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Photopattern Shapes of a Photodegradable Polyelectrolyte Monolayer Affected by an Ionic Strength of Aqueous Developer Solutions

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We describe the positive-type photopatterning method of an adsorbed monolayer formed from a new photodegradable macromolecular adsorbate of a Si-based cationic polyelectrolyte. The adsorption controllability of positively charged amino-modified polystyrene spheres by the photopatterned monolayer was investigated by fluorescence microscopy. It was revealed that a line width of sphere-adsorbed regions was larger than that of a used photomask, as the concentration of KOH in an aqueous developer solution was increased. This result indicated that the photopatterned adsorbed monolayer of the cationic flexible polysilane was shrunk on a substrate surface under a high ionic strength of the aqueous developer solution.

Key words: adsorbed monolayer, photochemistry, polysilane, zeta-potential, particle adsorption, ionic strength

1. INTRODUCTION

Patterned monomolecular surfaces to promote and resist tiny functional inorganic, organic and metallic materials have been increasing interests in nano device fabrication [1]. Self-assembled monolayers derived from organosilanes on silica and organothiols on silver and gold are widely accepted to fabricate patterned monomolecular surfaces due to their chemical stability. The patterned monomolecular surface to control surface properties is fabricated mainly by photolithography, soft-lithography (micro contact printing), and scanning probe microscope lithography. The photolithography using UV light is underutilized among these patterning methods, although reliable mass production of tailor-made photopatterned surfaces is possible. This situation probably arises from use of expensive light sources and organic solvents, unavailability of monolayer-forming molecules, and limitation of substrate choice for the monolayer preparation. To overcome these drawbacks, sophisticated photopatternable monomolecular layers should be formed from readily obtainable monolayer-forming molecules and should be compatible with a wider variety of substrates, milder solvents, and UV wavelengths available from inexpensive low-pressure Hg lamps.

We notice photoreactive ionic molecules and macromolecules with plural adsorption sites as monolayer-forming materials other than organosilanes and organothiols, due to their solubility and stability in environment-friendly water media and substrate variety. We reported the negative-type photopatterning method using an electrostatically adsorbed monolayer formed from a tetracation possessing two [2+2] photodimerizable 1,2-bis(4-benzylpyridinio)ethylene moieties [2]. The tetracationic molecule adsorbed by a negatively charged silica surface increases the number of adsorption sites per molecule by increasing the molecular weight arising from the photodimerization. As a result, the adsorption stability of the UV-exposed cationic molecule is markedly enhanced toward a NaCl-containing aqueous solution. Based on the principle, we successfully prepare the photopatterned adsorbed monolayer on a silica surface by imagewise UV exposure, followed by site-selective desorption of the unexposed tetracationic adsorbate with a NaCl-containing aqueous solution.

We have recently reported the positive-type photopatterning method using an adsorbed monolayer formed from a photodegradable multivalent cationic molecule as an opposite way [3]. The photodegradable multivalent cationic molecule of a chloromethylated decacyclopentasilane derivative quaternized with pyridine is adsorbed by silica and polyethylene terephthalate (PET) surfaces. The roles of the cationic pyridinium groups in the adsorbed monolayer separate into adsorption sites tethered to a negatively charged surface and adsorption-free sites to promote surface adsorption of negatively charged polystyrene spheres, due to its ball-like molecular structure. It is found that the adsorbed monolayer exhibiting a positive zeta-potential value is changed to an almost bare substrate surface exhibiting a negative zeta-potential value by UV exposure to cause degradation of the cyclopentasilane moiety and multiple rinses with deionized water to promote desoption of the UV-exposed adsorbate. The photoinduced polar transition of substrate surfaces enable us to prepare adhesive templates for site-selective surface adsorption of carboxy- and amino-modified polystyrene spheres charged with negative and positive sign, respectively.

In this paper, we investigated the positive-type photopatterning method using a new photodegradable Si-based cationic polymer adsorbate (Figure 1) and the controllability of sphere adsorption as an adhesive template. Polystyrene spheres showing a positive charge were adsorbed preferentially on UV-exposed areas in accordance with the adsorbate monolayer photopattern. During this study, we found that a line width of sphere-adsorbed regions was affected by an ionic strength of an aqueous solution to promote desorption of UV-exposed adsorbates. This result indicated that the shrinkage of the photopatterned

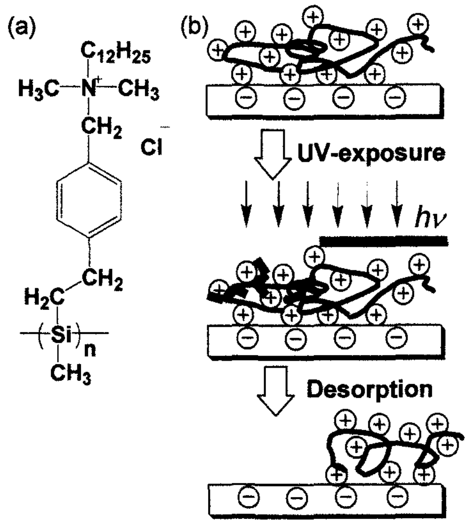

Figure 1. (a) Chemical structure of a photodegradable cationic polysilane and (b) a positive-type photopatterning method of an adsorbed polyelectrolyte monolayer on a substrate surface.

adsorbed monolayer formed from the Si-based cationic polymer adsorbate on a PET surface was brought about under a high ionic strength of the aqueous developer solution.

2. EXPERIMENT

2-1. Materials

A photodegradable Si-based cationic polyelectrolyte, poly[1-(2-(4-(N-dodecyl-N,N-dimethylazoniamethyl)-phenyl)ethyl)-1-methylsilane] [4], indicated in Figure 1a was used as a multivalent cationic macromolecular adsorbate in this study. Deionized water with resistivity of 18.0 MΩ·cm was prepared by a Milli-Q system and used throughout. Amino-modified fluorescent polystyrene spheres of 200 nm in diameter (Fluosphere F-8761) were purchased from Molecular Probe, Inc.

2-2. Preparation and photopatterning of polyelectrolyte adsorbed monolayer

A polyethylene terephthalate (PET) substrate (10 x 30 x 0.2 mm) was cleaned by a UV ozone cleaner (Nippon Laser Electronics Lab.) for 2 h. The cleaned substrate was immersed in a 1 wt% ethanol solution containing the cationic Si-based polyelectrolyte for 10 min, followed by multiple rinses with deionized water and drying by N_2 gas, to give an adsorbed monolayer of the cationic polysilane. The monolayer formation on a PET substrate was confirmed by zeta-potential measurement [3, 5]. The adsorbed monolayer on the PET plate was exposed through a photomask to UV light emitting from a 200-W Hg-Xe lamp (San-ei, Electric, Super Cure 202S), whose exposure dose of 0.1 J cm^{-2} was monitored at 254 nm. The imagewise exposed monolayer was treated with KOH aqueous solutions with various concentrations in range of 0.05 – 0.3 wt% for 60 s. After multiple rinses with deionized water and N_2-drying, a photopatterned monolayer was obtained.

2-3. Polystyrene sphere adsorption onto photopatterned monolayer

An acidic aqueous solution of pH 2 was prepared by addition of a dilute HCl solution. A dispersion of amino-modified fluorescent polystyrene spheres in water was diluted with the pH 2 aqueous solution, until a 0.4 wt% sphere-dispersion was obtained. A photopatterned monolayer on a PET plate was immersed in the sphere dispersion for 90 s, followed by rinses with deionized water and N_2-drying. Fluorescent spheres on the substrate were observed by fluorescent microscopy (Olympus, BX60) and low-vacuum scanning electron microscopy (Hitachi, S-3000N) without conductive metal coating.

3. RESULTS AND DISCUSSION

3-1. Photopatterning of adsorbed polyelectrolyte monolayer

Cationic polyelectrolytes possessing plural adsorption sites such as quaternary ammonium and pyridinium groups are adsorbed by a negatively charged substrate surface such as a silica plate, a surface-oxidized silicon wafer, and polymer plates through electrostatic interaction [6]. The cationic polymers adsorbed by the substrate surface in a multi-point adsorption manner exhibit high desorption resistance toward deionized water. We noticed the Si-based amphiphilic polymer with plural ammonium groups [4], indicated in part a of Figure 1, as a photodegradable multivalent cationic adsorbate on account of the following. Poly(alkylsilane)s are used as photodegradable positive-type photopolymers [7]. Accordingly, it is anticipated that the Si-Si main-chain included in the amphiphilic polymer is degraded by UV light through Si-Si bond cleavage into small-molecular-weight photoproducts, until the photoproducts can not absorb the actinic UV light [7]. The fragmentation to small molecular species will cause to lower adsorption stability of the photoproducts as a result of a decrease of adsorption sites per molecule, leading to desorption of the photoproducts from a substrate surface [3].

A UV/O_3-cleaned hydrophilic PET substrate exhibiting a negative zeta-potential value of -80 ± 13 mV at pH 7 and a contact angle of 15.5 ± 3 ° for water [3, 5] was immersed in an ethanol solution containing the photodegradable cationic polymer adsorbate. After the immersion, the hydrophilic PET surface turned to a hydrophobic surface with a contact angle of 80 ± 1°, which exhibited a positive zeta-potential value of +35 ± 7 mV. The change in surface properties of contact angle and zeta-potential indicated that an adsorbed monolayer of the photodegradable cationic polymer was formed on the negatively charged PET substrate surface.

The adsorbed monolayer of the cationic polymer on a PET plate was subjected to imagewise irradiation with UV light through a photomask. Taking into account that the Si-based cationic polymer on a silica plate showed an absorption band centered at 290 nm, it was anticipated that UV light at a wavelength of 254 nm generated from a Hg-Xe lamp caused a photochemical event. The imagewise UV-exposed monolayer on a PET was rinsed with an aqueous solution of 0.1 wt% KOH and dried by N_2 gas. To investigate the formation of a monolayer photopattern on a PET plate, we adopted a condensation figure method indicating surface heterogeneity of hydrophobicity and hydrophilicity reported by Whitesides et al. [8].

When water vapor was condensed on the PET plate, latent monolayered images in accordance with a shape of the used photomask emerged obviously. More water droplets were condensed on hydrophilic UV-exposed areas than hydrophobic unexposed areas. It was worthy to note that an exposure energy required to form the condensation figures was 0.1 J cm^{-2} at 254 nm, which was much smaller than that 10 J cm^{-2} in the case of an adsorbed monolayer formed from a multivalent cationic adsorbate of a decaphenylcyclopentasilane derivative possessing pyridnium groups reported in our recent paper [3]. This result implied that a chain-like Si skeleton included in the cationic polymer used in this study might be more readily degradable by UV light at 254 nm than a cyclic Si skeleton of the cationic decaphenylcyclopentasilane derivative. From the observation by the condensation figure method, it was anticipated that a hydrophobic photopatterned adsorbed monolayer of the photodegradable cationic polymer was formed on unexposed areas of the PET surface as illustrated in part b of Figure 1.

3-2. Site-selective adsorption of positively charged polystyrene spheres on photopatterned adsorbed monolayer.

Recently, we have reported that a positively charged adsorbed monolayer formed from a multivalent cationic molecule possessing plural quaternary pyridinium groups turns to a negatively charged substrate surface by photodegradation of the adsorbate and subsequent desorption from silica and PET substrate surfaces [3]. To confirm photoinduced polar transition of substrate surfaces achieved by the photodegradable multivalent cationic molecule, we investigated the photochemical event using the adsorbed monolayer formed from the Si-based amphiphilic polymer as another case.

We used commercially available fluorescent amino-modified polystyrene spheres of 200 nm in diameter as positively charged materials, to investigate a surface charge profile of the photopatterned adsorbed monolayer. The photopatterned adsorbed monolayer of the Si-based cationic polymer on a PET plate was immersed in an aqueous dispersion of pH 2 containing the fluorescent amino-modified spheres showing a positive zeta-potential value of +53 $\pm$ 1 mV. Fluorescent spheres adsorbed by the substrate were observed by fluorescence microscopy. Parts a and b of Figure 2 indicate the optical microscopy image of a used photomask with 5 μm lines and the fluorescence microscopy image of the polystyrene spheres adsorbed by the substrate, respectively. It was found that the positively charged amino-modified polystyrene spheres were preferentially adsorbed by the UV-exposed surface as illustrated in part c of Figure 2. The site-selective surface adsorption of the positively charged spheres presumably arises from electrostatic repulsion by a positively charged cationic polymer layer in the unexposed areas and electrostatic attraction by a negatively charged bare PET substrate surface as described in our recent paper [3]. It was addressed here that a line width of sphere-adsorbed regions indicated in Figure 2b was somewhat larger than a line width of the photomask indicated in Figure 2a.

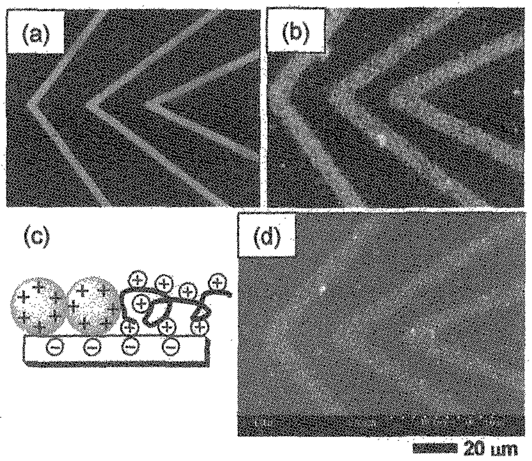

Figure 2. (a) Optical microscope image of a photomask, (b) fluorescence microscopy and (d) scanning electron microscopy images of polystyrene spheres (*d* 200 nm) adsorbed by the photopatterned polyelectrolyte monolayer, and (c) illustration of sphere adsorption on the photopatterned monolayer.

To observe directly the spheres on the PET substrate, we used low-vacuum scanning electron microscopy (LV-SEM). In the LV-SEM, electron charging-up disturbing SEM observation can be avoided even in the case of samples without conductive metal-coating. The result of LV-SEM observation was indicated in part d of Figure 2. It was found that the fluorescence microscopy image of the spheres (Figure 2b) was almost identical to the LV-SEM image (Figure 2d). This result clearly implies that the photopattern shape of the adsorbed polyelectrolyte monolayer was changed during the monolayer photopattern preparation.

3-3. Photopattern shape of polyelectrolyte monolayer affected by ionic strength of aqueous developer solutions.

It has been reported that conformation of polyelectrolytes adsorbed on a colloidal silica sphere, a polystyrene sphere, and a mica substrate is varied under a high ionic strength of their aqueous dispersion [9]. Hammond et al. have reported that the thickness and roughness of a polyelectrolyte single-layer in patterned multilayered films prepared by a layer-by-layer deposition technique are altered by ionic strengths of a polyelectrolyte-containing solution with an additive salt during multilayered film fabrication [10]. Taking the facts into consideration, it is anticipated that hydrophobic interaction in an aqueous solution of a high ionic strength is increased to cause some conformational change of the flexible Si-based cationic polymer possessing hydrophobic long-chain dodecyl groups.

To investigate the effect of an ionic strength on the monolayer pattern shape on the PET surface, we prepared four photopatterned monolayers of the Si-based cationic polymer by rinses with an aqueous KOH solution with a different concentration of 0.05, 0.1, 0.2 and 0.3 wt% KOH, and subsequently fluorescent

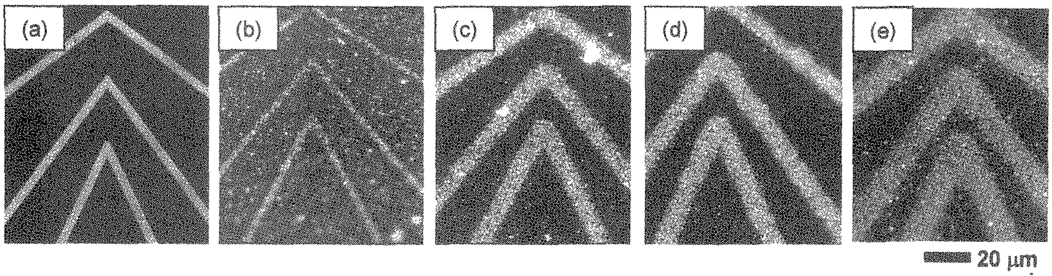

Figure 3. (a) Optical microscope image of a photomask and (b) fluorescence microscope images of polystyrene spheres adsorbed on the photopatterned polyelectrolyte monolayer by immersion in aqueous KOH solutions of (b) 0.05, (c) 0.1, (d) 0.2 and (e) 0.3 wt%.

amino-modified polystyrene spheres were adsorbed at pH 2 on each PET surface having the photopatterned monolayer. The KOH concentrations of 0.05, 0.1, 0.2 and 0.3 wt% correspond to ionic strengths of 0.0089, 0.018, 0.036 and 0.053, respectively. Part a of Figure 3 indicates the optical microscopy image of a used photomask. The other parts of Figure 3 indicate the fluorescence microscopy images of surface-adsorbed amino-modified polystyrene spheres, with results for 0.05, 0.1, 0.2 and 0.3 wt% KOH solutions shown in part b, c, d and e of Figure 3, respectively.

In all cases, the amino-modified spheres with a positive charge were preferably adsorbed on UV-exposed areas of the PET surface. When a 0.05 wt% KOH solution with an ionic strength of 0.0089 was used as a developer solution for the monolayer patterning, a line width of adsorbed spheres was almost identical to a line width of the used photomask. As the ionic strength of aqueous developer solutions was increased, a line width of sphere-adsorbed regions was larger. It was obvious from the fluorescence microscopy observation that the line width of sphere-adsorbed regions was affected by the ionic strength of the developer solutions.

In general, a Si-Si backbone of poly(alkylsilane)s showing thermochromism is flexible [7]. The Si-based cationic polymer (Figure 1a) used in this study possesses hydrophobic long-chain dodecyl groups. Taking the facts into consideration, it is anticipated that the photopatterned adsorbed monolayer of the Si-based cationic polymer remained in unexposed areas is shrunk during the rinse treatment with an aqueous developer solution containing KOH. As a result, the UV-exposed area to promote surface adsorption of the positively charged amino-modified spheres might be enlarged as illustrated in Figure 4. The shrinkage of the photopatterned adsorbed monolayer formed from the cationic polyelectrolyte is under investigation by direct observation using atomic force microscopy.

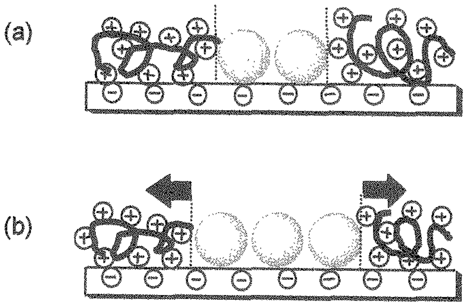

Figure 4. Illustration of adsorption behaviors of polystyrene spheres on the monolayer photopattern after immersion in an aqueous solution of (a) low and (b) high ionic strengths.

4. CONCLUSION

We described the positive-type photopatterning of an adsorbed monolayer formed from a photodegradable Si-based cationic polymer on a PET substrate and the site-selective adsorption of positively charged polystyrene spheres on the photopatterned adsorbed monolayer. It was found that the UV-exposed area to promote the sphere adsorption was enlarged as an increase in the concentration of KOH in the aqueous developer solutions. It is considered that the enlargement of sphere-adsorbing area is as a result of shrinkage of the adsorbed monolayer pattern under a high ionic strength of the developer solution.

5. REFERENCES

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