



# Preparation and characterization of emulsifier-free polyphenylsilsesquioxane-poly (styrene-butyl acrylate) hybrid particles



Ruiqin Bai, Teng Qiu\*, Feng Han, Lifan He, Xiaoyu Li\*

College of Materials Science and Engineering, State Key Laboratory of Organic-Inorganic Composites, Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, PR China

## ARTICLE INFO

### Article history:

Received 12 May 2012

Received in revised form 17 May 2013

Accepted 24 May 2013

Available online 30 May 2013

### Keywords:

Emulsifier-free

Polyphenylsilsesquioxane

Poly (styrene-butyl acrylate)

Hybrid particles

## ABSTRACT

The core-shell polyphenylsilsesquioxane-poly (styrene-butyl acrylate) hybrid latex particles with polyphenylsilsesquioxane as core and poly (styrene-butyl acrylate) as shell were successfully synthesized by seeded emulsion polymerization using polyphenylsilsesquioxane (PPSQ) latex particles as seeds. X-ray diffraction (XRD) indicated that the polyphenylsilsesquioxane (PPSQ) had ladder structure, and PPSQ had incorporated into the hybrid latex particles. Transmission electron microscopy (TEM) confirmed that the resultant hybrid latex particles had the core-shell structure. TEM and dynamic light scattering (DLS) analysis indicated that the polyphenylsilsesquioxane latex particles and obtained core-shell hybrid latex particles were uniform and possessed narrow size distributions. X-ray photoelectron spectroscopy (XPS) analysis also indicated that the PPSQ core particles were wrapped by the polymer shell. In addition, compared with pure poly (styrene-butyl acrylate) latex film, the polyphenylsilsesquioxane-poly (styrene-butyl acrylate) hybrid latex film exhibited lower water uptake, higher pencil hardness and better thermal stability.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Recently, inorganic-organic materials have attracted much attention owing to their unique properties and their application in many fields such as coatings, adhesives, plastics, rubbers, catalysis, biotechnology and diagnostics [1–11].

Polysilsesquioxanes (PSQ) are an important class of organic-inorganic hybrid materials with the empirical formula  $(\text{RSiO}_{1.5})_n$ , where R is hydrogen, methyl, ethyl, phenyl, or other substituted organic groups [12–15]. Among the polysilsesquioxanes, polyphenylsilsesquioxanes (PPSQ) are widely studied owing to their good properties, such as thermal resistance, flame retardancy and solubility in common organic solvents [16–18]. They can be potentially applied in many areas such as lithographic materials, coatings for electronic and optical devices, insulator layers for semiconductor devices, and additive powders to materials including cosmetics, polypropylene films, and methacrylic resins [18–20]. Poly (styrene-butyl acrylate) have many specific properties such as good film-forming, gloss, transparency, and mechanical properties, and they have been widely used as coatings,

paints, and adhesives [21–23]. However, in some circumstance, poor water resistance and thermal resistance, and low pencil hardness greatly limit their application. There are much research works that focused on the preparation and investigation of the inorganic-organic core-shell particles [24–27]. However, by far very little work has been done to prepare and characterize the inorganic-organic core-shell hybrid latex particles with PPSQ as core and poly (styrene-butyl acrylate) as shell.

In this work, core-shell polyphenylsilsesquioxane-poly (styrene-butyl acrylate) [PPSQ-P(St-BA)] hybrid latex particles were synthesized by seeded emulsion polymerization of styrene (St) and butyl acrylate (BA), using the polyphenylsilsesquioxane (PPSQ) latex particles as seeds. Firstly, PPSQ latex particles were prepared by the hydrolysis and polycondensation of phenyltrimethoxysilane (PhTMS) in the presence of the reactive emulsifier SE-10N. Secondly, 3-methacryloyloxypropyltrimethoxysilane (MAPTS), which contains reactive methacryloyloxy group, was used to modify the surface of the PPSQ latex particles and therefore there are reactive methacryloyloxy groups on the surface of PPSQ latex particles. Thirdly, the shell monomers including St and BA were added to perform emulsion polymerization on the surface of PPSQ latex particles, forming core-shell PPSQ-P(St-BA) hybrid latex particles. The polyphenylsilsesquioxane core particles and core-shell PPSQ-P(St-BA) hybrid latex particles were characterized by X-ray diffraction (XRD),

\* Corresponding authors. Tel.: +86 10 64419631; fax: +86 10 64452129.

E-mail addresses: [qiu teng@mail.buct.edu.cn](mailto:qiu teng@mail.buct.edu.cn) (T. Qiu), [lix y@mail.buct.edu.cn](mailto:lix y@mail.buct.edu.cn) (X. Li).

transmission electron microscopy (TEM), dynamic light scattering (DLS) analysis, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA), etc.

## 2. Experimental

### 2.1. Materials

Monomers of butyl acrylate (BA) and styrene (St), obtained from Tianjin Fuchen Chemical Reagent Factory (China), were distilled under vacuum before use. Phenyltrimethoxysilane (PhTMS) and 3-methacryloxypropyltrimethoxysilane (MAPTS) were, respectively, obtained from Qufu Chenguang Chemical Co., Ltd. (China) and Momentive Performance Materials Inc., and used as received. The reactive emulsifier, 1-nonylphenyloxy-2-deca(oxyethylene)-3-allyloxypropane ammonium sulfate (SE-10N), was received from Asahi Denka Industries Ltd. and used as received without further treatment. Sodium hydroxide (NaOH) and ammonium persulfate (APS) were obtained from Fuchen Chemical Reagent Factory (China) and used without further purification. Distilled water was used throughout the experiment.

### 2.2. Preparation of polyphenylsilsesquioxane (PPSQ) latex particles

The polyphenylsilsesquioxane (PPSQ) latex particles were prepared by the hydrolysis and polycondensation of phenyltrimethoxysilane in the presence of the reactive emulsifier. 250 g of water, 0.60 g of NaOH and 0.03 g of SE-10N were added into a 500 mL four-necked flask equipped with a mechanical stirrer, reflux condenser and thermometer. Then 40 g of PhTMS was slowly added into the flask. The mixture was stirred at room temperature for 24 h and then at 50 °C for another 24 h.

### 2.3. Modification of polyphenylsilsesquioxane (PPSQ) latex particles

After the preparation of polyphenylsilsesquioxane (PPSQ) latex particles, the silane coupling agent MAPTS, which contains reactive methacryloyloxy group, was used to modify the surface of PPSQ latex particles. MAPTS was slowly added into the above PPSQ latex emulsion. After the addition of MAPTS, the mixture was stirred for another 24 h.

### 2.4. Preparation of core-shell polyphenylsilsesquioxane-poly(styrene-butyl acrylate) [PPSQ-P(St-BA)] hybrid latex particles

All the experiments were carried out under nitrogen atmosphere in a 250 mL four-neck round-bottom flask equipped with reflux condenser, mechanical stirrer, dropping funnels and inlet for nitrogen gas. The flask was heated using a water bath. A portion of PPSQ emulsion (containing 1 g PPSQ), SE-10N and 90 g of water were charged into the flask. After the temperature was increased up to 80 °C, the shell monomers (4 g of BA and 6 g of St) were fed into the flask under starved-feed addition within 2 h. Simultaneously APS aqueous solution (0.07 g of APS dissolved in 10 g of water) was fed into the flask with an appropriate rate to initiate the polymerization of the shell monomers. After the feed of shell monomers and APS aqueous solution, the mixture was reacted at 80 °C for another 4 h. The total conversion of monomers was determined gravimetrically.

The PPSQ-P(St-BA) hybrid latex particles with different PPSQ content were prepared under similar method. The recipes for the synthesis of core-shell PPSQ-P(St-BA) hybrid latex particles were described in Table 1.

**Table 1**  
Recipes and properties of the core-shell PPSQ-P(St-BA) hybrid latex particles.

Sample code	S-1	S-2	S-3	S-4	S-5
PPSQ (g)	1	2	3	4	5
St (g)	6	6	6	6	6
BA (g)	4	4	4	4	4
SE-10N (g)	0.009	0.018	0.027	0.036	0.045
APS (g)	0.07	0.07	0.07	0.07	0.07
DI water (g)	100	100	100	100	100
Conversion (%)	98.25	96.42	93.28	89.46	85.33
Particle size (nm)	155.6	135.1	120.7	115.5	111.6
Polydispersity	0.026	0.012	0.008	0.009	0.013

### 2.5. Characterization

X-ray diffraction (XRD) data of PPSQ and core-shell PPSQ-P(St-BA) were obtained using a Rigaku D/max-2500 X-ray diffractometer with Cu K $\alpha$  radiation. The transmission electron microscopy (TEM) images of PPSQ and core-shell PPSQ-P(St-BA) were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The particle sizes and their distributions of the PPSQ and core-shell PPSQ-P(St-BA) latex particles were measured with dynamic light scattering (DLS) using a Zetasizer Nano ZS (Malvern Instruments, UK). The samples were highly diluted before testing. X-ray photoelectron spectroscopy (XPS) of PPSQ and the core-shell PPSQ-P(St-BA) were performed with a Thermo VG Scientific Escalab 250 electron spectrometer (East Grinstead, UK) using monochromatic Al K $\alpha$  radiation source. Hardness test of the dry latex film was determined using an apparatus (Tianjin Test Instrument Factory, China), employing a set of equivalent calibrated wood pencils meeting the scale of hardness from 6B (softer) to 6H (harder). Thermogravimetric analysis (TGA) was measured by a Perkin Elmer TGA 4000 under a nitrogen atmosphere at a heating rate of 10 °C/min from 30 to 800 °C. The water absorption was determined as follows. The latex films were dried at 80 °C until constant weight ( $W_{dry}$ ) was obtained. The latex films were immersed into deionized water at 25 °C for 24 h. Then the latex films were taken out and immediately weighted ( $W_{wet}$ ) after wiping out the surface water. The water absorption was calculated using the following formula:

$$\text{water absorption} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\%$$

## 3. Results and discussion

### 3.1. XRD analysis

The XRD patterns of PPSQ, PPSQ-P(St-BA) and pure P(St-BA) are shown in Fig. 1. In the diffractogram of the PPSQ (Fig. 1e), the relatively intense peak at about 7° with a spacing of about 1.26 nm correspond to the chain-to-chain distance, while a broad halo at about 19° with a spacing of about 0.46 nm correspond to the intrachain distance in the stereoregular double-chain structure of PPSQ [28,29]. The peak at about 7° can be considered as the characteristic peak of ladderlike PPSQ. Comparing the diffractograms of PPSQ and pure P(St-BA), it can be seen that the peak at about 7° cannot be detected in the diffractogram of pure P(St-BA). However, the characteristic peak at about 7° can be detected in all the diffractograms of PPSQ-P(St-BA), and the intensity of the peak increases as the amount of PPSQ increases, indicating that the PPSQ particles have effectively incorporated into the core-shell PPSQ-P(St-BA) hybrid latex particles.

Download English Version:

<https://daneshyari.com/en/article/5359692>

Download Persian Version:

<https://daneshyari.com/article/5359692>

[Daneshyari.com](https://daneshyari.com)