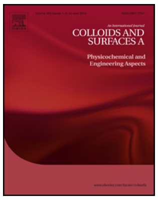
Colloids and Surfaces A: Physicochem. Eng. Aspects 497 (2016) 378–384

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Synthesis of sub-micron sized hollow, and nanoporous phenylsiloxane spheres through use of phenyltrimethoxysilane as surfmer: Insights into the surfactant and factors influencing the particle architecture

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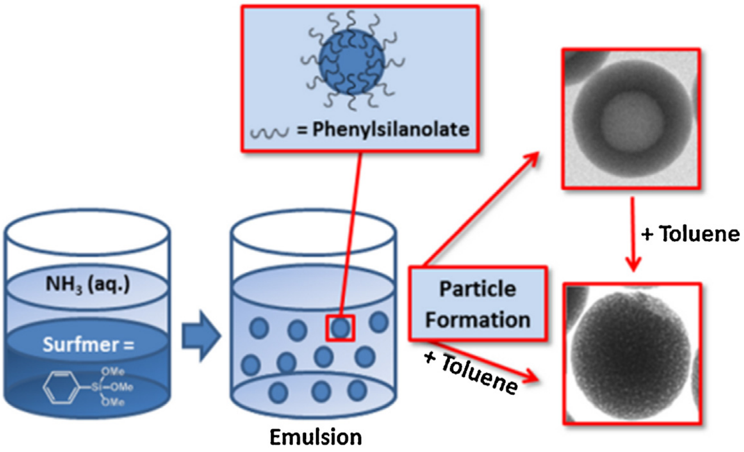
HIGHLIGHTS

- Surfactant formed through hydrolytic conversion of the Ph-TMS surfmer identified as a mixture of phenylsilanolates.
- Study on the formation of nanoporous spheres, focusing on the kinetics of formation of surfactant and siloxane network.
- Solubility of phenylsiloxane in toluene identified as cause for the switch in particle architecture.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 January 2016
Received in revised form 9 March 2016
Accepted 10 March 2016
Available online 15 March 2016

Keywords:
Emulsion
Phenylsilanolate
Hydrolysis
Polycondensation
Silica

ABSTRACT

Recently, our group reported synthesis routes for sub-micron sized hollow, and nanoporous phenylsiloxane spheres, in which phenyltrimethoxysilane is applied as surfmer. Here, we present insights into the surfactant formed through hydrolytic conversion of phenyltrimethoxysilane, and factors influencing the particle architecture.

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http://dx.doi.org/10.1016/j.colsurfa.2016.03.029

1. Introduction

The use of surfmers with reactive (meth) acrylic or styrene moieties in the emulsion-based synthesis of sub-micron sized polymer particles has been reported by a variety of research groups, amongst which the groups of Möller [1] and Armes [2]. In these syntheses, the surfmer is either a surfactant or forms a surfactant in the initial stage of the process through reaction with other components in the mixture, and subsequently reacts with other monomers to become covalently connected to the polymer particle. In this way, the use of conventional, non-covalently attached surfactants can be avoided, which is beneficial for further modification of the polymer particles with *e.g.* metals to form polymer-metal composites [1b], or in formulating the polymer particles into coatings and polymer matrices [3].

Despite the substantial amount of work on surfmers that can be applied in the synthesis of polymer particles, reports on the use of surfmers in the synthesis of inorganic or inorganic-organic hybrid particles are scarce [4]. Recently, our group reported a route for the synthesis of hollow phenylsiloxane spheres, in which phenyltrimethoxysilane (Ph-TMS) was used as surfmer [5]. This synthesis is based on an emulsion of Ph-TMS in aqueous ammonia, in which a surfactant is formed through hydrolytic conversion of the surfmer – Ph-TMS – in the initial stage of the particle synthesis. This stabilizes the emulsion, and through hydrolysis and condensation a phenylsiloxane shell was formed at the oil-water interface. This progressively grew towards the particle interior, and after extraction of unreacted and low-molecular weight core material with ethanol, a suspension of hollow phenylsiloxane spheres in water was obtained (Fig. 1).

Particle size and shell thickness could be tuned independently from each other, and hollow phenylsiloxane spheres with an average outer particle diameter (D_{av}) between 445 nm and 1020 nm, a narrow size distribution (0.036–0.083) [6], and shell thickness between 95 nm and 171 nm were obtained (Fig. 2A) [5]. Replacement of 50 vol.% Ph-TMS by toluene resulted in the formation of nanoporous spheres with an outer diameter of 341 nm, and a narrow size distribution of 0.10 (Fig. 2B) [5]. Please note: we do not consider the shell of the hollow spheres to be non-porous, but merely use the terms “hollow” and “nanoporous” to differentiate between the architectures of particles obtained with Ph-TMS and Ph-TMS/toluene mixtures, respectively.

To understand the formation of both types of phenylsiloxane spheres, we studied the surfactant formed through hydrolytic conversion of Ph-TMS in aqueous ammonia, and investigated factors that influence the particle architecture. Here, we report the findings of both studies.

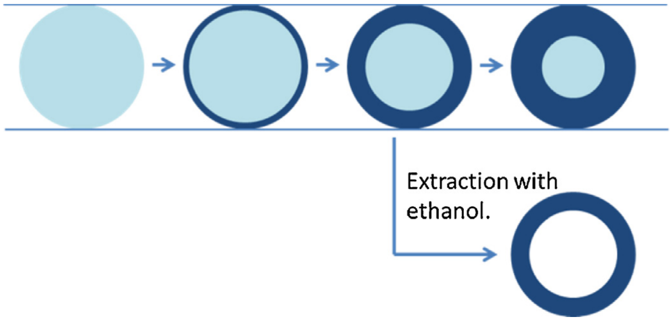

Fig. 1. Schematic representation of the formation of hollow phenylsiloxane spheres. [5].

2. Materials and methods

2.1. Materials

2.1.1. General

Ph-TMS (deposition grade, 98%) and ammonium hydroxide solution (30–33%) were ordered from Sigma-Aldrich. Nitric acid (65%) was ordered at Fluka. Ethanol (absolute, analytical reagent, dehydrated) and toluene (analytical reagent) were ordered from Biosolve. All chemicals were used as received.

2.2. Methods

2.2.1. Synthesis of hollow and nanoporous sub-micron sized phenylsiloxane spheres

For the synthesis of hollow spheres, MilliQ water (300 mL) was heated to 60 °C in a 500 mL reactor. Ammonium hydroxide solution (30–33%, 30 mL) was added in order to obtain a pH of 11. Ph-TMS (2.79 mL, 14.9 mmol) was added under mechanical stirring (250 rpm). Within approx. 3–6 min, a milky emulsion formed. The reaction was stirred at 60 °C for one hour. To stop the reaction, the reaction mixture was cooled on ice to room temperature. The reaction mixture was centrifuged at 3214*g* for 20 min, after which the supernatant was removed and the pallet redispersed in ethanol. The pallet was redispersed using an ultrasound bath for 15 min. Afterwards, the dispersion was again centrifuged at 3214*g* for 20 min, after which the supernatant was removed and the pallet was redispersed in MilliQ water.

For the production of nanoporous spheres, part of the Ph-TMS in the above procedure was replaced with toluene which was added to the reaction mixture directly before Ph-TMS. Particle dispersions prepared with only Ph-TMS (no toluene) have a solid weight percentage of approx. 0.3%.

2.2.2. Addition of toluene or Ph-TMS to hollow particle dispersion

Toluene (8.5 μL per mL hollow particle dispersion) or Ph-TMS (1.7, 8.5 or 42.5 μL per mL hollow particle dispersion) was added to an aqueous hollow particle dispersion (as prepared in Section 2.2.1). The mixture was stirred for 1 h. Subsequently, the mixture was centrifuged at 3214*g* for 20 min after which the supernatant was removed. The pallet was redispersed in ethanol and again centrifuged at 3214*g* for 20 min, after which the supernatant was removed. Thereafter, the pallet was redispersed in MilliQ water.

2.2.3. Electron microscopy

2.2.3.1. Scanning electron microscopy. Scanning electron microscopy (SEM) analyses (Figs. 3, 7 A, B, D, S12A, S12B, S12D and S12F) were carried out using a FEI quanta 600 microscope. Samples were prepared by drying a dispersion droplet on a cleaned microscope slide and were subsequently sputtered with a gold coating. The accelerating voltage used was 15 kV.

2.2.3.2. Transmission electron microscopy. Transmission electron microscopy (TEM) analyses (Figs. 2 A, B, 4, S2A and S2B) were performed using a FEI Tecnai 20 (type Sphera) microscope operating with a 200 kV LaB_6 filament and a bottom mounted 1024 × 1024 Gatan msc 794^{TM} CCD camera. Samples were prepared by drying a dispersion droplet on a 200 mesh Cu grid with Quantifoil R 2/2 holey carbon film (Quantifoil Micro Tools GmbH). Other TEM studies (Figs. 7 C, E, S3A, S3B, S12C, S12E and S12G) were performed using a JEOL ARM 200 probe corrected TEM, operated at 200 kV.

2.2.3.3. Scanning transmission electron microscopy. Scanning transmission electron microscopy (STEM) analyses (Fig. 4C, inset) were performed using a FEI NovaNano SEM 650 operated at high vacuum with a solid-state BSED (CBS). Beam deceleration (4 kV) is applied to