

# **Synthesis of Polystyrene@Silica Particles through Soap-Free Emulsion Polymerization and Sol-Gel Reaction on Polymer Surfaces**

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## **Abstract**

Polystyrene@silica particles were produced through soap-free emulsion polymerization (SFEP) of styrene and *N*-vinylacetamide (NVA) via the sol-gel reactions of tetraethyl orthosilicate (TEOS) on polymer particle surfaces. Different amounts of NVA were used to prepare polystyrene particles using the SFEP process. The particles covered with poly-NVA then underwent the Stöber process to form an outer silica shell. NVA was found to stabilize the polymer colloids and improve their stability by steric effects, even after the positive charge on the polymer surface was partially neutralized by the electrostatically adsorbed TEOS, which tends to induce particle aggregation. Further, the –NH functional groups on NVA catalyzed the hydrolysis of TEOS in the sol-gel reaction to form silica. Consequently, small, monodisperse, and stable core-shell particles were formed despite having a low zeta potential.

*Keywords:* Polystyrene@Silica Particle; Colloidal Stability; Sol-Gel Reaction; Surface Reaction

## 1. Introduction

Polymer particles are applied in various fields on the basis of fundamental research [1-4]. Particularly, soap-free emulsion polymerization (SFEP) was researched eagerly to clarify the nucleation and growth processes of polymer particles because it is a simple system without a surfactant and organic solvent [3, 5-8]. Recently, hybrid composite particles with both inorganic and organic components have been synthesized and displayed novel functionalities [9, 10]. For example, polymer particles were used as a core to prepare core-shell particles [9, 11, 12]. Often, a silica shell is created over the polymer core particles [11, 13]. When the polymer cores are removed by chemical dissolution or heating, hollow silica particles are synthesized [14, 15]. Therefore, these polystyrene@silica particles were utilized as thermal insulators [16, 17].

Many designs of composite particles have focused on the interaction between organic materials and inorganic silica with negative charge, using cationic surfactants to modify the surface of the polymer core particles. However, some surfactants such as hexadecyltrimethylammonium bromide are detrimental to the environment [18-21]. Furthermore, the composite particulate materials synthesized through only electrostatic interactions between the polymer and silica would not be stable in terms of colloidal stability according to the DLVO theory [22].

In this study, a new method to synthesize polystyrene@silica particles was developed that only uses non-toxic chemical reagents. We found that cationic polystyrene with low molecular weight is toxic to the bacteria *Micrococcus luteus* (see Supporting Information). However, the toxicity could

be controlled by using *N*-vinylacetamide (NVA) monomer to form a non-toxic hydration layer around the polymer particles, which maintains good colloidal stability without coagulation according to the electrostatic theory [23]. In addition, NVA has –NH functional groups that catalyze the reaction of tetraethyl orthosilicate (TEOS), enabling in situ electrostatic adsorption of TEOS to form silica shells on the polymer particles [24]. Therefore, we polymerized styrene and NVA monomers using a cationic initiator to prepare polymer core particles through SFEP.

## **2. Experimental**

### *2.1. Materials*

The water used for polymerization was purified using a distillation system (Auto Still WG250, Yamato), and nitrogen gas was then bubbled into the water to remove any dissolved oxygen. After the styrene monomer (FUJIFILM Wako Pure Chemical Corporation.) was rinsed with 10 wt% sodium hydrate (NACALAI TESQUE, INC.) solution to remove any polymerization terminators, it was purified by vacuum distillation. To fabricate polyNVA (PNVA) layers around the polystyrene cores, NVA monomer (Showa Denko K.K.) was polymerized during the polymerization of styrene. NVA monomers were so amphiphilic that the emulsification of styrene monomers were occurred at the initial stage of the polymerization reaction. Therefore, NVA monomers were not in the bulk, but gave the reaction places for the polymerization to make the emulsions. PNVA also served as a catalyst in the synthesis of silica and as a stabilizer to maintain the colloidal stability of the synthesized polymer

particles. 2,2'-Azobis(2-methylpropionamidine)dihydrochloride (V-50, FUJIFILM Wako Pure Chemical Corporation.), a typical cationic initiator, was used as received to render the polymers positively charged. Sol-gel reactions of TEOS (NACALAI TESQUE, INC.) dissolved in 1-propanol (NACALAI TESQUE, INC.) was carried out to prepare the silica shell.

## 2.2. Reactions

The NVA polymerization reaction was performed in a reactor, which contained a magnetic stirrer equipped with a heater (RCH-20L, EYELA) to control the rotation speed of the impeller and the temperature. The quantities of chemicals used for the polymerization reaction are shown in **Table 1**. The reaction time was set as 6 h because previous studies showed that polymerization was generally completed within this time [25].

**Table 1.** Experimental conditions of the polymerization

| Water [g] | Styrene [g] | NVA [g] | V-50 [mg] | Reaction temperature [°C] | Rotational velocity of impeller [rpm] |
|-----------|-------------|---------|-----------|---------------------------|---------------------------------------|
| 15        | 0.5         | < 1.0   | 8.3       | 70                        | 130                                   |

The polymerization experiments were carried out as follows. Given amounts of pure water and V-50 were poured into the reactor, and then, the monomers were added. The reactor was sealed with

a cap and heated to 70 °C using an electric heater. The reaction mixture was agitated at 130 rpm to facilitate the monodispersion of particles [5].

The sol-gel reaction [26] was conducted to form silica shells on the polystyrene surfaces as follows [1, 27]. First, 500  $\mu$ L of TEOS was dissolved in 10 mL of 1-propanol and heated at 40 °C. Then, 10 mL of the prepared polymer colloid was added to this TEOS solution at 1 mL/min via a burette, so that the polymer particles were covered with TEOS by electrostatic attraction. Although coagulation occurs easily under conventional conditions, in this case, the steric effects of the hydration layers formed by PNVA on the polystyrene surfaces helped maintain good colloidal stability [28]. The mixture was stirred for 2 days at 40 °C to synthesize polystyrene@silica particles. Finally, the synthesized polystyrene@silica particles were obtained from the colloid using a centrifugal machine (3700, KUBOTA) and dispersed again in water.

### *2.3. Characterizations*

The morphologies and sizes of the synthesized particles were determined by scanning electron microscopy (SEM, JSM-7500FA, JEOL) following the sample preparation steps described below. A drop of the solution from the reactor was placed on a freshly cleaved mica surface. The specimen was dried and covered with an osmium tetroxide film by chemical vapor deposition (OPC60A, Filgen, Inc.). The number-average particle size was calculated based on more than 300 particles seen in the SEM images. Transmission electron microscopy (TEM, JEM-2100F/HK, JEOL) along with energy

dispersive X-ray spectrometry (EDS) was used to observe the inner structure of the synthesized particles and analyze their elemental composition, respectively.

The zeta potential of the particles in suspension was measured by laser Doppler velocimetry [29] (Zetasizer Nano-ZS, Malvern Panalytical, Ltd.) after diluting the sample slurry with deionized water at a pH of ca. 7.0. The thermal properties of the silica-polymer particles were evaluated by differential thermal analysis (DTA, DTG-60AH, SHIMADZU) heating the sample to 500 °C at a rate of 10 °C/min.

### 3. Results and discussion

#### *3.1 Dependency of polymer particle properties on NVA concentration*

At first, the morphologies of the particles synthesized at an NVA concentration,  $C_N$ , of 392 mM, were observed by SEM before and after washing by centrifugation. As observed from the SEM images in **Fig. 1**, the particles before washing have rough surfaces because their surfaces were covered with PNVA (**Fig. 1a**), while the surfaces became smooth after PNVA removal (**Fig. 1b**), as shown in **Fig. 1c**, where polystyrene particles were captured through soap-free emulsion polymerization of styrene and V-50 without NVA monomer. From the different appearances, we inferred that PNVA was formed by reaction on the surfaces of the polystyrene particles. Because NVA monomer was disconjugate monomer, the copolymerization reaction with styrene was not proceeded. In our recent study, the coating of polystyrene by PNVA was also confirmed [23]. In our recent study, the thickness

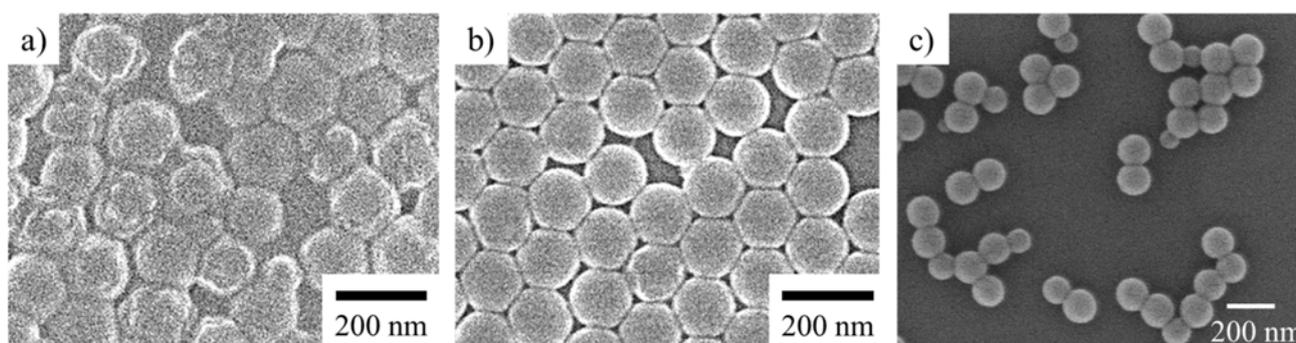
of this hydration layer was influenced by the hydrophobicity of the solvent [23]. As increasing the hydrophobicity of the solvent, the thickness was reduced. Therefore, the layers formed by PNVA had the nature of hydrophilicity, so called, hydration layers.

Next, as shown in **Fig. 2**, the effect of  $C_N$  on particle size was investigated. It was clear that the particle size decreased as the  $C_N$  increased. Being an amphiphilic monomer, NVA served as a surfactant to dissolve and stabilize the hydrophobic styrene monomer in the aqueous phase. Therefore, the number of polymerization sites increased, thereby reducing the size of the synthesized particle. After washing off the PNVA by centrifugation, the polystyrene particle size decreased. The error bar length was also reduced after washing because the PNVA layers gave the various sizes through the formation of the hydration layers.

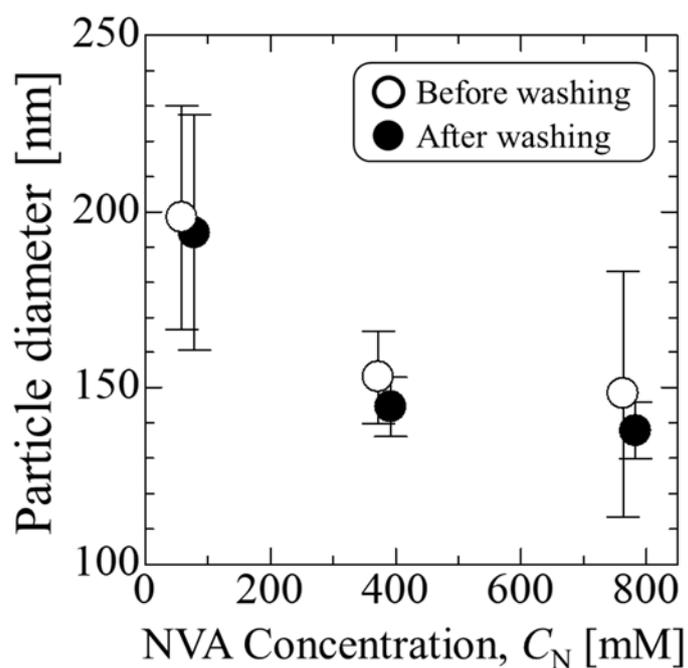
Finally, as shown in **Fig. 3**, the influence of  $C_N$  on zeta potential was investigated. It was found that the zeta potential of the particles decreased with increasing  $C_N$  during their synthesis, probably because the synthesized polystyrene with positive charge was covered with hydration layers formed by PNVA [30]. The thickness of the hydration layer on particle surface was increased with the concentration of NVA, the surface potential was decreased [23]. After washing off PNVA by centrifugation, the zeta potential increased slightly. Nevertheless, the zeta potential of the washed particles showed the same trend with  $C_N$  as the unwashed ones did, presumably because some PNVA remained on the core polystyrene particle even after washing by centrifugation.

Generally, a higher surface potential is necessary for reducing the particle size [31, 32].

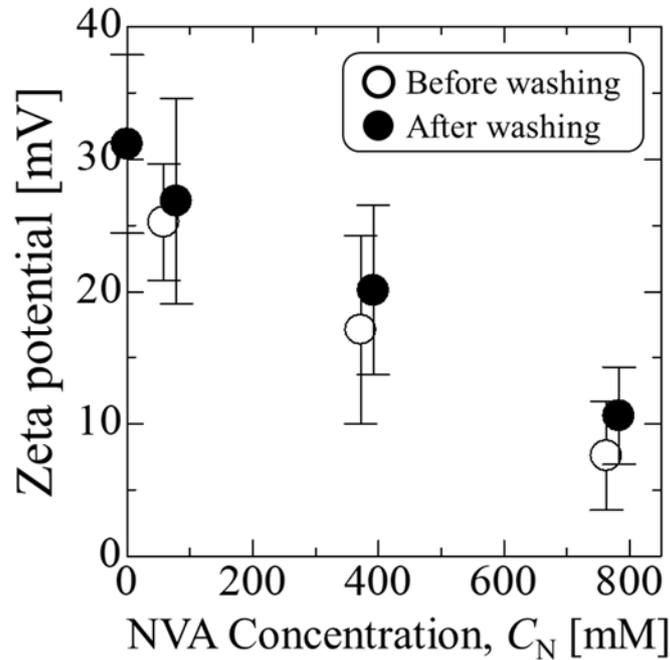
However, in this study, the particle size became small despite a reduction in surface potential. According to our previous work, this is because the PNVA coverage on the polystyrene surface produced a hydration layer and enhanced the dispersion stabilities [30]. Although the hydration layers reduced the surface potential, their steric effects prevented particle growth through coagulation during the reactions. The net result is a decreased size of the polymerized particles.



**Fig. 1 SEM images of polymer particles synthesized with  $C_N$  of 392 mM: (a) before washing, (b) after washing. (c) Reference SEM image of polystyrene particles synthesized with styrene monomer and V-50 in water without NVA monomer.**



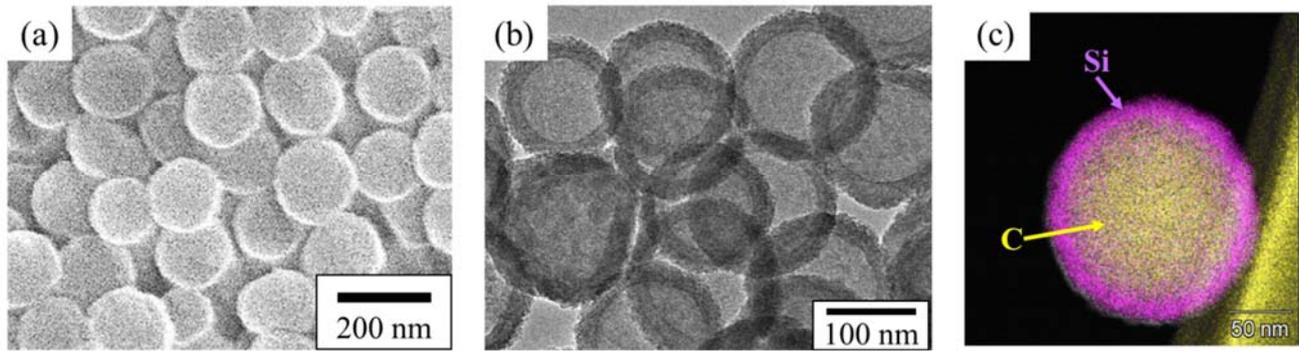
**Fig. 2** Effect of  $C_N$  on the size of polymer particles before and after washing.



**Fig. 3** Effect of  $C_N$  in the polymerization on the zeta potential of polymer particles before and after washing.

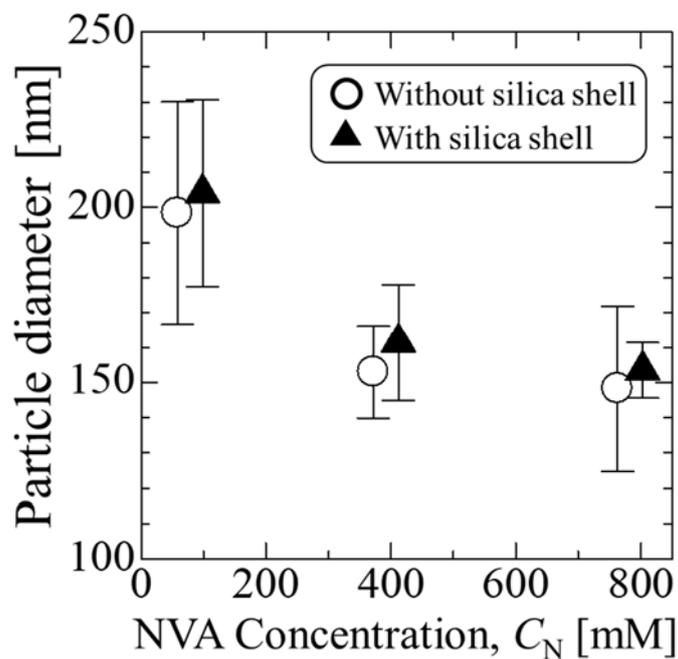
### 3.2 Function of NVA in silica shell synthesis

**Fig. 4** shows the electron microscopy images of the particles synthesized at a  $C_N$  of 392 mM. Highly monodisperse polystyrene@silica particles with a coefficient of variation of 10.3 % are shown in **Fig. 4a**. TEM observations of the particles clearly showed the core-shell internal structures (**Fig. 4b**). The shell was confirmed to be silica by the Si distribution from EDS analysis (see **Fig. 4c**), while carbon originating from the organic polymers was concentrated in the core of the synthesized particles.

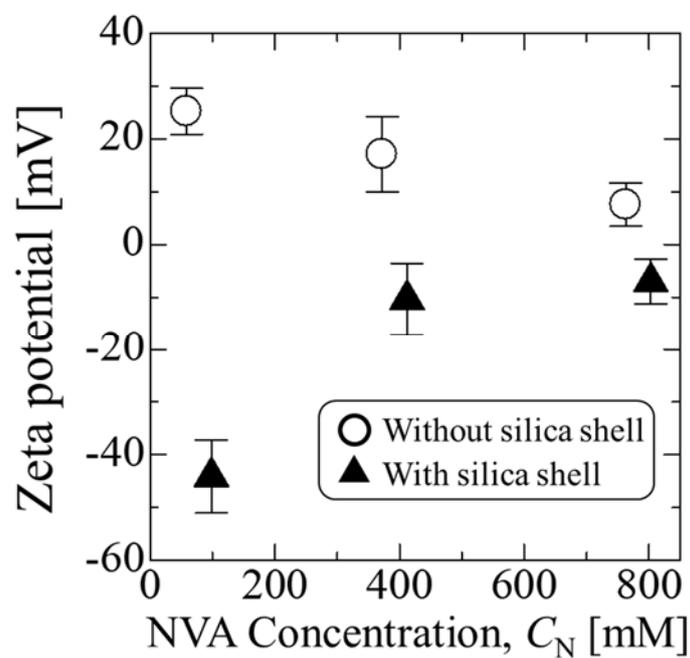


**Fig. 4** Electron microscopy images of the silica-polymer particles: (a) SEM image, (b) TEM image, and (c) EDS map.

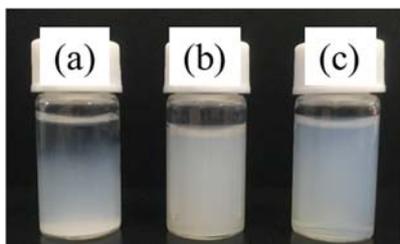
As shown in **Fig. 5**, the change in particle size with  $C_N$  was investigated. The increased size of the polymer particles after the sol-gel reaction was due to the silica coating. The negative zeta potential was attributed to the silica shell, as shown in **Fig. 6**. At a higher  $C_N$ , the presence of the silica shell had only a very small effect on the zeta potential. After waiting for 5 h to allow all reactions to complete, the colloidal dispersions were photographed, as shown in **Fig. 7**. Although the zeta potential was negatively higher for the sample synthesized with a  $C_N$  of 78.3 mM, some of the particles sedimented. On the other hand, the particles prepared with 392 or 783 mM NVA showed good colloidal stability even though their surface potentials were lower. To clarify this, EDS analysis was carried out, and carbon was detected both inside and on the surface of the silica shell (see **Figs. 8a and a'**). However, after washing via centrifugation as shown in Fig. 1, almost all the carbon on the silica shell was removed, indicating that it belonged to PNVA. The high dispersion stability resulted from steric effect by the hydration layers on the silica shells where PNVA on the polystyrene core had penetrated. As a result, the influence of silica on the zeta potential was smaller at higher  $C_N$ .



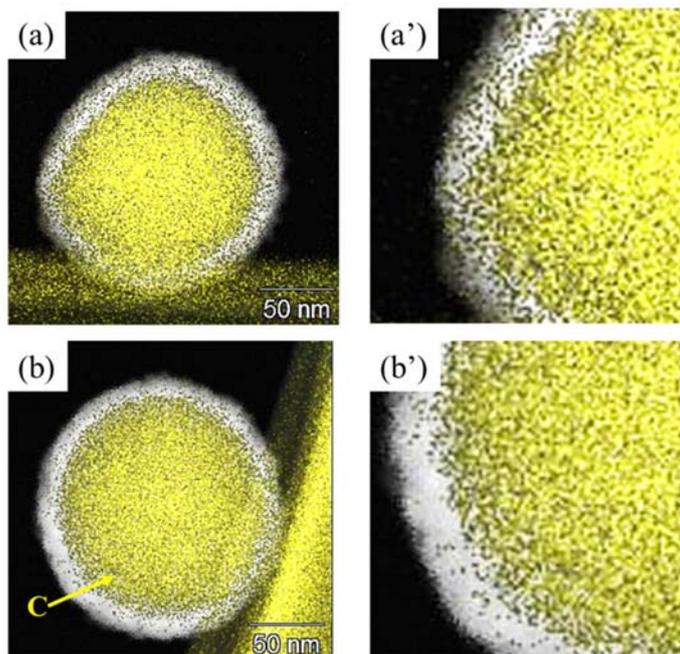
**Fig. 5** Effect of  $C_N$  on the size of polymer particles with and without silica shell.



**Fig. 6** Effect of  $C_N$  on zeta potential of polymer particles with and without silica shell.



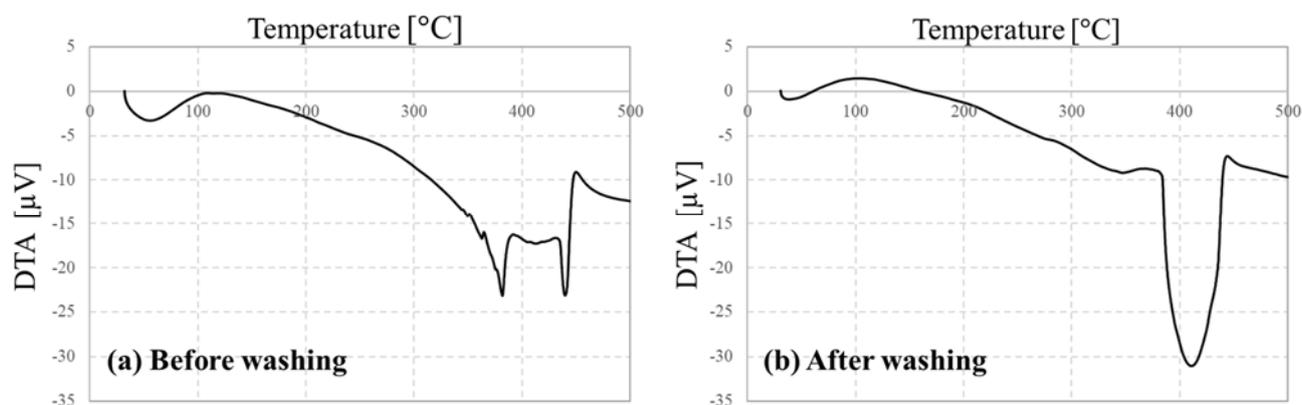
**Fig. 7 Comparison of dispersion stability of silica-polymer particles in water synthesized with  $C_N$  of (a) 78.3 mM; (b) 392 mM; and (c) 783 mM.**



**Fig. 8 Carbon maps of silica-polymer particle by EDS: (a) before and (b) after washing. (a') and (b') are magnified portions of (a) and (b), respectively.**

Finally, the thermal properties of the silica-polymer particles were evaluated by DTA. The results are shown in **Fig. 9**. For the particles before washing, two significant peaks were observed at temperatures of 381.9 and 439.8 °C. These peaks indicated the independent co-existence of polystyrene and PNVA that were not connected with each other by any chemical bond [23]. On the other hand, after washing by centrifugation to remove PNVA, only a single peak at 410.7 °C originating from mainly polystyrene remained. These experimental results confirmed that the polystyrene particles

were covered with PNVA and then coated with silica, and the intermediate PNVA layer was removed by centrifugal separation.



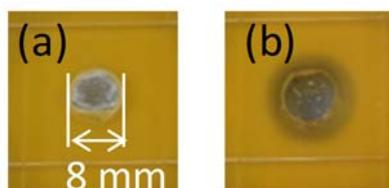
**Fig. 9 Thermal properties of silica-polymer particles measured by DTA: (a) before and (b) after washing.**

#### 4. Conclusions

Core-shell particles were synthesized through a newly developed SFEP and sol-gel reaction. At first, SFEP of styrene and NVA was conducted using V-50 to synthesize the polymer core particles. Next, the sol-gel reactions of TEOS were performed to prepare silica shells around the polymer particles, during which PNVA greatly contributed to not only the sol-gel reactions but also the colloidal stability. Furthermore, because PNVA on the polystyrene cores penetrated the silica shell, a hydration layer was formed to prevent coagulation in the sol-gel reactions on the polymer surface. Finally, microscopic analysis was performed to clarify the shell structures. The PNVA on polystyrene particles were found inside and outside the silica shell to form a hydration layer, whose steric effect resulted in good dispersion stability.

## Supporting Information

The low- and high-molecular-weight polystyrenes were classified by using a centrifugal separator. The polymer materials were obtained in the solid state by using a centrifugal separator, and were ultrasonically re-dispersed in pure water to prepare the polystyrene colloids. These materials were applied to cultures of *Micrococcus luteus*. No bacterial inhibition zone was observed for the polymer colloids synthesized using V-50, as shown in **Fig. S1a**. However, **Fig. S1b** shows that the supernatant produced noticeable inhibition zones.



**Fig. S1 Results of the bioassays of *Micrococcus luteus* using (a) 180-nm particles and (b) product supernatant after synthesis using styrene and V-50.**

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