Synthesis of polystyrene core/SiO2 shell composite particles and fabrication of SiO2 capsules out of them

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Abstract. Systemic studies on the dependence of the morphology of polystyrene core/SiO2 shell composite particles on the conditions of their fabrication have been performed. Spherical polystyrene particles synthesized in the presence of a cationic initiator of polymerization were used as cores. SiO2 shells were formed by modified Stober's method. Exposure of the synthesized composite particles to high temperatures has been shown to cause destruction of their polystyrene core, thereby allowing the formation of mesoporous SiO2 capsules with a mean pore diameter of ~3 nm and specific surface area of ~270 m²/g. Model experiments on loading the SiO2 capsules with amoxicillin have been carried out. Spectrophotometry in the UV and visible spectral regions has been used to estimate the kinetics of amoxicillin release from the SiO2 capsules.

1. Introduction

Hollow inorganic microbeads are used in various fields of science and technology, e.g., as containers for drugs [1–4], absorbents [5], and catalyzers [6]. An effective method for obtaining these capsules is removal of the cores from composite particles (CPs) of the organic core/inorganic shell type, polystyrene core/SiO2 shell CPs being the most commonly used. In this case, the morphology of the resultant capsules is determined by the CP structure.

The methods for obtaining these CPs may be divided into two main groups: one-stage and two-stage. In the methods of the former group, CPs are synthesized without separation of the target product (the CPs) from the template (polymer particles). In general, polymerization reactions involving different type of initiators (neutral [7], cationic [7], or anionic [8]) are used to synthesize polystyrene (PS) particles and simultaneously form SiO2 shells by adsorbing preliminarily synthesized SiO2 nanoparticles (NPs) onto the PS particle surface [9, 10]. However, the resultant CPs are usually polydisperse with respect to size and have a heterogeneous surface.

Two-stage methods of synthesis are used more frequently than one-stage ones. These methods consist in successive obtaining PS particles and formation of the SiO2 shell (and subsequent fabrication of SiO2 capsules out of these CPs). Two-stage methods are advantageous in that they yield
monodisperse CPs with controllable morphology. For example, in [11], CPs were formed by successive deposition of alternately charged polyelectrolyte and SiO₂ NP layers onto PS particles.

Stober’s method [12] is one of the most common ones used to form SiO₂ shells on PS particles. This method, based on the reaction of tetraethyl orthosilicate (TEOS) hydrolysis, is reasonably simple and yields SiO₂ shells of uniform thickness [13]. In Ref. 13, it was used to form a SiO₂ layer on PS particles whose surface carried NH₂ groups. However, obtaining the particles with surface amino groups is a rather sophisticated procedure.

It should be noted that, despite common interest in obtaining PS core/SiO₂ shell CPs (and SiO₂ capsules out of these particles), most researchers confine themselves to studying the effect of one or two parameters of synthesis on the particle morphology. For example, the effects of the dichloromethane concentration and the PS particle to TEOS ratio on the structure of the SiO₂ shells formed [14] and the effects of the polarity of the medium and the TEOS concentration (C(TEOS)) on the structure of the SiO₂ layer on the PS particles [15] have been estimated. In another study, the type of precursor in the synthesis of PS core/SiO₂ shell CPs was varied (either TEOS or a mixture of TEOS with vinyl triethoxysilane was used) [16]. In one of the most comprehensive studies [17], the effects of three parameters of the process, namely, C(TEOS), pH of the reaction medium, and reaction temperature, on the structure of the SiO₂ shells formed on PS particles have been used. Note that the reaction was carried out at a low pH (~2.5), relatively high temperature (60–70°C), and prolonged reaction time (5 h).

Polyvinylpyrrolidone (PVP) is rather frequently used for forming pores in the SiO₂ layer on PS particles [18]. For example, it has been shown that SiO₂ shells with controllable porosity and specific surface can be obtained by varying the PVP concentration C(PVP) in the solution [19, 20]. The use of PVP also allows PS particles of controllable size to be made [21].

Here, we propose a method for forming homogeneous SiO₂ shells over preliminarily PVP-modified positively charged PS particles synthesized in the presence of a cationic polymerization initiator. These approaches to obtaining PS core/SiO₂ shell CPs have been used separately in different studies, but we suggest that they be combined. We also plan integrated systemic studies on the dependence of the morphology of SiO₂ shells formed on PS particles on the synthesis conditions (the time of synthesis of SiO₂ shells, pH of the reaction medium, and the concentrations of the precursor and pore-forming agent). The CPs can be used to obtain hollow SiO₂ capsules and carry out model experiments on loading them with a drug (amoxicillin) and subsequent release of the drug from the capsules incubated in physiological saline.

2. Materials and methods

2.1 Materials

We used styrene monomer (99.5%), 2,2’-azobis(2-methylpropionamidine) dihydrochloride (ABMPAD) (97%), PVPs with molecular weights (MWs) of 10, 30, 55, and 340 kDa, TEOS (98%), aqueous solution of ammonium hydroxide (30 wt %), and amoxicillin from Sigma-Aldrich (United States). Simulated body fluid (SBF) was prepared according to Ref. 22. The salts for preparing SBF were high-grade (Khimreaktiv, Russia).

2.2 Synthesis of PS Beads

PS beads with a positively charged surface were synthesized by the surfactant-free emulsion polymerization method. ABMPAD served as a cationic initiator of the reaction. The necessary amount of styrene (12.5 g) was added to 250 g of deionized water (resistivity, 18.2 MΩ·cm; Millipore Direct-Q, France), after which oxygen was removed from the reaction mixture by bubbling gaseous nitrogen for 30 min. The reaction mixture was heated to 65°C, and the necessary amount of ABMPAD (0.35 g) was added. The reaction was performed at a temperature of 65°C for 24 h with permanent nitrogen bubbling. The reaction products were sedimented by centrifugation at 8000 rpm for 10 min and repeatedly washed with methanol and deionized water. The precipitate was air-dried.
2.3 Synthesis of PS Core/SiO$_2$ Shell CPs

100 mg of PS was dispersed in 200 ml of a water–ethanol mixture (volume ratio, 35:165). PVP was gradually added to the dispersion while stirring to a final concentration of 3 to 10 g/l. The pH of the mixture was controlled by adding ammonium hydroxide. Then, the necessary amount of TEOS was added to the reaction mixture while intensely stirring. The resultant mixture was heated to 50°C and stirred for 6 h. The conditions of the synthesis of different samples are shown in the Table 1. After the reaction was completed, CPs were washed from excess PVP and TEOS in four cycles of sedimentation by centrifugation and resuspension in water. The precipitate obtained at the final stage was dried at room temperature.

| Sample | TEOS concentration in ethanol–water mixture, M | Reaction time, h | pH |
|--------|-----------------------------------------------|------------------|----|
| 1      | 0.2                                           | 3                | 10.0 |
| 2      | 0.2                                           | 3                | 11.0 |
| 3      | 0.2                                           | 3                | 12.5 |
| 4      | 0.2                                           | 1                | 11.0 |
| 5      | 0.2                                           | 6                | 11.0 |
| 6      | 0.05                                          | 3                | 11.0 |
| 7      | 0.1                                           | 3                | 11.0 |
| 8      | 0.4                                           | 3                | 11.0 |

2.4 Formation of SiO$_2$ Capsules

The dried CPs were exposed to a temperature of 400°C in the air for 6 h. In estimating the effect of the thermal treatment on the specific surface area of SiO$_2$ capsules and pore size, the temperature was varied from 200 to 1200°C.

2.5 Loading of the SiO$_2$ Capsules with Amoxicillin

The necessary amount of preliminarily dried SiO$_2$ capsules was dispersed in 50 ml of a 20 mg/l aqueous solution of amoxicillin (with the resultant amoxicillin to SiO$_2$ weight ratio of 2:1). The dispersion was intensely stirred for 48 h at room temperature. Then, the SiO$_2$ capsules were sedimented by centrifugation (12,000 rpm for 15 min), washed with acetone three times as described in Ref. 23, and vacuum-dried at 35°C. The amount of the drug loaded into the capsules was monitored by measuring the light absorbance of the supernatant at a wavelength of 245 nm using a Cary 50 spectrophotometer (Varian, United States).

Amoxicillin release was induced by dispersing the loaded SiO$_2$ capsules in physiological saline and stirring the dispersion at 37°C for 20 h. At predetermined intervals, the amoxicillin concentration was estimated by measuring the light absorbance of the supernatant obtained after centrifugation of the dispersion (12,000 rpm for 15 min) at 245 nm.

2.6 Instrumental techniques

The morphology of the particles was studied using the transmission (TEM) and scanning (SEM) electron microscopy methods. The TEM measurements of CPs were performed using a Technai G2 20 FEG microscope (FEI, Netherlands). Before the measurements, preliminarily dried CPs were thermally treated (400°C for 6 h). The residue was redispersed in 500 μl of ethanol. A drop of the dispersion was applied onto the surface of carbon-coated 300-mesh copper grids for TEM 3 mm in diameter. SEM studies were performed using a Quanta 200 microscope (FEI, Netherlands). A drop of the dispersion was applied onto a silicon substrate. After evaporation of the dispersion medium, a layer of gold was applied onto the sample surface by means of magnetron sputtering.
In thermogravimetric analysis (TGA) (TGA/STDA 851, Mettler-Toledo, United States), approximately 10-mg samples were used. The heating mode was 20°C/min in a nitrogen atmosphere (flow rate, 50 ml/min).

The specific surface area (S) and volumes of pores of CPs and SiO$_2$ capsules were determined by the method of low-temperature nitrogen adsorption (ASAP-2010N, Micromeritics, United States). The S values were calculated by the Barrett–Joyner–Halenda (BJH) method [24]. The S and size distribution of the pores were calculated using the desorption arm of the adsorption–desorption isotherm.

The $\xi$-potential of the particles and their size (determined by the dynamic light scattering (DLS) method) were measured by means of a ZetaSizer Nano device (Malvern, United States).

For measurements by the method of Fourier transform infrared spectrometry (MAGNA 550, Nicolet, United States), the necessary amount of dried particles was mixed with KBr powder, and the mixture was pressed into a tablet.

3. Results and discussion

Figure 1a shows a microphotograph of the PS particles synthesized. The particles are spherical, with a smooth surface, 120 ± 10 nm in diameter. A cationic initiator was used in the styrene polymerization reaction. As a result, the surface of the PS particles was positively charged (at pH 7.0), with a $\xi$-potential of about +74 mV.

At the next stage, SiO$_2$ shells were formed on the PS particle surface by Stober’s method. We found that, at pH $\ll$ 11.0 (at C(TEOS) = 0.2 M and reaction time of 3 h), the TEOS hydrolysis and condensation reaction rates were too low to form a SiO$_2$ layer on the particle surface (Figure 1b). According to TGA data, the weight of the solid residue of the CPs synthesized under these conditions was as small as 0.55% of the initial amount. An increase in the pH of the reaction mixture to 11.0 led to an increase in the TEOS hydrolysis rate and formation of a continuous, smooth SiO$_2$ shell ~9 nm in thickness (Figure 1c). Further increase in pH (to 12.5) caused not only an increase in the SiO$_2$ shell thickness (to ~13 nm), but also an undesirable increase in its roughness and heterogeneity compared to the shell obtained at pH 11.0 (Figure 1d). Apparently, the nucleation of SiO$_2$ NPs occurred not only on the surface of the PS particles and the SiO$_2$ layer formed at early reaction stages, but also in the bulk reaction medium. We believe that this is related to, first, an increase in the number of nucleation centers of SiO$_2$ particles (due to a high TEOS hydrolysis rate) and, second, adsorption of SiO$_2$ NPs formed in the reaction medium with pH 12.5 onto the positively charged surface of PS particles, followed by their incorporation into the SiO$_2$ shell during its formation, which decreases the shell heterogeneity. Subsequent experiments were performed in the reaction mixture with pH 11.0.
Note that, to perform TEM measurements, the CPs synthesized were dried and exposed to a temperature of 400°C in the air for 6 h. This resulted in the destruction and elimination of the PS core, as confirmed by IR spectrometry (Figure 2). The spectrum of the original PS particles (after the addition of PVP before the SiO$_2$ shell formation) contained absorption bands at 3100–2900 (aliphatic C–H bonds), 1600–1500 (aromatic C=C bonds), and 800–700 cm$^{-1}$ (aromatic C–H bonds). After the formation of the SiO$_2$ shells, the intensities of these bands were considerably decreased. In addition, an intense band with a peak at 1090 cm$^{-1}$ corresponding to Si–O–Si bonds appeared in the spectrum, which confirmed the formation of a SiO$_2$ layer on the surface of PS particles. After thermal treatment of the CPs, the absorption bands characteristic of PS disappeared, which indicated its complete elimination. The elimination of the PS core allowed the contrast of TEM images to be considerably increased and the analysis of the SiO$_2$ shell morphology to be improved. In addition, bands characteristic of the C=O and C–N bonds (1660–1680 cm$^{-1}$) can be seen in Figures 2a and 2b, which is explained by the presence of PVP molecules on the PS particle surface and in the CPs. After thermal treatment, these bands disappeared, which indicated thermal destruction of PVP.

We established that the thickness of the synthesized SiO$_2$ shells increased with increasing TEOS hydrolysis reaction time (at pH 11.0 and C(TEOS) = 0.2 M). Non-continuous SiO$_2$ shells were formed on PS particles within 1 h; continuous shells ~9 nm in thickness, within 3 h, and 14-nm shells, within 6 h. Further increase in the reaction time did not lead to thickening of the SiO$_2$ shells. Note that the thickness of the synthesized SiO$_2$ shells was smaller than the calculated value. This was related to the formation of small SiO$_2$ NPs in the reaction mixture in the course of shell growth. However, subsequent washing entirely eliminated these NPs, which was confirmed by SEM and TEM data.

The results of TGA showed that the weight content (ω) of SiO$_2$ in CPs increased with increasing reaction time. The ω(SiO$_2$) was approximately 2, 11, and 27% after 1, 3, and 6 h of the reaction, respectively. These data reasonably agree with the thicknesses of SiO$_2$ shells indicated above.
We also found that the SiO$_2$ content of the CPs increased with increasing C(TEOS) (Figure 3a). The TGA curves for CPs synthesized at different C(TEOS) values show a drastic decrease in the sample weight at a temperature of ~420°C and a plateau at temperatures higher than 500°C.

As seen from TEM images (Figures 3b-3d), continuous, almost defect-free SiO$_2$ shells from ~4 to 17 nm in thickness formed on PS particles at C(TEOS) from 0.05 to 0.4 M, respectively (reaction time, 3 h; pH 11.0). At the C(TEOS) of 0.05 and 0.1 M, the SiO$_2$ layers had about the same thickness of 4–5 nm, whereas an increase in C(TEOS) to 0.2 and 0.4 M led to their thickening to ~9 and 17 nm, respectively. Note that it was earlier shown [21] that the diameter of SiO$_2$ NPs increased with increasing C(TEOS) in the reaction mixture. This agrees with the dependence of the SiO$_2$ shell thickness on C(TEOS) observed in our study. Therefore, an increase in the SiO$_2$ content of the samples was entirely accounted for by an increase in the SiO$_2$ shell thickness. Figure 4a shows the dependence

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**Figure 2.** The IR spectra of (a) PS particles after addition of PVP to the reaction mixture and (b, c) PS core/SiO$_2$ shell composite particles (b) before and (c) after thermal treatment.
of the S of CPs exposed to temperatures from 200 to 1200°C calculated using the BJH model, as well as the pore size distribution (at a thickness of the SiO$_2$ shell of ~17 nm). All the nitrogen adsorption–desorption isotherms belong to type IV, which is characteristic of mesoporous materials (see the inset in Figure 4b). The mean size of the pores was ~3 nm. Note that the pore size distribution curve of none of the samples has a second maximum in the region of larger sizes, which indicates the absence of pores larger than 3–4 nm.

Figure 3. (a) TGA curves of PS core/SiO$_2$ shell composite particles (the numbers at the curves correspond to the ordinal numbers of the samples in the table; see the “Materials and methods”) and original PS particles. (b–d) TEM images of SiO$_2$ shells obtained after thermal treatment of the composite particles synthesized at different TEOS concentrations: (b) 0.05 M, (c) 0.2 M, and (d) 0.4 M.

Obviously, the pores were formed by PVP molecules adsorbed onto the PS particles and incorporated in the SiO$_2$ shells. PVP added to the reaction medium was adsorbed onto the positively charged surface of the particles, a certain amount of PVP remaining in the solution. During the formation of a thin SiO$_2$ layer (at short TEOS hydrolysis reaction times), PVP molecules were adsorbed on this layer due to hydrogen bonding between the carbonyl groups of PVP and OH groups formed on the SiO$_2$ surface [25]. Further growth of the shell (with increasing reaction time) was accompanied by incorporation of more PVP (apart from that adsorbed on the PS particles) into the SiO$_2$ shells.

TGA showed that the temperature of the thermal destruction of PVP, as well as that of PS, was ~400°C. The PVP elimination upon thermal treatment at 400°C resulted in the formation of pores. The C(PVP) in the reaction mixture was 4 mg/ml and its MW was 55 kDa in all samples.
With increasing temperature of the thermal treatment from 200 to 400°C, the S of the CPs increased from 15 to 270 m²/g. The reason was that exposure to a temperature of 200°C did not cause destruction of the PS core or the PVP molecules incorporated in the SiO₂ shell, whereas heating to 400°C resulted in their complete elimination and formation of pores and a cavity within the SiO₂ shell, thereby increasing S. Exposure to temperatures of 600°C and higher caused a considerable decrease in S because of sintering of the pores.

An increase in the concentration of PVP (MW = 55 kDa) introduced into the system before the formation of SiO₂ shells from 1 to 7 mg/ml led to an increase in S from ~40 to 270 m²/g (Figure 4c). At C(PVP) = 3 mg/ml, it reached the maximum value and did not change with further increase in C(PVP) to 7 mg/ml. This indicated that the surface of the PS particle was completely saturated with PVP at C(PVP) = 3 mg/ml. The pore diameter remained unchanged (~3 nm) in the entire C(PVP) range studied.

Figure 4. (a) Dependence of the specific surface area (S) on the temperature of treatment of PS core/SiO₂ shell composite particles. (b) Size distribution of the pores in the SiO₂ capsules obtained by treatment of the composite particles at 400°C. The inset shows a typical adsorption–desorption isotherm of a sample of these SiO₂ capsules. (c) Dependence of the S value of the composite particles exposed to a temperature of 400°C on the PVP concentration in the reaction mixture.
Porometry data showed that an increase in the PVP MW from 10 to 340 kDa only slightly affected the pore diameter (Figure 5a). For example, the mean pore diameter was ~3 nm at PVP MW = 10 kDa and ~4 nm at PVP MW = 340 kDa. In all cases, C(PVP) was 7 mg/ml; i.e., it was considerably higher than the concentration at the saturation of the PS surface with PVP molecules. These data agree with the results of other studies [20, 26]; however, the authors of those studies do not suggest any explanation to this effect.

It was demonstrated that the amounts of the polymer adsorbed onto TiO$_2$ [27] and PS [28] particles are independent of the PVP MW (in the range from 10 to 360 kDa). Photon correlation spectroscopy has shown that the thickness of the adsorbed PVP layer is considerably smaller than the diameter of a globule of the polymer with the corresponding MW [27]. This has led to the conclusion that the most part of each PVP polymeric chain (irrespective of the MW) is adsorbed on the PS surface [27]. The other part of the molecule, which does not interact with the PS particle, is oriented perpendicular to the surface. Apparently, this latter part of the molecule is involved in the formation of pores in the SiO$_2$ layer. This explains the independence of the diameter of pores formed in the SiO$_2$ layer on the PVP MW observed in our study. It should be noted that additional studies are necessary to reliably determine the cause of this nontrivial phenomenon.

**Figure 5.** (a) - Size distribution of the pores in the SiO$_2$ capsules formed in the presence of PVP with different molecular weights: 1, 10 kDa; 2, 22 kDa; 3, 340 kDa. (b) – dependence of the amoxicillin concentration in the physiological saline on the square root of the time of incubation of loaded SiO$_2$ capsules.

Loading of amoxicillin into SiO$_2$ capsules and its release. We performed model experiments to estimate the possibility of using SiO$_2$ capsules formed by means of thermal treatment of PS core/SiO$_2$ shell CPs as containers for drug delivery. In these experiments, capsules made out of CPs with a shell thickness of ~17 nm were used; amoxicillin served as a model loaded substance. The SiO$_2$ capsules were dispersed in SBF and incubated at room temperature for different periods of time while intensely stirring. After different periods of incubation in physiological saline (0.5, 1, 2, 6, 9, and 24 h), the SiO$_2$ capsules were sedimented by centrifugation. The degree of amoxicillin release was determined from the light absorbance of the supernatant at the wavelength corresponding to the peak of amoxicillin light absorbance (245 nm). The temperature and pH of the physiological saline were maintained at the levels close to physiologically normal ones (37°C, pH 7.4) to simulate the release of amoxicillin from SiO$_2$ capsules in the human body.

With increasing time of incubation of amoxicillin-loaded SiO$_2$ capsules in SBF, the light absorbance of the supernatant increased due to an increase in the amoxicillin concentration in SBF. Approximately 50% of the amoxicillin loaded into the capsules was released within 30 min of incubation. As the incubation time increased to 24 h, another ~30% of the drug was released into the solution. The release of another 15% of amoxicillin took substantially more time (about five days).

Figure 5b shows the dependence of the amount of amoxicillin released into SBF on the square root of the incubation time. As seen in the figure, this dependence is close to linear, which suggests that the
release of the drug from SiO$_2$ capsules is a diffusion-controlled process and can be satisfactorily approximated by Higuchi's diffusion model [29, 30]. Note that this dependence would have been linear in the case of a purely diffusion process. The deviation from the linear pattern in our case may have resulted from partial dissolution of SiO$_2$ in the physiological saline [31] and change in the diffusion coefficient in the course of the release of the amoxicillin load.

4. Conclusions

Stober's method has been used to synthesize PS core/SiO$_2$ shell composite particles. The dependences of the SiO$_2$ shell structure (its thickness, roughness, homogeneity, continuity, and porosity) on the conditions of its formation, including pH, TEOS concentration, reaction time, and PVP concentration and molecular weight, have been determined. It has been demonstrated that variation of these conditions makes it possible to obtain SiO$_2$ shells with thicknesses from ~4 to 17 nm and different morphologies on the surface of PS particles.

The PVP molecules preliminarily adsorbed on the PS particles have been shown to be incorporated into the SiO$_2$ shell in the course of its growth, which results in the formation of pores ~3 nm in diameter. Variation of the PVP concentration in the reaction medium allows the number of pores and the specific surface area of both PS and SiO$_2$ capsules made out of them to be changed within wide ranges.

We have demonstrated that the resultant mesoporous SiO$_2$ capsules can be used as containers for delivery of drugs (as exemplified by amoxicillin). The kinetics of the release of amoxicillin loaded into SiO$_2$ capsules under simulated physiological conditions (capsules incubated in physiological saline) has been studied. The characteristic stages of this process have been determined.

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