Synthesis and characterization of poly(sodium-p-styrenesulfonate)/modified SiO₂ spherical brushes

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Abstract. The multistep procedures for preparing novel anionic spherical polyelectrolyte brushes (ASPB) by grafting sodium-p-styrenesulfonate (SSS) from the surface of γ-methacryloxypropyl trimethoxy-silane modified SiO₂ nanoparticles were demonstrated. The morphology of ASPB was characterized by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). The core radius R_c and hydrodynamic radius R_h of ASPB measured by Zeta Potential/Particle Sizer (ZLS) were ca. 50nm and (84.5±1) nm respectively. The percentage of grafting (PG%) of polyelectrolyte brushes was 4.3% investigated by Thermo-gravimetric analysis (TGA). Detailed characterizations on ASPB were performed by cleaving the grafts from the anchoring surface. The molecular weight (M_w) and polydispersity (M_w/M_n) of brushes were $1.788 \cdot 10^3$ g/mol and 1.6 respectively from Gel Permeation Chromatography (GPC) measurements. Moreover, R_h and ζ-potential of ASPB in the presence of aqueous NaCl solutions of different concentrations were discussed.

1. Introduction

Polyelectrolyte brushes consist of polyelectrolyte chains attached to planar or curved surfaces. Owing to novel properties brought about by the strong electrostatic interaction between the densely grafted highly charged chains, an intense research on these systems has been done in the past twenty years. The field of polyelectrolyte brushes is explored as one of the most active fields in polymer science [1, 2]. If the polyelectrolyte chains affix to the surface of spheres, spherical polyelectrolyte brushes (SPB) result [3, 4]. With the advantage of spherical symmetry or quasi-symmetric structure, SPB have been used in a variety of areas, such as organic-inorganic composite materials [5], carrier system of nanoparticles [6], biocompatibility [7], papermaking [8], etc. Hence, the synthesis of novel SPB to meet the

application needs has attracted considerable attention recently.

In general, the synthesis of SPB by chemically grafted polyelectrolytes [9, 10] mainly involves two different strategies: 'grafting to' and 'grafting from'. The former method is applied by attaching polyelectrolyte chains with appropriate functional end or side groups to reactive surfaces. The grafting density of brushes formed is limited in this fashion because of the steric hindrance among the preformed polymers [11–13]. The latter strategy, the so-called 'grafting from' technique [14–17], is based on the surface modified by polymerization initiators. Due to bearing initiator functionalities on the surface of core, it can lead to a dense layer of chemically bound polyelectrolyte chains.

In this study, we have succeeded in grafting sodium-p-styrenesulfonate (SSS) from the surface of modified SiO_2 using conventional free radical polymerization. Compared with the methods which are widely used in synthesizing polyelectrolyte brushes, such as ATRP (atom transfer radical polymerization) polymerization and RAFT (reversible addition-fragmentation chain transfer) polymerization, this approach is more simple, practicable and maneuverable. In other words, this technique is of significance for extensive industrial applications due to its low cost.

2. Experimental
2.1. Materials
Tetraethyl orthosilicate (TEOS), γ-methacryloxy-propyl trimethoxy-silane and sodium-p-styrenesulfonate (SSS) were purchased from Sinopharm Chemical Reagent Ltd.. 2,2-Azo-bis-iso-butyronitrile (AIBN) purchased from Shanghai Chemical Co., Ltd. was recrystallized from ethanol and dried under vacuum. Other chemicals and solvents including Hydrochloric acid (HCl, 34 wt%), Ammonia (NH_3 (aq), 25–28 wt%), Sodium hydroxide, toluene and ethanol were analytical reagents. They were used without further purification.

2.2. Preparation and modification of SiO_2 nanoparticles
Monodisperse spherical SiO_2 nanoparticles (ca. 100 nm) were prepared using tetraethoxysilane by sol-gel method [18]. The γ-methacryloxypropyl tri-methoxy-silane was used to introduce ethylene groups onto the surface of SiO_2 nanoparticles and create a cleavable group for grafted polyelectrolyte chains. In a typical run, 4.2 g of γ-methacryloxy-propyl trimethoxy-silane was dissolved in 100 ml of ethanol/water (10/1, v/v) mixture, followed by

adjusting pH to 4 with HCl for the hydrolysis of γ-methacryloxypropyl trimethoxy-silane. The hydrolysis reaction proceeded at room temperature for 1h. After the complete addition of 100 g of 4 wt% SiO_2 dimethylcarbinol suspension, the reaction mixture was stirred vigorously at 70°C for 5 h. The products were then separated from the mixture with a high-speed centrifuge (TG16-II, Changsha PINGFAN Instruments and Meter Co., Ltd.), and washed with ethanol three times by repeated centrifugation. The resulting products were dried in vacuum at 65°C for 12 h.

2.3. Synthesis of ASPB
The surface-initiated polymerization of SSS monomer on modified SiO_2 nanoparticles was carried out in the presence of a small amount of sacrificial initiator AIBN under a nitrogen atmosphere. The reaction protocol in Figure 1 clearly shows the sequence used to synthesize the brushes and cleave them from the silica particles. An amount of 10 g of 4 wt% modified SiO_2 ethanol/water (10/1, v/v) mixture was appended into a three-necked flask containing 100 ml of toluene, followed by addition of 12 mg of initiator [AIBN] with vigorously stirring. After the mixture was heated to 40°C, 400 mg of monomer [SSS] was then added. Polymerization was allowed to proceed for 24 h. The synthesized ASPB were separated from toluene, and subjected to three sequential washings with ethanol and distilled water before finally being dried in vacuum at 65°C for 12 h. The products were stored in a desiccator for other analytical experiments.

2.4. Cleavage of grafted polyelectrolyte chains
The chemistry for cleaving long polyelectrolyte chains from the surface of modified SiO_2 nanoparticles was also illustrated in Figure 1. The ASPB
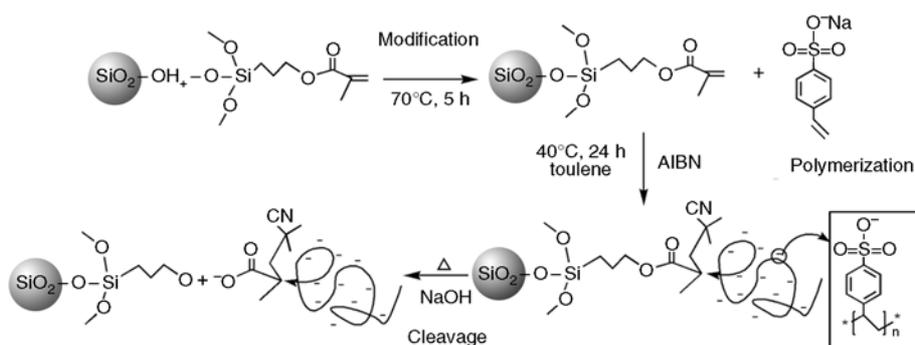
Figure 1. The reaction scheme for the synthesis of ASPB and the hydrolysis of PSS chains

were hydrolyzed by refluxing in 2M of NaOH (aq) at 85°C for 48 h. The SiO₂ cores and grafted poly-electrolyte brushes in the reaction mixture were then carefully separated by centrifuging. The PSS chains were obtained by extraction, neutralization and concentration of supernatant.

2.5. Characterization methods

Fourier transform infrared spectrum (FTIR) was recorded using a Nicolet AVATAR 360FT [Japan] spectrometer in region between 4000 cm⁻¹ and 500 cm⁻¹. The morphologies of samples were characterized by Transmission electron microscopy (TEM) and Scanning electron microscopy (SEM). TEM measurements were performed on a JEM-100CX II transmission electron microscope at an acceleration voltage of 100 kV. SEM images were made with a high resolution Quanta 200 scanning electron microscope operated at 30 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a FEI 'Quanta 200' instrument operating at a voltage of 30 kV with MnKα radiation. The $PG\%$ of polyelectrolyte brushes was calculated by Thermo-gravimetric analysis (TGA). TGA measurements were conducted with a SETSYS-1750 [SETARAM] instrument at the heating rate of 10°C/min from 25 to 750°C under a nitrogen atmosphere. The average initial sample mass was ca. 5 mg. The $PG\%$ of polyelectrolyte brushes could be defined by Equation (1) [19]:

$$PG\% = \frac{m_1}{m_2} \cdot 100\% \qquad (1)$$

where m_1 is the weight of all grafted PSS brushes, m_2 is the weight of SiO₂.

Gel Permeation Chromatography (GPC) was performed on Spectra SERIES P100 to obtain the molecular weight distribution of brushes. The surface grafting density could be defined as moles of polymer graft per gram [mole/g] or per square [mole/m²] of the matrix. Knowing the average molecular weight (M_w) and the $PG\%$ of polyelectrolyte brushes, the surface grafting density σ was calculated using Equation (2) [20]:

$$\sigma = \frac{PG}{M_w} \qquad (2)$$
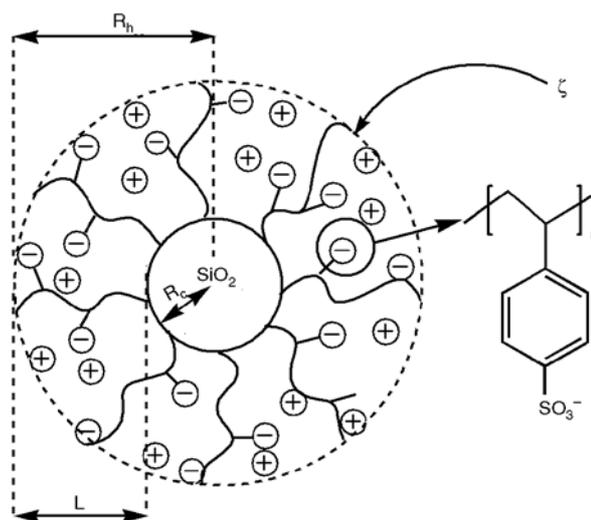
Figure 2. A sketch of ASPB in this study

Considering the surface area of silica particles, the calculation of surface grafting density could also be achieved by chains per square nanometer surface.

The Zeta Potential/Particle Sizer (ZLS, Nicomp 380, USA) was used to measure the ζ-potential and R_h of ASPB. Figure 2 displayed this model system termed ASPB. The core radius R_c consisted of the radius of SiO₂ and the thin layer thickness of γ-methacryloxypropyl trimethoxy-silane, from which polyelectrolyte chains (PSS) were grafted. L denoted the thickness of the brush layer, R_h the hydrodynamic radius and ζ the zeta potential.

3. Results and discussion
3.1. FTIR and XPS analyses

Figure 3 shows the FTIR spectra of SiO₂ (a), modified SiO₂ (b), cleaved PSS chains (c) and SSS (d).
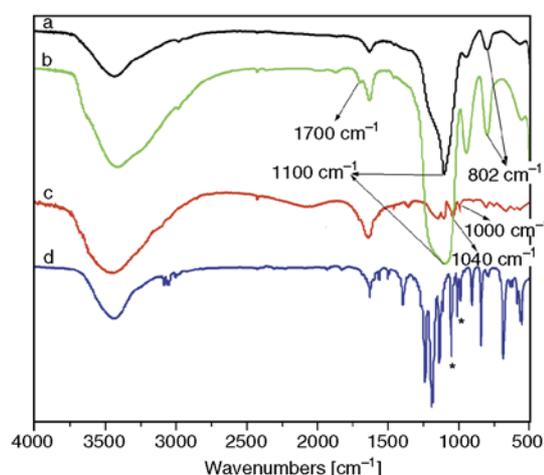
Figure 3. FTIR curves of SiO₂ (a), modified SiO₂ (b), cleaved PSS chains (c), and NaSS (d)
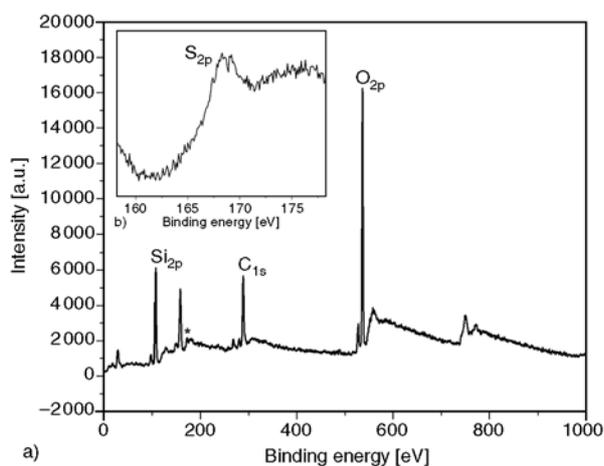
Figure 4. XPS spectra of wide region spectroscopy (a) and S 2p (b) of ASPB

The characteristic peaks at 1100 and 802 cm^{-1} for both SiO_2 (Figure 3a) and modified SiO_2 (Figure 3b) are visible, attributed to the Si–O–Si stretching vibration. The spectrum of modified SiO_2 (Figure 3b) displays the characteristic absorption bands at 1700 cm^{-1} of C=O stretching vibration of the carboxyl group (–COO–), which suggests that γ-methacryloxypropyl trimethoxy-silane interacts with SiO_2. The FTIR spectra of cleaved PSS chains and SSS are shown in Figure 3c and Figure 3d, respectively. Compared with the characteristic peaks in the FTIR spectrum of SSS, major characteristic peaks appear in the FTIR spectrum of cleaved PSS chains. The peaks at 1000 and 1040 cm^{-1} are attributed to the S=O stretching vibration [21] confirming the existence of PSS chains on modified SiO_2 surface. Thus the FTIR spectra clearly support the surface modification reaction and polymerization given in Figure 1.

Figure 4a shows a typical XPS wide-scan spectrum for ASPB in which the exhibited peak at 168.5 eV is observed. The narrow spectrum of S 2p is also displayed in Figure 4b. Thereby, the appearance of sulfur signal further supports the surface modification reaction.

3.2. Morphologies and particle size distribution

The TEM and SEM images clearly indicate the morphologies of SiO_2, modified SiO_2 and ASPB. As shown in Figure 5, they are well dispersed and
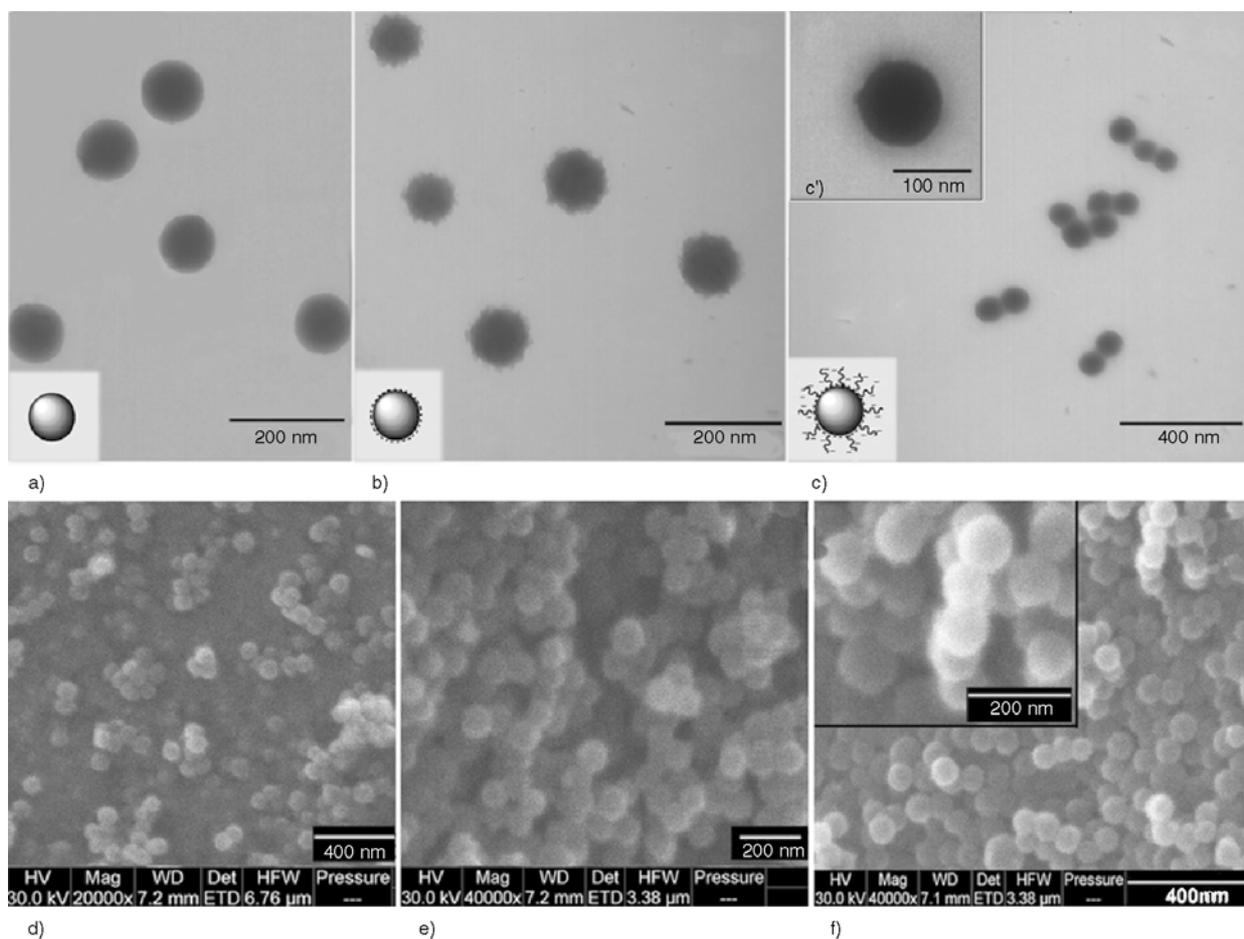
Figure 5. TEM and SEM images of SiO_2 (a, d), modified SiO_2 (b, e), ASPB (c, f) and an enlargement of c (c')

have uniform spherical structure. The average diameter of SiO_2 core is ca.100 nm. Figure 5c and Figure 5f display the TEM and SEM images of ASPB. The blurring and hair edges can be observed in Figure 5c' which is an enlargement of Figure 5c. The hydrodynamic radius R_h of ASPB is (84.5±1) nm determined by ZLS, which demonstrates that the polyelectrolyte brushes have been anchored onto modified SiO_2 cores successfully.

3.3. Determination of percentage of grafting (*PG%*)

For any brush polymer system *PG*% is an important factor which is related to the morphology of brushes and determines the properties of the system. In order to calculate the *PG*% of PSS brushes on the surface of modified SiO_2 cores, TG-DTG is employed (Figure 6). Compared with the SiO_2, the main weight losses for modified SiO_2 (10.1%) and ASPB (13.4%) have occurred between 200 and 750°C. The TGA thermogram of γ-methacryloxypropyl trimethoxy-silane is also displayed as insert (Figure 6d) to assess the thermal decomposition temperature of products. As shown in Figure 6d, the weight loss of γ-methacryloxypropyl trimethoxy-silane occurs in the temperature range of 90–190°C which may be because of the thermopolymerization. The decomposition temperature sections of modified SiO_2 and the number of DTG peaks of ASPB are different. For the modified SiO_2, only one endothermic peak at 458°C is observed, attributed to the decomposition of γ-methacryloxypropyl trimethoxy-silane with 90.2% residues. In the case of ASPB, a new endothermic peak appears at higher
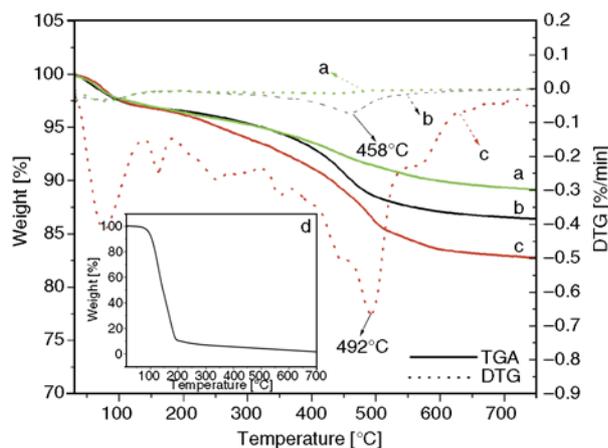
Figure 6. TG-DTG curves of SiO_2 (a), modified SiO_2 (b), and ASPB (c); the insert shows the TGA curve of γ-methacryloxypropyl trimethoxy-silane (d)

temperatures (490°C) [22] with 88.1% residues. It may be due to the thermal insulating property of SiO_2 particles. More energy is required, which suggests that the polymer has been bonded to modified SiO_2 nanoparticles. The *PG*% is 4.3% calculated from Equation (1).

3.4. Molecular weight and surface grafting density

After cleaving the polyelectrolyte chains from the surface of modified SiO_2 nanoparticles, the molecular weight distribution of PSS brushes is measured by GPC. The GPC curve of cleaved PSS chains is shown in Figure 7. Taking 0.1 M NaCl (aq) as mobile phase, PEG is used as the internal standard at room temperature. The M_w and polydispersity (M_w/M_n) are $1.788 \cdot 10^3$ g/mol and 1.6 respectively. The surface grafting density σ is $2.013 \cdot 10^{-5}$ mol/g or 0.047 μmol/nm².
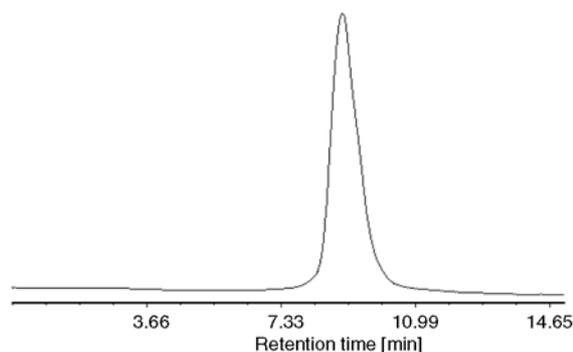
Figure 7. GPC curve of cleaved PSS chains

3.5. ζ-potential and R_h

Figure 8 illustrates the ζ-potential and R_h of ASPB as a function of aqueous NaCl solutions of different concentrations. It is shown that the magnitude of ζ-potential and R_h decrease with increasing salt concentration. At the lowest salt concentration (10^{-4} M), electrostatic interaction prevails and the grafted polyelectrolyte chains adopt an extended conformation. Intermediate salt concentrations result in a partial screening of the electrostatic interaction and a shrinking of the brush layer. As shown in Figure 8, when salt concentration is around 0.1 M, contraction of the brush layer becomes pronounced ($R_h \approx$ 60 nm). This effect can be well captured by the theory of Hariharan *et al*. [23]. In case of ASPB, the electrostatic screening increases with increasing salt concentration resulting in a reduced elec-
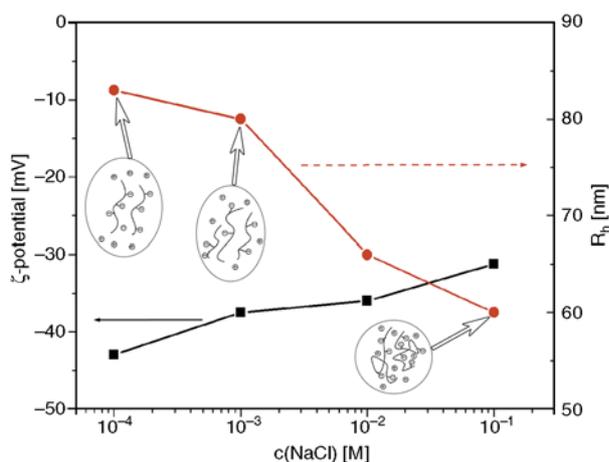
Figure 8. ζ-potential and R_h of ASPB as a function of aqueous NaCl solutions of different concentrations ($T = 25°C$, pH = 6, c(ASPB) = 1 mg/ml)

trophoretic mobility [24]. This is presumably due to the fact that continuous collapse of the brush layer with salt concentration has the effect of moving the shear plane closer to the surface, thus the ζ-potential of particles decreases [25]. In monovalent electrolyte solution (aqueous NaCl solutions), the value of ζ-potential at salt concentration of 0.1 M is still below -30 mV.

4. Conclusions

In this paper, novel ASPB have been successfully synthesized using conventional free radical polymerization. Different characterization and analytical methods confirm PSS brushes have been attached to the surface of modified SiO_2 cores. The synthesized ASPB are well dispersed and have uniform spherical structure, high grafting density and a narrow molecular weight distribution. Upon adding sodium ions (Na^+) the brush layer responds by contracting, and the ζ-potential of particles decreases.

Acknowledgements

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