Synthesis and characterization of silica-polyvinyl imidazole core–shell nanoparticles via combination of RAFT polymerization and grafting-to method

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The silica–polyvinyl imidazole core–shell nanoparticles (silica/PVI NPs) with controlled shell thickness and narrow distribution size were fabricated via a “grafting-to” method. First, O-ethyl xanthate terminated PVI with various chain lengths was produced via the reversible addition–fragmentation chain transfer (RAFT) polymerization using O-ethyl-S-phenyl dithiocarbonate (EPDC) as RAFT agent. Next, three synthesized PVI of different molecular weights (3.4, 6.6, and 11 kg/mol) were successfully grafted to the methacrylate modified silica NPs from solution by radical mediated grafting-to method. These core–shell NPs were then characterized by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectrum measurements (XPS), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). Polyvinyl imidazole molecular weight, reaction time, polymer concentration, and reaction temperature were all used to control the grafting reaction for PVI grafting densities and shell thicknesses. The highest grafting density obtained was close to 1.2 chains/nm\(^2\) and was achieved for 3.4 kg/mol PVI at 80°C. The prepared silica/PVINP displayed efficient antifouling properties and stability in concentrated sodium chloride aqueous solutions over a broad pH range for a period of at least 7 days. Copyright © 2017 John Wiley & Sons, Ltd. Additional Supporting Information may be found online in the supporting information tab for this article.

Keywords: core–shell; silica nanoparticle; polyvinyl imidazole shell; RAFT polymerization; grafting to

INTRODUCTION

Over the past few decades, core–shell structured silica/polymer nanoparticles (NPs)\textsuperscript{[1–7]} attracted much attention due to their unique properties such as surface functionality, encapsulation capability, and tunable surface permeability. To date, two main routes including physical\textsuperscript{[8–12]} and chemical\textsuperscript{[13–15]} methods have been exploited for constructing of core–shell material polymeric shells. Among them, chemical methodologies are preferred due to polymer layer stability in adverse conditions.

Polymer substances can be chemically immobilized to various substrates via two main approaches namely the "grafting-from"\textsuperscript{[16,17]} and the "grafting-to"\textsuperscript{[18,19]} approaches. In the "grafting-from" approach, polymerization is directly initiated from initiator-functionalized surfaces. However, grafting-from methods not only tend to produce polydisperse brushes but also require relatively complicated chemical synthesis, and conventional polymer characterization methods cannot be utilized. On the other hand, the "grafting-to" approach involves the tethering of prefabricated polymer chains to substrates via a chemical reaction between functional groups of the polymer chains and the surface. Reversible addition–fragmentation transfer (RAFT) polymerization\textsuperscript{[20–22]} has received increasing interest as a widespread method to prepare well-defined polymers with advanced architectures. Reversible addition–fragmentation transfer route not only has attractive characteristic of free radical polymerization but also as a sustainable process meets the almost all of required criteria in the field of green chemistry.\textsuperscript{[23]} In fact, using grafting-to method in combination with RAFT route techniques, preparation of fully characterized and optimized polymer for construction of well-defined and controlled polymer brushes is more feasible.

Polynimide (PVI) and its derivatives have been investigated due to unique physical and chemical properties with potential applications in various fields such as absorption,\textsuperscript{[24]} enzyme immobilization\textsuperscript{[25,26]} and gene delivery systems.\textsuperscript{[27,28]} Nowadays, PVI core–shell composites with inorganic materials such as silica,\textsuperscript{[29]} iron oxide,\textsuperscript{[24]} and montmorillonite\textsuperscript{[30]} also have gained attention due to improved properties of these materials in various aspects as compared to the corresponding pure and cross linked PVI. Peng et al.\textsuperscript{[5]} recently prepared silica/poly (N-vinylimidazolium) nanospheres by combined RAFT polymerization and thiol-ene click chemistry; however, the mechanism of grafting and effect of various factors on shell tackiness and shell density remain unclear. In this paper, we present a more detailed study of the controlled synthesis of silica/PVI NPs using combination of
radical mediated grafting-to and RAFT polymerization method. O-ethyl xanthate terminated PVI with various chain lengths was first prepared via RAFT polymerization, and then a series of silica/PVI NPs were prepared by radical mediated grafting of PVI on the surface of methacrylate-functionalized silica NPs. Then, the formation of the PVI shell was investigated with the Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectrum (XPS), and transmission electron microscopy (TEM) analyses. The effects of reaction time, the polymer molecular mass, temperature, and polymer concentration on the silica/PVI characteristics were studied using dynamic light scattering (DLS) and TGA analyses. Aggregation properties as well as stability of the silica/PVINPs in aqueous solutions were assessed in the next experiments.

EXPERIMENTAL SECTION

Materials
Silica NPs with average particle size of 12 nm were purchased from Aldrich. 1-Vinylimidazole (VI, Aldrich, 99%) was distilled under reduced pressure and used as the monomer. 2, 2'-Azobis (2-methylpropionitrile) (AIBN, Aldrich, 98%) was recrystallized from methanol (Merk, 99.9%) before use. Toluene was refluxed over sodium slices and benzophenone as indicator. 3-(Trimethoxysilyl) propyl methacrylate (MPS, Aldrich, 98%), absolute ethanol (Merk, 99.5%), potassium hydroxide pellets (Aldrich, 85%), anhydrous carbon disulfide (Merk, 99.9%), benzyl bromide (Merk, 98.0%), and diethyl ether (Merk, 99.7%) were used as received. O-ethyl-S-phenyl dithiocarbonate and methacrylate-functionalized silica NPs (MPS-silica NPs) were prepared following previously described route elsewhere.[31,32] For dialysis, regenerated cellulose membranes (MWCO 3400) were used. All other chemical reagents were purchased from either Aldrich or Fisher and used without further purification.

RAFT polymerization of polyvinyl imidazole
Monodisperse, O-ethyl dithiocarbonate end-functionalized PVI of different molecular weights (Mn, 3400, 6600, and 11,000 g/mol) were obtained by RAFT polymerization of vinyl imidazole by the following general method. In a typical reaction, VI (2.7 g, 29.3 mmol), AIBN (30 mg, 0.048 mmol), and 0.042 g (0.48 mmol) of EPDC were taken in a 50-ml vial in 30 ml of ethanol, and the solution was deoxygenated by the nitrogen bubbling for 10 min. The vial was sealed with a rubber septum under vacuum, and it was agitated at 70°C for 3 h. The polymerization was stopped by rapid cooling of reaction vessel with liquid nitrogen, and then the resultant mixture was precipitated in a large excess of acetone in ice bath and then isolated by filtration. The resulting product was dried under vacuum at ambient temperature to yield PVI with RAFT pendant groups as a white powder. The polymer was characterized by gel permeation chromatography (GPC) using polystyrene calibration.

Synthesis of silica/polyvinyl imidazole nanoparticles
A number of different batches of silica/PVI NPs were synthesized during the course of this study. A typical synthesis of silica/PVI NPs is described as follows: methacrylate-functionalized silica NPs (50 mg, 0.011 mmol of the initiating sites), PVI (100 mg, 0.011 mmol), and methanol (2.44 ml) were added to a polymerization tube equipped with a magnetic stirring bar. The NP mixture were then dispersed by ultrasonication for 20 min. Afterward, 7.9 mg (0.055 mmol) of AIBN was introduced into the reaction vessel, and the solution was degassed at 0°C by nitrogen injection for 20 min. After overnight stirring at 70°C, the reaction was stopped upon flask immersion into iced water. The obtained modified NP colloid was purified by three centrifugation/redispersion cycles with methanol (14,000 rpm, 20 min) and dried for 2 days at 50°C in a vacuum oven.

Characterization of silica/polyvinyl imidazole nanoparticles
The FTIR spectra of silica/PVI NPs samples were recorded using a Bruker Vector-22 FTIR spectrometer. Thermogravimetric curves were recorded between 25 and 800°C with heating rate of 10°C/min in N2 atmosphere on a SDT Q600 thermogravimetric analyzer. All samples were dried under vacuum at 80°C overnight prior to TGA runs. Considering the residue in the TGA curve as the weight fraction of the silica component, the graft density of the grafted PVI chains on silica surface can be estimated from following equations:

\[ G_r = \frac{W_{S/P,100^\circC}}{W_{S/P,800^\circC}} \]  
\[ G_p = \frac{G_r}{M_w,\text{GPC}(g)} \]
The molecular weight and polydispersity index (PDI, PDI = $M_w/M_n$) of the synthesized polymers were determined by an Agilent 1100 GPC system equipped with the PL Aquagel-OH MIXED-H columns and a Agilent 1260 Infinity II Refractive Index Detector. Water/acetonitrile mixer was used as eluent at flow rate of 1.0 ml/min at 20°C. Gel permeation chromatography system was calibrated using narrow-polydispersity polyethylene oxide standards with $M_n$ values ranging from 1620 to 71,100 (Varian Inc., UK). The data were processed using Agilent GPC/SEC software (32bit version 2.0).

The particle stability experiments with PVI-coated silica NPs were conducted (NaCl) electrolyte over a range of concentrations. The pH conditions of the bare and PVI-coated silica NPs were maintained at 4.5 (under which the colloidal particles were stable at low ionic strengths). Before an experiment, the stock NPs was dispersed using ultrasonication for 20 min. The stock dispersion was then added to the water samples to achieve the target concentrations. Particle size at different stages of the aggregation process was determined via DLS.

**RESULTS AND DISCUSSIONS**

**Synthesis of polyvinyl imidazole via reversible addition–fragmentation chain transfer polymerization**

The PVI with various molecular mass was successfully synthesized using standard RAFT procedure by adapting synthetic procedures previously reported in the literature.[33] O-ethyl-S-phenyl dithiocarbonate (EPDC) is a xanthate RAFT CTA that allows for high addition/fragmentation rates and stable radical leaving groups when used with vinyl imidazole, vinylpyrrolidone, and vinyl acetate monomers, which promotes polymer monodispersity. For these features, EPDC has been used for controlled growth of PVI. Due to steric limitation of already attached polymer chains in grafting-to method, only relatively short chains were used (Scheme 1).

The resulting polymers were characterized by size-exclusion chromatography (SEC) to determine the molecular weights and polydispersity indices of RAFT-synthesized PVIs. Characteristics of the PVI investigated in this study are presented in Table 1 with all polymers exhibiting low PDIs (<1.3) (Fig. 1). The presence of the characteristic absorption band of thiols at 2400 cm$^{-1}$ was confirmed by FTIR (Fig. 2).

**Synthesis of 3-(trimethoxysilyl) propyl methacrylate-silica nanoparticles**

The synthesis of methacrylate-functionalized silica nanoparticles is presented in Scheme 2. The amount of methacrylate group incorporated in the silica NPs, determined by TGA (Supporting Information, Fig. S1), shows the concentration of methacrylate to be 1.9 mmol/g for silica NPs. The high loading is probably indicative of a multilayer grafting of the methacrylate moiety. The presence of a trace amount of moisture solution probably led to the precondensation of the MPs in solution, leading to high grafting of methacrylate moiety onto silica NPs. The structure of MPS-silica NPs was established using FTIR and NMR as discussed later. The FTIR spectrum of MPS-silica displays the characteristic absorption around 1700 cm$^{-1}$, due to a carbonyl group in conjugation with a C=C group (Fig. 3). The absence of this peak in silica is indicative of surface-bound methacrylate group. The solid-state $^{13}$C CP-MAS NMR results of MPS-silica NPs (Fig. 2) also confirm grafting of propylmethacrylate moiety and are consistent with acquired results from FTIR.

![Scheme 1. Polymerization of vinyl imidazole via RAFT technique.](wileyonlinelibrary.com/journal/pat)
Radical coupling between 3-(trimethoxysilyl) propyl methacrylate-modified silica nanoparticle and xanthate end polyvinyl imidazole

The methacrylate functionalized silica NPs were subjected to radical grafting reaction with prepared O-xanthate end PVI produced by RAFT procedure (Scheme 2)\(^{[23,34,35]}\). All coupling reaction were conducted during 70 hr at 60°C in ethanol using AIBN as radical source (0.04 and 0.16 wt%, respectively). The silica/PVINPs were analyzed by FTIR techniques for monitoring the reaction progress. The introduction of the PVI chains on the MPS-silica surface resulted in shifting of carbonyl stretching vibrations of methacrylate moiety from 1700 to 1720 cm\(^{-1}\) (Fig. 3). This result agrees reasonably with PVI addition onto the double bond which reduces its conjugation to the adjacent carbonyl group. Furthermore, one additional characteristic peak that appeared at 1493 cm\(^{-1}\) corresponds to C\(=\)N stretching of PVI (Fig. 5).

The addition product silica/PVINPs, formed upon reaction of MPS-silica and PVI, were further characterized by SEM, TEM, and XPS analyses. Figure 4 displays a SEM micrograph of silica/PVI core shell particles with a diameter of approximately 25 nm. The silica/PVINPs in the cast films have intrinsic spherical shape with a diameter somewhat larger than that of bare silica. Moreover, no free polymer globules can be observed in the SEM images. This result suggests that the PVI grafted to silica surface.

The morphology of the silica/PVI50 NPs was observed using TEM, and the contrast between the PVI shell and silica core was increased using CsI (Fig. 4). The dark silica cores in the structure of the silica/PVI NPs are surrounded by a light gray

**Scheme 2.** Grafting of PVI to MPS-silica NP. [Colour figure can be viewed at wileyonlinelibrary.com]

**Figure 3.** FT-IR spectra of (a) bare SiO\(_2\), (b) SiO\(_2\)-g-MPS, (c) SiO\(_2\)/PVI NPs, and (d) PVI. [Colour figure can be viewed at wileyonlinelibrary.com]

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PVI shell. The average size of the core NPs is about 20 nm in diameter. Measurements of the shell thickness in the dried state according to Fig. 4 reveal the value of about 10.4 nm, and the overall radius of the silica/PVI NPs is about 30.4 nm.

X-ray photoelectron spectrum measurement spectra of PVI, bare silica, and silica/PVI NPs are compared in Fig. 5. As shown in Fig. 5a, the peaks at 100, 150, and 529 eV are related to the Si 2p, Si1s, and O 1s binding energies, respectively, corresponding to bare silica characteristic regions. After silica modification with PVI shell (Fig. 5a), the Si peaks had almost disappeared, while new peaks at 400, 285, and 163 eV have appeared assigned to N1s, C1s, and S2p, respectively, which is in good agreement with the presence of a xanthate end PVI layer on the silica substrate. Furthermore, the N1s narrow XPS scan of silica/PVI NPs was fitted by two main components at 400 and 402 eV (Fig. 5b) with a 1:1 ratio of the integrated areas, which corresponds to the two nitrogen atoms in imidazole. The core level C1s spectrum of silica/PVI NP also segregated into two components at 284.7 and 285.3 eV related to sp and sp3 hybridized carbon atoms, respectively (Fig. 5c). Thermogravimetric analysis also confirmed the presence of PVI on the silica NP as evidenced by an additional 20% weight loss corresponding to the grafted polyvinylimidazole (Fig. 2d). In summary, all of these observations are direct evidence of thick PVI layer formation on silica surface.

Kinetic dynamic light scattering and thermogravimetric measurements

The PVI with varied lengths (PVI50, PVI100, and PVI150, Table 1) has been chosen to study the effect of polymer chain length on produced silica/PVINP hydrodynamic diameter (Dh) and grafted polymer density on methacrylate-functionalized silica NPs. Two methods, DLS and thermogravimetric analysis, were used to analyze the hydrodynamic diameter and grafted polymer density, respectively.

For tracing the grafting reaction, samples were removed from the reactor at 10, 15, 25, 50, 70, and 90 hr of reaction for characterization. To achieve the high surface coverage of silica NPs, the molar ratios between the PVI and MPS-silica were all 50:1. The Dh increases of the all silica/PVI NPs included the two successive regimes and follows a similar trend (Fig. 6). Results show that more than 60% of the Dh increase was obtained during the first 15–25 hr of the reaction until a layer of overlapping chains is formed. As soon as the already grafted PVI chains begin to overlap and form an activation barrier, the kinetics enters the second regime, in which the film thickness continued to grow though at a slower rate.

As shown in Fig. 7, the grafting-to reaction is mainly governed by a diffusion process in both regimes. In the first regime, the reaction is limited by the PVI segmental diffusion. Obviously, for the longer PVI chains with a greater gyration radius, the grafting is slower due to greater average distance between the polymer xanthate group and the surface double bonds. In later stages of the reaction, grafting density rate was progressively reduced and approaches a plateau because all end-functional groups in the vicinity of the grafting interface were consumed and the grafting reaction limitations are changed from segmental diffusion limits to translational diffusion limits.

The Dh of silica/PVI NPs was observed to increase from 28 to close to 35 nm and then decreased slightly below 32 nm as the PVI molecular weight increased from 3.4 to 11 kg/mol. However, the grafting density decreased as the molecular weight increased (Fig. 6). A combination of several factors is behind this experimental observation. Among them are the size of polymer coil and polymer chain entanglement due to increasing PVI molecular weight that affect diffusion. In fact, the maximum grafting density was obtained at PVI molecular weight of 3.4 kg/mol.

Concentration of polymer has been shown to have a substantial effect on grafting density and grafting thickness of produced polymer brushes.[36] Measurements of Dh and grafting density of the resulting silica/PVI as a function of PVI concentration are summarized in Fig. 8. The results clearly demonstrate that the number of chains tethered per unit area of substrate was enhanced significantly with increasing PVI concentration. This is because with an increase in the solution concentration, more polymer chains are adsorbed onto the...
MPS-silica NPs; therefore, there is a commensurate increase in the number of reactive chain ends in the vicinity of the surface, ready to undergo chemical reaction with the active sites there. Figure 8 also shows that the \( \text{D}_h \) and grafting density of produced silica/PVI appear to reach a plateau at high polymer concentration. This reveals that continued increases in solution concentration beyond a certain point are ineffective in increasing the tethered chain density.

We perform further study and find that the surface coverage of silica particles is influenced by reaction temperature. Figure 9 shows the hydrodynamic diameters and grafting density of silica/PVINPs conducted at 60, 70, and 80°C. It was found that grafting at elevated temperatures led to higher amounts of grafted PVI and larger hydrodynamic diameter resultant silica/PVINPs. This may be due to the increment in segmental diffusion of PVI with increasing temperature. We concluded that thickness and density of the PVI nanoshell over the silica core can be controlled by grafting at various grafting conditions.

**Stability of silica/polyvinyl imidazole nanoparticle dispersions**

The stability of core shell NPs in an aggressive environment is a crucial prerequisite upon which hinges the successful use of its antifouling properties. In this study, DLS measurements were conducted to monitor the changes in the hydrodynamic diameter of the silica/PVI NPs during their incubation in electrolyte solutions to evaluate their stability. According to literature,[37] in the presence of sodium chloride, the bare silica NPs flocculated immediately and extensively through electrostatic destabilization as described by the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. The stability of the
Silica/PVI NPs was investigated in 0.1 wt% dispersions by DLS at different electrolyte concentrations and pH, as shown in Fig. 10. The z-average particle diameter changes little as the concentration of sodium chloride is increased from 0 up to a saturated solution (Fig. 10a). This demonstrates the highly effective steric stabilization of these particles even at extreme ionic strengths.

Figure 10b shows the time dependence of the average particle diameter when dispersed in a 5 wt% in aqueous solution of sodium chloride. The NPs showed no increase in their size over 7 days. The surface attached PVI layer has to be sufficiently thick to provide a steric barrier that counterbalances the attractive van der Waals forces responsible for particle agglomeration. The influence of pH on the colloid stability of the PVI/silica NPs is shown in Fig. 10. The particles are stable over the very wide pH range of 1–12. Measurements taken 24 hr after adjusting the pH of the NP dispersions show no noticeable differences in the sizes of the particles in the pH range 4–12.

**CONCLUSION**

We demonstrated grafting of PVI on the methacrylate functionalized silica NPs based on radical mediated grafting-to method. The polymer grafting was confirmed by FTIR, XPS, and TEM analyses. Dynamic light scattering and TG results also indicated that grafting thickness and grafting density depended on grafting time, length of incoming chains, concentration of polymer, and reaction temperature. Furthermore, silica/PVI NPs are stable at 25°C for at least 7 days in high ionic strength solutions over a broad pH range. Therefore, the tunable tackiness and stability in various conditions, combined with the reported properties of this polymer make these PVI-grafted silica NPs to be potential candidates for new types of adaptive surfaces, and apply in heavy metal adsorbent, drug carriers, catalyst supports, and other technologies.

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**REFERENCES**


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