

Relationship of Zeta Potential to Molecular Structure of Multivalent Cationic Adsorbates on Silica and PET Substrates

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The formation of an organic adsorbed monolayer on a substrate surface of silica and poly(ethylene terephthalate) (PET) was investigated by zeta potential measurements of substrates after immersion in solutions containing multivalent cationic molecules and polymers. Silica and PET substrates cleaned by the UV-irradiation from a low-pressure Hg lamp exhibited large negative zeta potentials, on which the multivalent cationic adsorbates of rod-like tetrapyrindinium **1**, ball-like cyclopentasilane derivative **2**, and random-coiled polysilane **3** could be adsorbed from their dilute solutions. Accompanied with the adsorbed monolayer formation through electrostatic forces, the zeta potential values of substrates adsorbing **1-3** turned positive, regardless of the kind of substrates. The small positive zeta potential values observed for **1** caused an obvious suppressive effect on further adsorption of negatively charged polystyrene particles. These zeta potential and particle-adsorption studies indicated that when the multivalent cationic adsorbates with a different feature in their molecular structures form an adsorbed monolayer, the role of cationic functional groups included in the adsorbates is divided into substrate-adsorption sites and particle-adsorption sites according to adsorption manners of the multivalent cationic molecules and polymers.

Key words: surface adsorption, multivalent cationic adsorbate, zeta potential, contact angle, particle adsorption

1 INTRODUCTION

The methods to control surface properties by chemical modification of an outermost surface of solid matters with an organic monolayer have begun to attract notice. This situation arises from the recognition that such a nanometer-sized organic monomolecular layer is an ultimate material to handle solid materials from submicron to nanometer sizes, readily available in nanotechnology [1]. The chemical modification of substrate surfaces has been carried out up to the present through the formation of self-assembled monolayers (SAMs), the deposition of Langmuir-Blodgett (LB) monolayers, and the adsorption of polyelectrolytes by layer-by-layer techniques [2]. In the case of using SAMs formed from organosilanes on silica and organothiolates on gold and silver, the limitation on combinations between a layer-forming molecule and a substrate often causes to decrease use of their SAMs. In the case of LB monolayers, expensive apparatuses and skilled techniques are required for their fabrication. Moreover, there is a problem that a LB monolayer deposited physically on a substrate surface lacks desorption-resistance toward chemicals including solvents. One has best prepare a widely usable and stable monolayer in a convenient, inexpensive and environmentally benign way.

We have recently taken notice of an adsorbed monolayer formed from multivalent cationic molecules and polymers on a negatively charged silica surface. We demonstrated that the adsorbed monolayers formed by cationic molecules possessing four pyridinium units showed high desorption-resistance toward deionized water through multi-point electrostatic interaction [3, 4]. It was found that the adsorbed monolayers were applicable to the photoalignment of nematic liquid crystals [4] and the adsorption photocontrol of nano-sized silica particles [3]. During systematic studies on the adsorption behaviors of colloidal polymer and silica particles on substrates adsorbing multivalent cationic adsorbates **1-3** as indicated in Figure 1, We noted that the tetrapyrindinium **1** exhibited peculiar behaviors differing from the substrates adsorbing

cationic cyclopentasilane **2** and polysilane **3**. It was anticipated that surface charges controlling the adsorption of colloidal particles were different among the substrates adsorbing **1-3**.

In this paper, we investigated the zeta potential values of silica and PET substrates that were cleaned by UV-irradiation and treated with solutions containing the multivalent cationic adsorbates **1-3**. We studied on the correlation of the zeta potential values with the adsorption behaviors of negatively charged polystyrene particles to the substrates. From these studies, we led to the conclusion that the multivalent cationic adsorbates **1-3** formed an adsorbed monolayer on substrate surfaces in a different adsorption manner depending on features in their molecule structures.

2 EXPERIMENT

2.1 Materials

Chemical structures of multivalent cationic adsorbates used in this study are displayed in Figure 1. Tetrapyrindinium **1** and polysilane **3** with quaternary ammonium groups were prepared according to our previous reports [3, 5]. Cyclopentasilane with pyridinium groups **2** was synthesized from decaphenylcyclopentasilane, donated by Osaka Gas Co. Ltd., through two steps of reactions consisting of the chloromethylation with chloromethyl methyl ether and SnCl₄ and the quaternization with pyridine. The cationic cyclopentasilane having quaternized pyridiniums of approximately nine units, **2**, which was characterized by ¹H-NMR and elemental analysis measurements [6], was used in this study. The detailed procedures to prepare **2** will be published elsewhere.

Deionized water was purified with a Milli-Q system prior to use. Fluorescent carboxyl-modified polystyrene particles of 200 nm in a diameter (Molecular Probe, Fluosphere, F-8811) were purchased from Funakoshi.

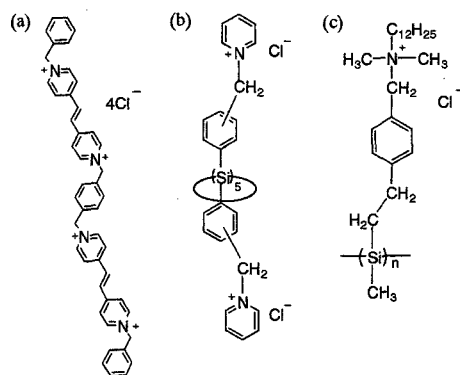


Figure 1. Chemical structures of (a) tetrapyridinium 1, (b) cyclopentasilane with pyridinium units 2, and (c) polysilane with ammonium units 3.

2.2 Preparation of substrates for surface adsorption

A silica plate (10 x 30 x 1 mm) to fabricate an adsorbed layer was cleaned with an ozone cleaner (Nippon Laser & Electronics Lab.) for 2 h. Silica substrates exhibiting a water contact angle below 5°, measured by a contact angle meter (Kyowa Kaimen Kagaku, CA-X) were used in this study. A substrate (10 x 30 x 1 mm) of polyethylene terephthalate (PET) was used for surface adsorption after three kinds of following methods, which were (1) the UV-treatment with an ozone cleaner, (2) the acid-treatment with piranha solution (H₂SO₄/H₂O₂ 7:3 (v/v)), and (3) the alkaline-treatment with an 1 mol dm⁻³ NaOH aqueous solution. PET substrates after each treatment at room temperature were rinsed with deionized water thoroughly and dried by N₂ gas. The optimal conditions to obtain a hydrophilic PET substrate using each treatment were determined by monitoring a water contact angle as a function of treatment time.

2.3 Formation of an adsorbed layer on substrates

Cleaned substrates of silica and PET were immersed in a solution containing an adsorbate of 1, 2 and 3 for 1 h, rinsed with pure solvent and dried with N₂ gas. In the case of cationic adsorbate 1 and 3, an aqueous solution of 10⁻⁴ mol dm⁻³ 1 and an ethanol solution of 1 wt% 3 were used for the surface adsorption, respectively, according to our previous reports [3, 7]. In the case of 2, an aqueous solution containing 3 wt% 2 at 50 °C was used.

2.4 Zeta potential measurements

Zeta potentials of fluorescent carboxyl-modified polystyrene particles and silica and PET substrates before and after the surface adsorption of adsorbates 1-3 were measured at 25 ± 1 °C with an electrophoretic light scattering spectrophotometer (Otsuka Electronics, ELS-8000). HPC-coated (hydroxyl propyl cellulose coated) polystyrene particles of 520 nm in a diameter were used as standard monitor particles for the zeta potential determination of substrates. Commercially available HPC-coated particles were diluted 500 times by adding a 10 mmol dm⁻³ NaCl aqueous solution, whose pH value was adjusted by adding a dilute solution containing either HCl or NaOH.

2.5 Surface adsorption of fluorescent polystyrene particles to substrate surfaces

Silica and PET substrates cleaned and treated with the solutions of multivalent cationic adsorbates 1-3 were immersed pH 7 for 90 sec in an aqueous dispersion containing fluorescent

carboxyl-modified polystyrene particles. After multiple rinses with deionized water and dried by N₂ gas, particles-adsorbed substrates were observed by a microscope (Olympus, BX60) in a fluorescence mode.

3 RESULTS AND DISCUSSION

3.1 Zeta potential changes of silica substrates through adsorbed layer formation and adsorption behaviors of polystyrene particles

The formation of adsorbed monolayers of tetrapyridinium 1 and cationic polysilane 3 on a cleaned silica plate could be confirmed by UV-visible spectral measurements as reported in our previous reports [3, 7]. In the case of cationic cyclopentasilane 2, it was found by UV-visible spectroscopy that a densely packed adsorbed monolayer was formed on a silica plate after immersion in the aqueous solution of 2, under the assumption that a molecular extinction coefficient in solution was not altered in a film state [6].

The zeta potential values at pH 7 observed for a cleaned silica substrate and substrates after the adsorption of multivalent cationic adsorbates 1-3 with different molecular structures were summarized in Table 1. The cleaned silica plate having an isoelectric point of pH 2-3 [8] exhibited a negative zeta potential of -73 ± 5 mV, while the zeta potential value of a silica substrate after immersion in a solution containing each cationic adsorbate and multiple rinses turned positive. When the multivalent cationic adsorbates of 1, 2 and 3 were used, the zeta potential values of +6 ± 1 mV, +35 ± 5 mV, and +40 ± 13 mV were observed, respectively. The silica substrate after surface adsorption of 1 showed a smaller zeta potential value than the others. It was supported from zeta potential and UV-visible spectral studies that no desorption of each cationic adsorbate from a silica substrate took place even after immersion in the electrolyte aqueous solution containing NaCl to measure the surface potential. Therefore, these results imply that the zeta potential values of silica plates after the surface adsorption are dependent on the chemical structure of multivalent cationic adsorbates.

It seems that there are some relationships between the zeta potential value of surface-adsorbed silica plates and the molecular structure of cationic adsorbates. We further investigated adsorption behaviors of polystyrene latex particles with a negative charge onto the three kinds of silica substrates adsorbing 1-3 which exhibited different positive zeta potentials, in order to comprehend the correlation of substrate zeta potentials with adsorption ability of the oppositely charged particles. The silica substrates after the surface adsorption of multivalent cationic adsorbates were immersed for 90 seconds in a neutral aqueous dispersion containing fluorescent carboxyl-modified polystyrene particles (*d* 200 nm) with a negative zeta potential of -36 ± 2 mV at pH 7. After multiple rinses with deionized water thoroughly and dried by N₂ gas, the silica substrates were observed with a fluorescent microscope.

Figure 2 shows fluorescent microscope images of the silica substrates after the immersion in the particle suspension.

Table 1 ζ-potentials (mV) of silica and PET substrates before and after immersion in solutions containing 1-3.

	Cleaned substrate ¹	1	2	3
Silica	-73 ± 5	+6 ± 1	+35 ± 5	+40 ± 13
PET	-80 ± 13	+6 ± 1	+32 ± 13	+35 ± 7

1: Silica and PET substrates cleaned by the UV treatment.

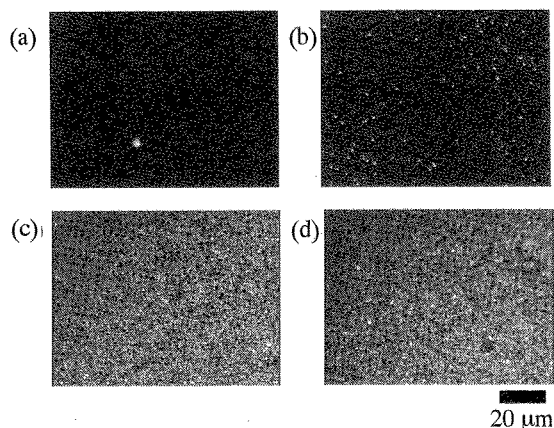


Figure 2. Fluorescent microscope images of polystyrene particles (d 200 nm) adsorbed on (a) a cleaned silica substrate and silica substrates forming an adsorbed layer of (b) **1**, (c) **2** and (d) **3**.

Particle adsorption was not observed for the cleaned silica substrate at all (Figure 2a) and hardly observed for the silica substrate adsorbing tetrapyrindinium **1** (Figure 2b). On the other hand, a lot of polystyrene particles were densely adsorbed on the silica substrates adsorbing cationic cyclopentasilane **2** and polysilane **3** as indicated in Figure 2c and 2d, respectively. The adsorption behaviors of negatively charged polystyrene particles on the substrate surfaces were clearly related to surface charges measured by the zeta potential studies. The cleaned silica substrate shows a large negative zeta potential due to dissociation of surface silanol groups at neutral pH 7. This situation causes electrostatic repulsion between surfaces of silica and polystyrene particles with a negative charge, to prevent the polystyrene particles from being adsorbed on the silica surface. In the case of tetrapyrindinium **1**, the silica substrate has a zeta potential of about zero, so that the particles are hardly adsorbed because of weak electrostatic interaction. On the contrary, the adsorbed layers formed by cationic cyclopentasilane **2** and polysilane **3** exhibit such large positive zeta potentials of approximately +40 mV that electrostatic attraction between surfaces of the adsorbed layer and the particle is induced, to result in a lot of particle adsorption, until the surface positive charge is neutralized. Consequently, we found that the silica substrates adsorbing the multivalent cationic adsorbates provided different surface zeta potentials depending on their chemical structures, even when the adsorbed monolayers were formed similarly on a silica plate. The resulting surface charges had influence on the adsorption ability of latex particles.

3.2 Adsorbed monolayer formation on PET substrates

The adsorbed monolayer exhibiting desorption-resistance on a silica surface could be formed from the multivalent cationic adsorbates **1-3** with more than four cationic pyridinium and ammonium units through multi-point electrostatic interaction [3, 4]. It is anticipated that an adsorbed single-layer will be formed similarly on negatively charged substrate surfaces in addition to a silica surface, because the adsorbed layer formation is mainly based on electrostatic interactions between a substrate surface and adsorbate molecules. We chose a polyethylene terephthalate (PET) substrate as a flexible, light-weight, and inexpensive polymer film. This is because the PET films are utilized in the many industrial fields such as printing materials, electrical

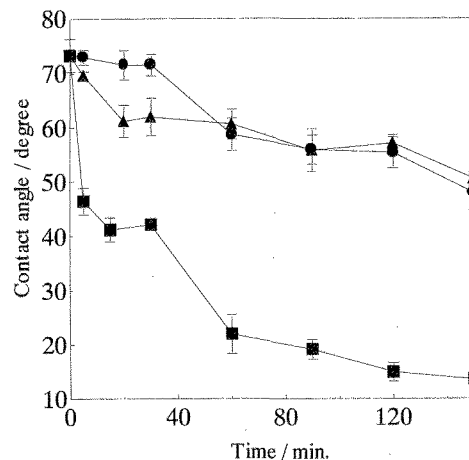


Figure 3. Water contact angles of PET substrates after (■) the UV treatment, (●) the acid treatment, and (▲) the alkali treatment.

products, and food packages. In this section, we investigated the formation of adsorbed layers on a PET substrate. At first, we researched how to prepare a cleaned PET substrate with a negative charge by contact angle and zeta potential measurements. Then, the adsorbed layer formation was investigated through zeta potential studies because it was difficult to investigate the layer formation by UV-visible spectroscopy due to no transmittance of PET films in a UV region.

It is generally known that a PET substrate surface is cleaned by three methods of UV-treatment, acid-treatment, and alkali-treatment. Figure 3 shows the changes of water contact angles on PET substrates as a function of each treatment time. A PET surface became hydrophilic until approximately 50° after the treatment with strong acid and alkali solutions for 2 h, while the most hydrophilic PET surface showing a water contact angle about 15° was obtainable after the UV-treatment for a shorter time. The zeta potential measurements at pH 7 revealed that the largest negatively charged PET surface with a zeta potential value of -80 ± 13 mV could be prepared by the UV-treatment for 2 h, and the PET surfaces after the treatments with acid and alkali for 2 h exhibited zeta potentials of -47 ± 8 mV and -49 ± 11 mV, respectively. We found that the hydrophilicity expressed by a water contact angle has a good relationship to a negative value of zeta potential. In the UV-treatment using a low-pressure Hg lamp, photodegradation of ozone (O_3) occurred, to form active atomic oxygen, which attacks hydrocarbons located at a PET surface. The photochemical events cause the formation of carboxyl and hydroxyl groups showing negative charges in neutral water [9].

The adsorption of multivalent cationic adsorbates **1-3** on the negatively charged PET surface prepared by the UV treatment for 2 h was carried out in the same manner as a silica substrate. As seen in Table 1, the zeta potential values observed for the PET substrates after the surface adsorption were well consistent with those for the silica substrates. Moreover, the adsorption behaviors of carboxyl-modified particles to the PET surfaces were almost same when the silica surfaces were used (data not shown). These results clearly indicate that the multivalent cationic adsorbates **1-3** formed an adsorption monolayer on the cleaned PET substrate as well as on the silica substrate.

3.3 Relationship of zeta potential to molecular structure of multivalent cationic adsorbates

The zeta potential values of substrates adsorbing **1-3** were obviously dependent on the kinds of cationic compounds, even when different substrates of silica and PET were used. We noticed that the three kinds of adsorbates **1-3** have each different feature in their molecular structures, when their CPK models are made. The multivalent cationic adsorbates are classifiable to a rod-like low-molecular-weight compound for **1**, a ball-like medium-molecular-weight compound for **2**, and a random-coiled macromolecule for **3**. To form an adsorbed monolayer on negatively charged substrate surfaces, cationic substrate-adsorption sites are required for the molecular structures of adsorbates. In order for the negatively charged particles to be adsorbed on the organic monolayer, particle-adsorption sites are furthermore required except for the substrate-adsorption sites, even after the molecules are adsorbed.

Considering that positive zeta potential values mean the existence of particle-adsorption sites not neutralized electrostatically, it is anticipated that all of four cationic pyridinium units included in tetrapyrindinium **1** are used as substrate-adsorption sites, as illustrated in Figure 4a, because the substrates after the adsorption of **1** have a zeta potential of approximately zero. In a flat-laid adsorption manner of the rod-like molecule **1**, negatively charged particles cannot be adsorbed on the substrate surface at any longer, for lack of particle-adsorption sites. The cyclic compound **2** possessing about nine pyridinium units in upper and lower rims of its cyclopentasilane ring forms a densely packed monolayer on substrate surfaces, where the pyridinium units were separated into substrate-adsorption-sites and particle-adsorption sites, as illustrated in Figure 4b, as a result of the ball-like molecular structure of **2**. In the case of the cationic polysilane **3**, the random-coiled macromolecules form an adsorption monolayer, as indicated in Figure 4c, so that many particle-adsorption sites are remained. In these adsorption manners of the ball-like molecule **2** and the random-coiled macromolecule **3**, zeta potential values of the substrates adsorbing **2** and **3** will become positive, and the assembly of negatively charged particles on the substrates will be promoted. The discussion on the adsorption manners of the multivalent cationic adsorbates **1-3** is supported by the zeta potential and particle adsorption studies as described above. Accordingly, we lead to a conclusion that we must consider the substrate-adsorption sites and the particle-adsorption sites for adsorbate molecules and polymers, when such multivalent cationic adsorbates are designed and used to form an adsorbed monolayer on a substrate surface.

4 CONCLUSION

We disclosed the zeta potential values of silica and PET substrates adsorbing the multivalent cationic adsorbates **1-3** with a different feature in their molecular structures. The adsorbates having more than four cationic pyridinium and ammonium units formed a stable adsorbed monolayer on a PET surface as well as a silica surface. It was suggested that the rod-like molecule **1** was adsorbed on the substrate surface in a flat-laid adsorption manner, which differed from the ball-like molecule **2** and the random-coiled macromolecule **3**. In the flat-laid adsorption manner, the zeta potential value of the substrate reached to zero because of neutralization of surface charges, causing a suppressive effect on the surface adsorption of colloidal particles. Accordingly, we will be able to control

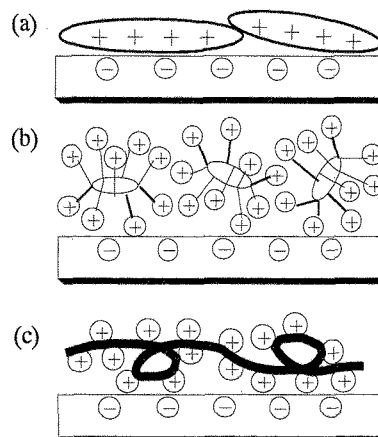


Figure 4. Illustration of adsorption manners of adsorbates of (a) **1**, (b) **2**, and (c) **3** on silica and PET substrates.

the surface charges on demand by changing chemical structures, orientations, and adsorption manners of multivalent cationic adsorbates through photochemical events.

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(Received December 21, 2002; Accepted April 28, 2003)