

## Polysilane–Silica Hybrid Nanoparticles

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**ABSTRACT:** Polysilane–silica hybrid nanoparticles were prepared by chemical attachment of polysilane–poly(methacrylic acid) block copolymer onto aminopropyl-modified silica particles. [DOI 10.1295/polymj.37.1]

**KEY WORDS** Polysilane / Block Copolymer / Silica / Composite / Cross-linking /

Organic–inorganic hybrid materials have attracted interest in the last decade because of potential applications in nonlinear optics and mechanically reinforced lightweight components.<sup>1–3</sup> These hybrid materials also show great promise, as they can provide the necessary stability and processability for these important applications. Many approaches to the synthesis of hybrid materials have been reported. For example, a sol–gel method is one of the most efficient methods.<sup>5–7</sup> Another method is *in situ* polymerization in the presence of silica and the graft polymerization from or onto the silica to produce hybrid materials.<sup>8,9</sup> The layer-by-layer method may also be applied to the synthesis of hybrid materials.<sup>10</sup> Silica plates or silica particles with micro- or nanometer dimensions were usually employed as the template for the synthesis of the hybrid materials, because silica with a variety of sizes is commercially available and it is easy to functionalize the surface.

Recently, we have succeeded in synthesizing poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(methacrylic acid) by a sequential anionic polymerization of masked disilenes,<sup>11</sup> and in constructing unique nano-architectures based on self-assembly of the block copolymer.<sup>12</sup> The block copolymer has reactive carboxylic acid groups on the PMAA block, and hence cross-linking of the polymer is possible. The cross-linking reaction with the block copolymer and silica nanoparticles could provide polysilane–silica composite nanoparticles. Polysilanes have attracted considerable interest in the past few decades because of their interesting electronic and photophysical properties and potential applications in the field of materials.<sup>13</sup> The unusual properties of polysilanes are attributable to  $\sigma$ -conjugation along the main chain, and hence they are extremely sensitive to the polymer conformation. Manipulation of the structure and composition of macromolecules at the nanometer level provides new possibilities for the application of nanomaterials.<sup>14</sup>

We report in this paper the synthesis of polysilane–silica hybrid nanoparticles using a chemical attachment of the polysilane–poly(methacrylic acid) block copolymer to the surface of silica particles. The hybrid nanoparticles may find interesting applications as opto-electronics materials because of the unique structural features of the nanoparticles and chemical durability of polysilane.<sup>15</sup>

### EXPERIMENTAL

#### *Apparatus*

<sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra were recorded on a Bruker DPX 300 FT NMR spectrometer at frequencies of 300, 75.4, and 59.6 MHz, respectively. The <sup>1</sup>H and <sup>13</sup>C chemical shifts were measured relative to residual CHCl<sub>3</sub>. The <sup>29</sup>Si chemical shift was referenced to an external Me<sub>4</sub>Si (0 ppm) standard. The GLC data were recorded on a Shimadzu GC-8A chromatograph. The molecular weight distributions of the polymers were measured using a Shimadzu LC 10 HPLC equipped with PL-gel mixed-C columns, and calibrated using polystyrene standards with THF as the eluent. Dynamic light scattering (DLS) was performed using an Otsuka Electronics DLS-700. IR spectra were measured on a Horiba FT-IR 720. UV spectra were recorded on a HP Agilent 8453 spectrometer. Atomic force microscopy (AFM) was performed using a Digital Instruments Nano Scope III.

#### *Materials*

All solvents were dried using standard procedures. THF, diethyl ether, and toluene were dried and distilled from a sodium/benzophenone mix just before their use. Trimethylsilyl methacrylate was purchased from Aldrich and distilled from calcium hydride just before use. Tetraethoxysilane (TEOS), 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride and aminopropyltrimethoxysilane were purchased from Wako

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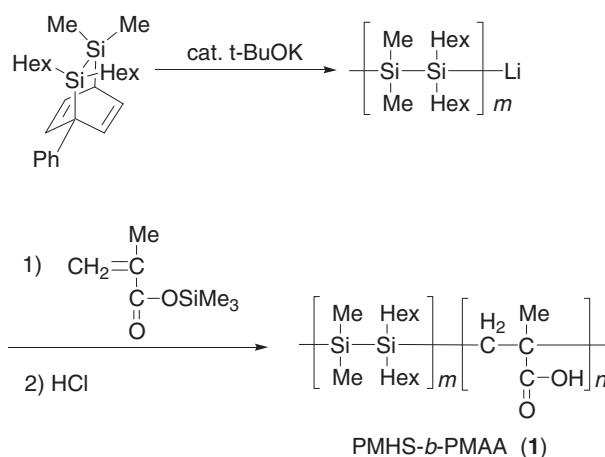
Chemicals and used as received. THF and H<sub>2</sub>O used for the spectroscopic measurements were of commercial UV spectral grade, and were used without further purification.

*Preparation of 1-Phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (masked disilene).* 1-Phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was synthesized as described previously.<sup>16</sup> Reaction of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane with lithium biphenylide in THF at -78 °C gave the masked disilene in 62% yield. The monomer was purified by distillation and subsequently used for the polymerization.

*Synthesis of Poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(methacrylic acid), 1.* All reactions were performed under an atmosphere of argon. A THF solution of potassium *t*-butoxide (5 mol %) was added to 1-phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (masked disilene, 2.3 g, 5.6 mmol) and THF (20 mL) at room temperature. After the mixture was stirred for 20 min, trimethylsilyl methacrylate (90 mg, 0.56 mmol) was added to the reaction mixture at room temperature. The mixture was stirred for 90 min and then a few drops of 1.5 M HCl solution were added to the mixture. After removal of the solvent, fractional precipitation followed by drying *in vacuo* gave polymer **1** as a white powder (220 mg, 12%). The molecular weight was estimated by GPC with a methyl-esterified copolymer prepared from the reaction the obtained copolymer with trimethylsilyldiazometane.  $M_n = 1.6 \times 10^4$ ,  $M_w/M_n = 1.21$  (polystyrene standards, THF as eluent); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz,  $\delta$ ) 0.05–0.30 (br, -SiMe<sub>2</sub>), 0.74–1.31 (br, -SiHex<sub>2</sub>, C-Me), 1.79 (brs, -CH<sub>2</sub>-C).

*Synthesis of Aminopropyl-modified Silica Particles.* A mixture of silica (150 mg), prepared by TEOS with 28 wt % aqueous ammonia,<sup>17</sup> and 5 wt % aminopropyltrimethoxysilane in toluene was heated under reflux for 24 h. The mixture was cooled to room temperature and evaporated to give the aminopropyl-modified silica particles as a white powder (130 mg). IR (KBr) 3541, 3425, 2344, 1928, 1595, 1473, 1089, 795 cm<sup>-1</sup>; DLS 167 nm (0.2 g L<sup>-1</sup>, in THF, 25 °C, Ar 488 nm).

*Preparation of Polysilane–Silica Hybrid Particles 2.* A mixture of **1** (9.9 mg, 6.3 × 10<sup>-4</sup> mmol), **2** (15 mg), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (1.8 × 10<sup>-2</sup> mg, 9.4 × 10<sup>-5</sup> mmol) in dichloromethane (15 mL) was heated under reflux for 24 h. The mixture was cooled to room temperature and evaporated to give **2** as a white powder (14 mg). IR (KBr); 3361, 1744, 1645, 1512, 1099 cm<sup>-1</sup>; <sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 300 MHz,  $\delta$ ) 0.2–0.4 (br, -SiMe<sub>2</sub>), 0.9–1.4 (br, -SiHex<sub>2</sub>); UV (THF)  $\lambda_{\max}$  310 nm (0.2 g L<sup>-1</sup>).



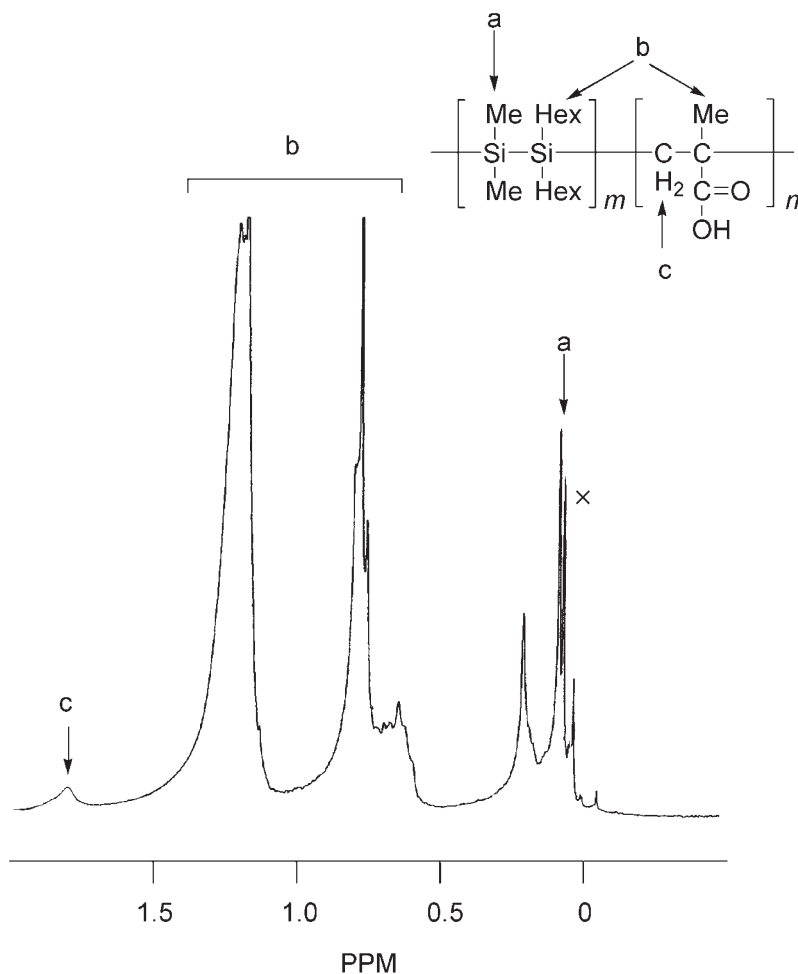
**Scheme 1.**

## RESULTS AND DISCUSSION

Poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(methacrylic acid) (PMHS-*b*-PMAA, **1**) was prepared by the sequential anionic polymerization of the masked disilene and trimethylsilyl methacrylate, followed by hydrolysis of the trimethylsilyl protecting group (Scheme 1).<sup>11</sup> The molecular weight and structure of the block copolymer were determined using GPC and NMR spectroscopy. The obtained polymer was converted to methyl-esterified copolymer by the reaction with trimethylsilyldiazometane and the molecular weight of the polymer was estimated by GPC calibrated with polystyrene standards with THF as eluent. The molecular weight of the block copolymer was 15 700 ( $M_n$ ,  $M_w/M_n = 1.20$ ). Figure 1 shows the NMR spectrum of the obtained block copolymer. In the spectrum, the signals of both PMAA and PMHS units were observed. The ratio of PMHS to PMAA, estimated by <sup>1</sup>H NMR in CDCl<sub>3</sub>, was 2:1. Because signals of the head-to-tail sequence were observed, but signals of the head-to-head sequence were almost not, as demonstrated in the <sup>13</sup>C and <sup>29</sup>Si NMR spectra, indicating that the PMHS block unit of the block copolymer has a highly regulated structure in relation to the repeating unit.<sup>17</sup>

The block copolymer is soluble in organic solvents such as hexane and THF, but not in water, because the block copolymer has a long sequence of PMHS units. In THF, the block copolymer was self-assembled to form polymer aggregates, with an intensity-averaged particle diameter of 210 nm in THF (0.2 g L<sup>-1</sup> at 25 °C) by DLS analysis. In the polymer aggregates, the PMHS block exists in a corona being exposed to THF, a good solvent for PMHS, while the PMAA block exists in a core (reverse polymer micelles).

Since the block copolymer has reactive carboxylic acid groups on the PMAA block, the cross-linking re-



**Figure 1.**  $^1\text{H}$  NMR spectrum of poly(1,1-dimethyl-2,2-dihexyldisilene)-*b*-poly(methacrylic acid) (PMHS-*b*-PMAA, **1**) in  $\text{CDCl}_3$ .

**Table I.** XPS analysis of aminopropyl-modified silica particle and polysilane–silica nanoparticle **2**

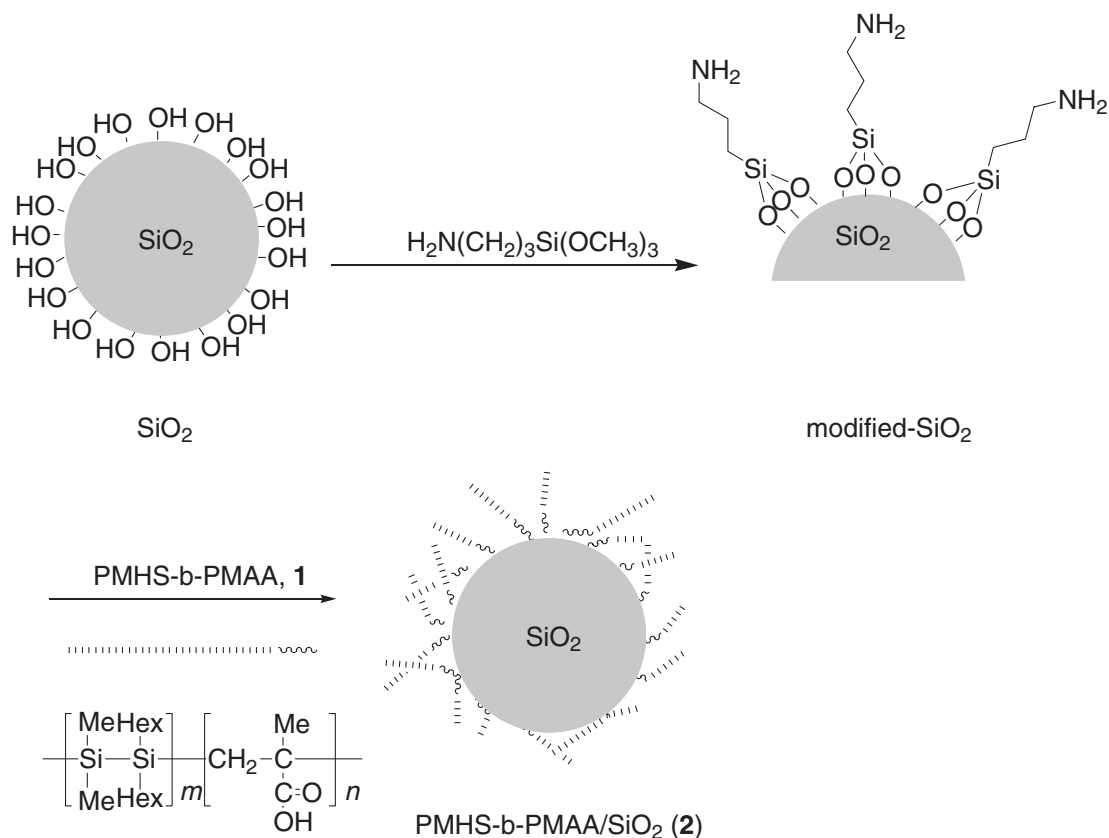
Sample	Atomic concentration (%)				
	C 1s	Si–O: Si(2p)	NH <sub>2</sub> : N(1s)	O(1s)	Si–Si: Si(2p)
Modified-SiO <sub>2</sub>	18.23	19.4	3.25	54.79	— <sup>a</sup>
PHMs- <i>b</i> -PMAA/SiO <sub>2</sub> ( <b>2</b> )	45.18	12.32	2.07	35.35	3.78

<sup>a</sup>Not observed.

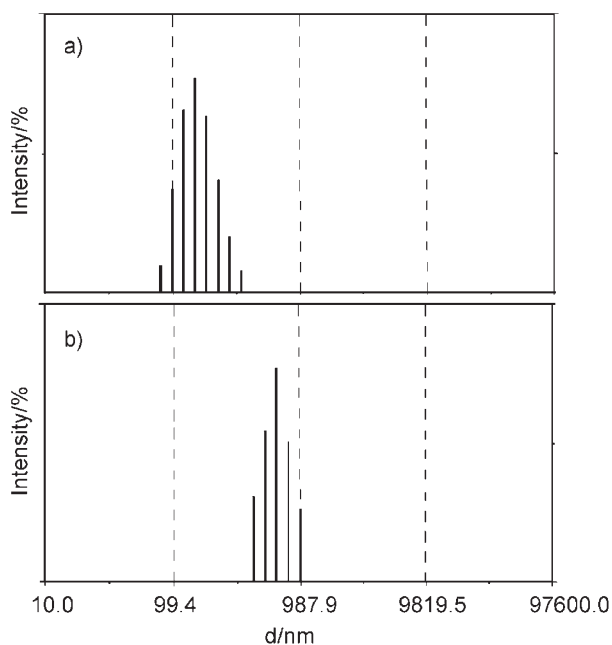
action of the polymer with an amino-activated surface of silica was examined, as shown in Figure 2. The modified silica was prepared by the reaction of silica particles with 3-aminopropyltrimethoxysilane.<sup>18</sup> The diameter of the silica particles was 160 nm as determined by DLS (Figure 3a). The surface-modified nanoparticles, thus prepared, were then used in a cross-linking reaction with the block copolymer. The cross-linking of the partial carboxylic acid on the PMAA block of **1** was achieved by reaction with the aminopropyl-modified silica and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride to give the polysilane–silica hybrid particles **2**. Spectroscopic studies demonstrated the formation of the polysilane–silica nanoparticles. In the  $^1\text{H}$  NMR spectrum of **2** in  $\text{THF-}d_8$ , signals of the hexyl and methyl groups on the

polysilane block were found, but no signal from the PMAA was observed, due to its colloidal nature. The IR spectrum of **2** showed absorption bands for the amide groups at 1645 and 1512  $\text{cm}^{-1}$  (Figure 4). In the XPS analysis, a peak of Si–Si ( $\text{Si}_{2p}$ ) was observed for **2**, but not for the modified-SiO<sub>2</sub> and the percentage of the Si–O ( $\text{Si}_{2p}$ ) atomic ratio decreased. The N(1s) and O(1s) atomic ratio Si–O ( $\text{Si}_{2p}$ ) decreased to 64%. In the UV spectrum of **2** in THF, **2** shows an absorption maximum at 310 nm (Figure 5), indicating that the PMHS block takes a random-coil conformation.

A DLS study showed the average diameter of the polysilane–silica particles to be 660 nm and the size distribution was relatively broad (Figure 3b). The particle size was found to be larger than the expected

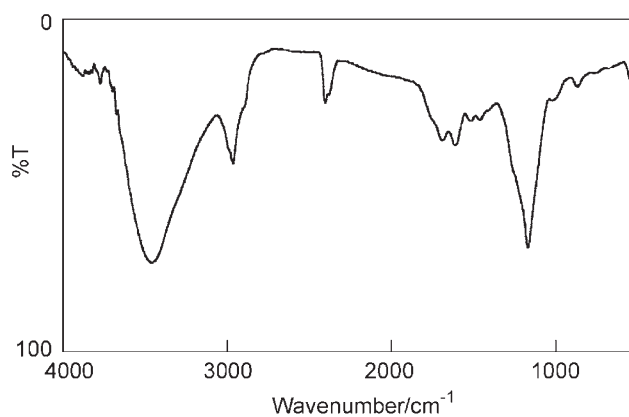


**Figure 2.** Schematic drawing of the synthetic pathway for polysilane-silica nanoparticles derived from polysilane-polymethacrylate block copolymers (PMHS-*b*-PMAA, **1**).



**Figure 3.** DLS analysis of (a) the aminopropyl-modified silica and (b) the polysilane-silica hybrid particles **2** in THF.

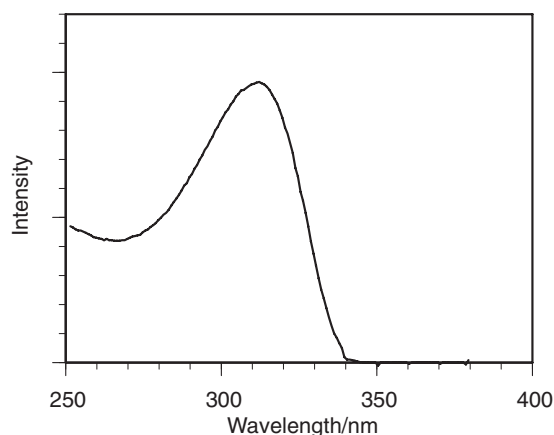
value, where the size of the modified silica was about 160 nm from the DLS analysis and the calculated size of the block copolymer **1** is 68 nm. This means the interparticle coupling reaction of **1** and the amino-



**Figure 4.** IR spectrum of the polysilane-silica hybrid particles **2** (KBr).

modified silica took place under this set of conditions. Further work to improve the reaction conditions is required.

An AFM image of the polysilane-silica particles **2** provided information on their size and shape. Samples for AFM measurement were prepared by placing a drop of **2** in water on the surface of either a hydrophobic or hydrophilic Pyrex glass plate, which was treated with hexamethyldisilazane or with water, respectively, and allowing it to dry in air. Figure 6 shows the AFM image of **2** on a Pyrex glass plate when operat-



**Figure 5.** UV absorption spectrum of the polysilane–silica hybrid particles **2** ( $0.2 \text{ g L}^{-1}$ , THF).

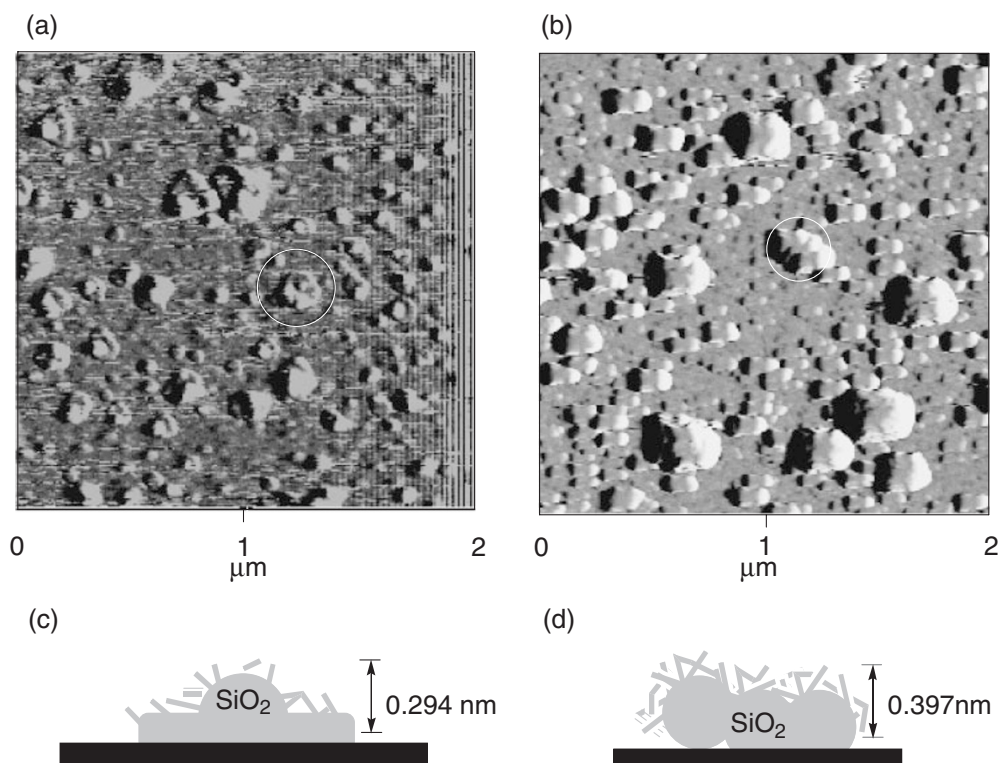
ing in the contact mode. **2** was observed as aggregated nanoparticles, confirming the DLS study. In addition, a considerable difference in morphology was observed in these images depending on the surface properties of the plates used.<sup>19,20</sup> On the hydrophobic plate, **2** was observed as particles with the spread PMHS blocks on the silica surface. A schematic vertical sectional view estimated from the AFM image is also shown in Figure 6c. On the hydrophilic plate, however, **2** was observed as a conglomerate consisting of a few particles, because the hydrophobic PMHS corona

eventually shrunk on the silica.

AFM analysis of the amphiphilic block copolymer on the  $\text{SiO}_2$  surface indicated that different morphologies were formed when located on the hydrophobic and hydrophilic plates, respectively. We speculated that the polymer was stretched out from the surface and each polymer chain is flexible enough to permit the conformational change. When the particle located on hydrophilic plate, the PMHS block would aggregate on the surface. Instead, when the particles located on hydrophobic plate, the PHMS block might spread on the top surface. The diverse morphologies of the block copolymer on the  $\text{SiO}_2$  induced by the surface properties of substrates and interchain interactions are interesting since opt or electro properties of polysilane usually depend on their conformation.<sup>13</sup> Further studies are currently in progress.

## CONCLUSIONS

We have synthesized polysilane–silica hybrid nanoparticles by integrating colloid and nanoparticle syntheses with a chemical attachment of the polysilane–poly(methacrylic acid) block copolymer to the surface of aminopropyl-modified silica particles. Because of the unique structural features of the nanoparticles, they may find interesting applications as opto-electronics materials.



**Figure 6.** AFM images of polysilanes attached to silica nanoparticle **2** on Pyrex glass with (a) hydrophobic treatment and (b) hydrophilic treatment ( $1.22 \text{ mg mL}^{-1}$  of a THF solution, AFM with contact mode). Schematic illustration of virtual profile of the AFM images of (c) the particles shown in (a) and (d) shown in (b). The values in the Figures were estimated from the AFM images.

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