h. Magnification: **(a)** and **(b)**, ×15,000

electric double layer of particles is compressed. As a result, the electrostatic repulsion between particles on the substrates becomes weaker to form more closely packed, aggregated type of particle monolayers. The resulting particle monolayers were easily peeled off by adhesive tape. On the other hand, CN particle monolayers annealed at 120 °C above T_g of the particles were not peeled off. Thus, the adhesive strength of particle monolayers can be improved by annealing at temperatures above T_g of the particles.

Fabrication of microlens array using polymer particles was reported. Hayashi and Hirai self-assembled polystyrene beads into 2D lattices on glass substrates, and demonstrated their use as arrays of microlenses in imaging [4]. Xia and colleagues prepared 2D microlens array of polystyrene beads by templating against substrates having cylindrical holes and annealing at temperatures slightly higher than T_g of the particles of monolayers [5]. We found that the particles transform by annealing at temperatures above the T_g of adsorbed particles. The dispersed type of particle monolayers (shown in Fig. 8b) was annealed to fabricate lens-shaped particle monolayers. Figure 11 shows the CN-1.0 particle monolayers before and after annealing at 140 °C for 1 h. Such lens-shaped particle monolayers could be readily formed by tuning annealing temperature and time. They may be applied as microlens array.

Conclusions

Cationic particle monolayers bearing quaternary ammonium groups were effectively formed on hydrophobic solid substrates through hydrophobic interaction. The coverage and morphology of particle monolayers could be controlled by changing the ionic strength, temperature and hydrophilic–hydrophobic balance of particles. Self-organization of CN particles on alkylated glass plates characteristically occurred only over a certain latex concentration range, and the behavior is greatly different from that of self-organization on unmodified glass plates through electrostatic interaction. Adhesive strength of particle monolayers was improved by annealing at temperatures above T_g of particles. Lens-shaped particle monolayers were easily fabricated by annealing the dispersed particle monolayers.

The monolayer formation of polymer particles through hydrophobic interaction has a lot of analogous points to the adsorption of proteins or organic pollutants to polymeric materials. Therefore, the adsorption of polymer particles on hydrophobic solid substrates may provide useful information for these systems. Furthermore, polymer films can be used as hydrophobic solid substrates for the fabrication of particle monolayers, and hence this method can be also applied to the surface modification of polymer films.

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