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polymer

Polymer 47 (2006) 947–950

www.elsevier.com/locate/polymer

Polymer Communication

One-step preparation of organosilica@chitosan crosslinked nanospheres

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Received 26 October 2005; received in revised form 13 December 2005; accepted 19 December 2005

Abstract

A one-step way to prepare organosilica@chitosan crosslinked nanospheres was developed through self-assembly of amphiphilic copolymers synthesized by concurrent grafting polymerization and sol–gel reaction. The core 'organosilica' was formed by hydrolysis and condensation of an alkyloxosilane-3-(trimethoxysilyl) propyl methacrylate (TMSPM) that was simultaneously polymerized using chitosan/*tert*-butyl hydroperoxide (TBHP) as redox-pair initiator. The well-defined nanospheres had adjustable sizes below 100 nm, and had not harmful residues impeding medical applications. This synthesis method simplified the preparation of silica@polymer spheres by eliminating the previous core-forming step, and could apply many water-soluble biopolymers containing $–NH_2$ groups as the shell materials.

Keywords: Polymer composite materials; Core–shell nanospheres; Biopolymer

1. Introduction

Inorganic–organic core–shell nanospheres have attracted a great deal of attention because of their potential applications in cosmetics, inks, paints, optics and electronics [1,2]. In these studies, silica is the material most often selected as core. The silica-polymer core–shell (silica@polymer) nanospheres have been fabricated by several methods: (a) surface-initiated polymerizations initiated by functional groups on cores, such as –OH, $–NH_2$, $–CH{=}CH_2$, and –R-Br, etc. [3]; (b) layer-by-layer adsorption technique, of which oppositely charged species were alternatively deposited on charged cores [4]; and (c) in situ emulsion and dispersion polymerizations employed to directly entrap inorganic nanospheres in the reaction media [5,6]. Despite the success of these approaches, there are still some drawbacks, such as tedious multiple-step syntheses [3,4], necessity of suitable surfactants [4] and very low surface grafting efficiency or encapsulation efficiency [3,5].

Among the various shell polymers, biocompatible and biodegradable polymers [7] have recently been covalently bonded to silica for applications in the biomedical areas, such as passivation of prosthetic devices and implants, and coating of drug-delivery devices [8]. However, these reported biodegradable shell polymers were limited in aliphatic polyesters, and the use of metal catalysts in most syntheses of biodegradable polyesters resulted in metallic residues impeding medical applications [9]. Therefore, we intended to develop a facile pathway, by which silica core could be covalently covered with suitable polysaccharides and proteins.

Chitosan is a versatile bio-polysaccharide widely applied in medical and pharmaceutical fields. Many hybrids of chitosan and silica have been prepared for applications such as protein chips, heterogeneous catalysis, gene deliveries, and biomedical scaffolds [10–12]. However, silica@chitosan crosslinked nanospheres have not been reported. In this communication, we reported a facile and bottom-up method to synthesize organosilica@chitosan crosslinked nanospheres. The core 'organosilica', different from the silica derived from tetraethoxy silane, was developed by hydrolysis and condensation of an alkyloxosilane: 3-(trimethoxysilyl)propyl methacrylate (TMSPM) that was simultaneously polymerized using a *tert*-butyl hydroperoxide (TBHP)/amino group ($–NH_2$) initiation system. TBHP/$–NH_2$ system has been reported as an efficient redox pair, which can generate radicals on the nitrogen atom of $–NH_2$ at low temperatures [13]. Although some copolymers have been prepared using this redox pair [14,15], the work presented here is the first one employing it to develop hybrid nanospheres.

2. Experimental part

Chitosan (medium molecular weight, 77% deacetylation determined by an elemental analysis), acetic acid,

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doi:10.1016/j.polymer.2005.12.063

3-(trimethoxysilyl) propyl methacrylate (TMSPM), and *tert*-butyl hydroperoxide (TBHP, 70% solution in water) were all purchased from Aldrich, and used as received. Freshly deionized and distilled water was used as the dispersion medium.

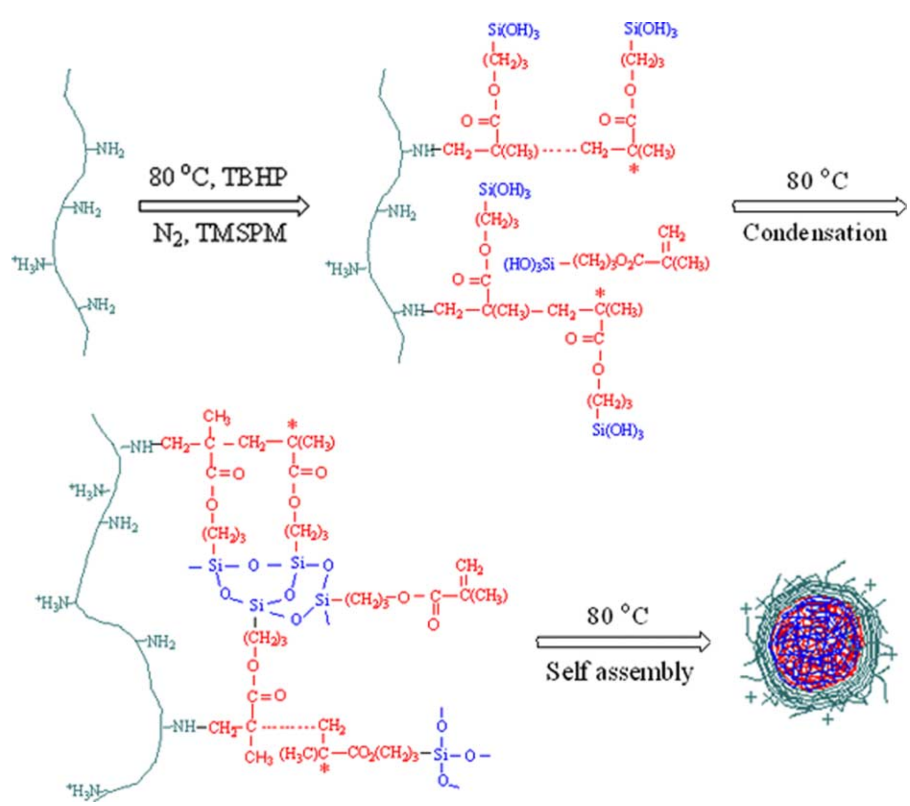
A typical synthesis of organosilica@chitosan crosslinked spheres was described as follows. In a flask equipped with a condenser and a nitrogen inlet, stirred chitosan solution (0.5 wt%, 100 mL) containing acetic acid (0.6 wt%) was purged with nitrogen for 30 min. About 2 mL TMSPM monomer was added at 80 °C and dissolved into water in 5 min. Then 1 mL 20 mM TBHP aqueous solution was added in one time. The mixture was stirred for 4 h under nitrogen. Finally, stable latex was obtained. The organosilica@chitosan hybrid nanospheres were carefully purified by repeated centrifugation, followed by decantation and resuspending in acetic acid solution (0.6 wt%). This procedure was repeated until conductivity of the supernatant was equal to that of the solution used.

The ζ-potential of obtained nanospheres was measured with a Brookheaven Zeta Plus Analyzer. FTIR spectra were recorded on an IR spectrometer (Perkin–Elmer, System 2000). The nanosphere morphology was observed under a scanning electron microscope (SEM) (Leica Cambridge Ltd, Stereoscan 440), and their core–shell structures were studied with a transmission electron microscope (TEM) (Philips, CM-20) at an accelerating voltage of 120 kV. Thermogravimetric (TG) curves were recorded by a thermal analyzer Netzsch TGA/DSC (STA 449 C Jupiter), with a heating rate of 10 °C/min and air atmosphere.

3. Results and discussion

The one-step synthesis process of organosilica@chitosan crosslinked nanospheres can be described as follows (Scheme 1). In the acidic aqueous solution of chitosan, TMSPM was quickly hydrolyzed into silanols and dispersed into aqueous phase. After TBHP was added, radicals generated on the N atom of chitosan $–NH_2$ groups, and the silanols with active vinyl groups were grafted onto chitosan chains. With the poly(vinyl silanol) side chains increasing, in situ condensation between adjacent Si–OH groups preferentially proceeded and microgels formed. As a result of the local gelation, the hydrophobicity of poly(propyl methacrylate) side chains became dominant and the amphiphilic copolymers self-assembled into core–shell sphere with chitosan as shell and organosilica as core. In practice, the transparent solution changed into translucent latex in about 30 min. This period was longer than the time for normal initiation of radical polymerization and shorter than the time for normal gelation of silanols. The fully reacted latex was stable over several months. However, when the reaction was stopped in 1 h, the latex agglomerated during storage. It was due to the large quantity of unpolymerized silanols and uncondensed Si–OH groups. The ζ-potential of the stable latex was measured with 1 mM NaCl solution as the dilution fluid. A highly positive ζ-potential value +68 was obtained, confirming the presence of chitosan on the sphere shells.

The obtained stable latex was dried and characterized by FTIR spectrometer. In the obtained FTIR spectra (Fig. 1), the absorption of TMSPM C=C at 1639 cm^{-1} clearly decreased



Scheme 1. Schematic description of the development of organosilica@chitosan crosslinked nanospheres.

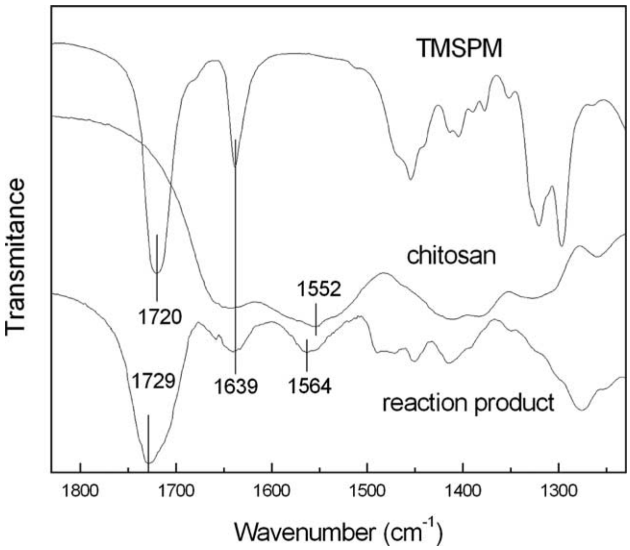


Fig. 1. FTIR spectra of pure TMSPM, pure chitosan and the synthesized hybrids.

after the reaction, using the absorption of TMSPM C=O as internal standurd; the C=O of TMSPM gave an absorption at 1720 cm^{-1}, while in latex product it moved to 1729 cm^{-1}, which was a characteristic of polymethacrylates. These results indicated a transition of the TMSPM vinyl monomer into polymer. For chitosan, its C=O had an absorption at 1641 cm^{-1}, and no change was found after reaction; the N–H in-plane bending had an absorption at 1552 cm^{-1} [12], while after reaction its absorption clearly moved to 1564 cm^{-1}, indicating the grafting at $–NH_2$ groups. The FTIR results approved the successful graft polymerization of vinyl silanols onto chitosan. Although some C=C groups remained in the product, the ungrafted monomers must have been incorporated into the organosilica cores by gelation, considering the good stability of the latex.

The organosilica@chitosan hybrid nanospheres were purified, dried on a silica wafer and observed under a SEM. Separate monodisperse particles with diameter around 100 nm were observed, as shown in Fig. 2(a). For TEM study, the sample was prepared by wetting a carbon-coated copper grid with a drop of dilute latex, and drying at room temperature before analysis. In Fig. 2(b) and (c), core–shell structure of the nanospheres was clearly observed, with dark organosilica core and gray chitosan shell. The sphere size was adjusted by changing the amount of TMSPM. When 0.5 mL TMSPM was used, the sphere size is about 30–50 nm, with shell of 10 nm thickness. When 2 mL TMSPM was used, the sphere size is distributed in 70–100 nm, with shell of 10 nm thickness.

Thermal stability of the purified nanospheres (obtained from 2 mL TMSPM) were evaluated with TG analysis, comparing to that of pure chitosan and TMSPM gel (the TMSPM was gelated in 0.6 wt% acetic acid solution and dried at 100 °C). From the TG curves in Fig. 3, following informations were deduced: decomposition of pure chitosan started at 230 °C; while in the hybrid particles, the decomposition of chitosan was clearly delayed. This delay should be caused by the grafting of silane

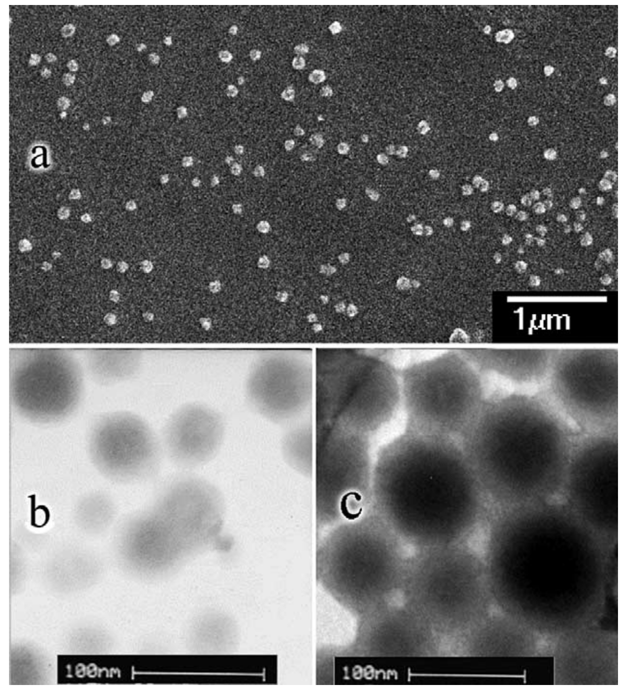


Fig. 2. Images of organosilica@chitosan nanospheres prepared in one-step: SEM image when 2 mL TMSPM was added (a); TEM image when 0.5 mL TMSPM was added (b) and when 2 mL TMSPM was added (c).

onto chitosan, the gelation of residual silanol groups in the core and the evaporation of produced water molecules, which consumed large amount of heat and thusly delayed the decomposition of chitosan. Similar phenomenon was observed in a previous report [2]. Because the temperature ranges of chitosan degradation and organosilica degradation overlapped, their weight losses cannot be clearly divided in the case of hybrid particles. Supposing the TMSPM gel and the core–shell hybrid particles had similar gelation degree, their gas losses in gelation and weight losses in organosilica degradation should be similar. In thus way, the chitosan weight percent in hybrid particles was estimated by subtracting the weight loss of

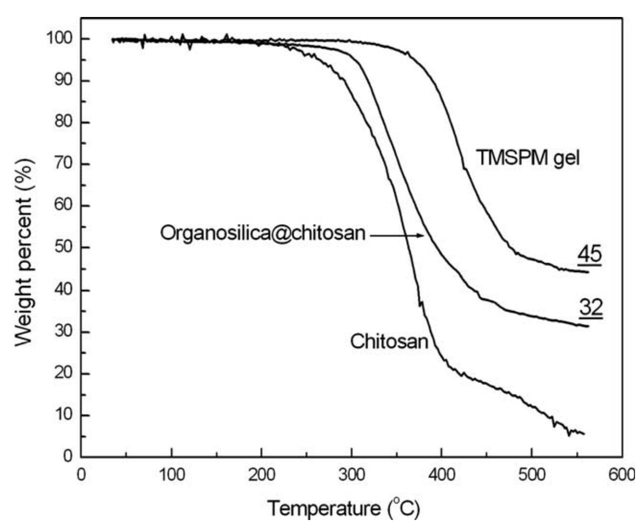


Fig. 3. TG curves of pure chitosan, pure TMSPM gel and the organosilica–chitosan nanospheres when 2 mL TMSPM was added.

organosilica (55%) from that of hybrid particles (68%). Finally, 13 wt% chitosan was deduced for the measured hybrid particles. This result is in consistant with the scales of the core–shell structure observed by TEM.

An interesting phenomenon worth to mention is that colors from pink to brown were observed for the produced latex (especially with low TMSPM content), dried film from the latex and sintered (600 °C) powders from the latex, while both pure chitosan and pure TMSPM gel were colorless. According to the report in the Science [16], these nanospheres should be highly emissive broadband phosphors, which were simply synthesized from gelation of alkyloxysilane in the presence of organic carboxylic acid (in our case, it is the acetic acid). Therefore, these core–shell nanospheres may also find applications related to optics.

4. Conclusion

Novel organosilica@chitosan nanospheres were synthesized in a one-pot way, basing on synergic grafting polymerization, sol–gel reaction and amphiphilic self-assembly. The core 'organosilica' was formed by hydrolysis and condensation of TMSPM that was simultaneously polymerized using $-NH_2$/TBHP as redox-pair initiator. The nanospheres had adjustable sizes below 100 nm, depending on the ratio of TMSPM to chitosan. This synthesis method simplified the preparation of silica@polymer nanospheres by eliminating the previous core-forming step, and by employing natural biopolymer as shell materials. Since a large quantity of bio-molecules contains $-NH_2$ groups (e.g. gelatin and casein), this method sheds new light on the preparation of a variety of silica@biomolecule hybrids. Thus synthesized organosilica@biopolymer nanospheres have not harmful residues, and are hopefully applied in heterogeneous catalysis, gene deliveries, and antibacterial technologies.

Acknowledgements

This work was supported by the Innovative Technology Funding ZP0D from the Hong Kong SAR government and the Postdoctor fellowship of the Hong Kong Polytechnic University.

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