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Synthesis of well-defined structurally silica–nonlinear polymer core–shell nanoparticles via the surface-initiated atom transfer radical polymerization

Jiucun Chen[a,*], Min Hu[a], Wendong Zhu[b], Yaping Li[a]

[a] *Department of Chemistry and Chemical Engineering, Ankang University, Ankang, Shaanxi 725000, China*
[b] *Department of agriculture and life sciences, Ankang University, Ankang, Shaanxi 725000, China*

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ABSTRACT

We report on the synthesis of the well-defined structurally silica–nonlinear polymer core–shell nanoparticles via the surface-initiated atom transfer radical polymerization. At first, 3-(2-bromoisobutyramido)propyl(triethoxy)-silane (the ATRP initiator) was prepared by the reaction of 3-aminopropyltriethoxysilane with 2-bromoisobutyryl bromide. The ATRP initiator was covalently attached onto the nanosilica surface. The subsequent ATRP of HEMA from the initiator-attached SiO_2 surface was carried out in order to afforded functional nanoparticles bearing a hydroxyl moiety at the chain end, SiO_2-g-PHEMA-Br. The esterification reaction of pendent hydroxyl moieties of PHEMA segment with 2-bromoisobutyryl bromide afforded the SiO_2-based multifunctional initiator, SiO_2-g-PHEMA(-Br)-Br, bearing one bromine moiety on each monomer repeating unit within the PHEMA segment. Finally, the synthesis of SiO_2-g-PHEMA(-g-PSt)-b-PSt was accomplished by the ATRP of St monomer using SiO_2-g-PHEMA(-Br)-Br as multifunctional initiator. These organic/inorganic hybrid materials have been extensively characterized by FT-IR, XPS, TG, and TEM.

1. Introduction

In the past two decades, considerable efforts have been made in both the academic and engineering fields to explore applications of inorganic/polymer hybrid materials, because these new materials have the potential to afford novel and excellent physicochemical properties due to the combination of an organic polymer shell and an inorganic core. Core–shell materials have attracted a great deal of attentions due to their improved physical and chemical properties over their single-component counterparts. Great potential is, therefore, expected from such materials in a wide range of applications, such as in molecular diagnostics [1–3], drug delivery [4–6], bioimaging [7,8], and electronic/photonic device fabrication [9,10]. Many methods have been developed to fabricate core–shell materials, such as layer-by-layer (LBL) technique [11,12], oriented deposition [13,14], chemical coprecipitation [15], in situ polymerization [16–18], emulsion polymerization [19,20], dispersion polymerization [21] and miniemulsion polymerization [22,23].

Radical polymerization, and especially atom transfer radical polymerization (ATRP), is a very suitable procedure to grow polymer brushes from a surface because it allows a good control over the grafting density and brush thickness [24,25]. The surface-initiated atom transfer radical polymerization (SI-ATRP) technique had been successfully used for the grafting of well-defined homopolymers [26,27], diblock copolymers [28,29], graft copolymer [30], star polymers [31], and hyperbranched polymers [32] from the nanoparticles, nanotubes, nanowires, and clays. As for the fabrication of the diblock copolymer brushes, the “living” chain ends of the initial homopolymer brushes were used as the macroinitiators for the ATRP of the second monomer [28,29].

Silica spheres have good mechanical strength and thermal stability, and can be synthesized easily in a controllable way by hydrolysis of organic silicate at room temperature, which makes them one of the most commonly used inorganic cores. Accordingly, SiO_2-coated particles are advantageous for applications in the field of biomedicine, because silica is easy to functionalize, nontoxic, and can protect the surface of the particles from oxidation. Recently, Okano and co-workers described the preparation of high-density thermo-responsive anionic copolymer brush comprising P(N-isopropylacrylamide-co-acrylic acid-co-tert-butyacrylamide) on silica surfaces using surface-initiated atom transfer radical polymerization (SI-ATRP) [33]. Characterization of the dense cationic copolymer brush surfaces on silica was also investigated by chromatographic analysis using catecholamine derivatives and anigotensin peptides as model basic analytes. Hong and co-workers reported that poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA) was selected to functionalize the mesoporous silica nanoparticles through SI-ATRP of DEAEMA [34]. The release behav-

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* Corresponding author. Tel.: +86 915 3261415; fax: +86 915 3261415.
E-mail address: chenjiucun@163.com (J. Chen).

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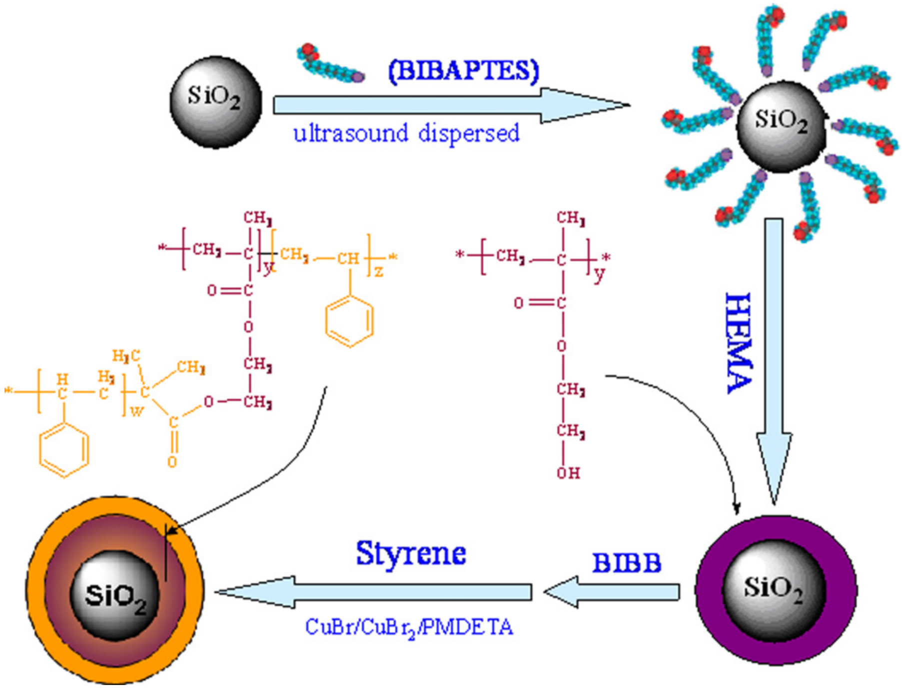

Scheme 1. Synthetic procedure of well-defined structurally silica–nonlinear polymer core–shell nanoparticles via the surface-initiated atom transfer radical polymerization.

iors of the guest molecules from this nanocarrier were investigated at three selected pHs and the results showed that release of the guest molecules could be well controlled. So this nanocomposite delivery system should have potential applications in targeted drug release and gene delivery. Save and co-workers demonstrated that hybrid materials were synthesized by grafting polymer chains from the surface of ordered mesoporous silica particles via SI-ATRP of methyl methacrylate or styrene [35]. This study not only provides for the first time a mechanistic insight into the SI-ATRP from ordered mesoporous silica of various shapes but also may find applications in material science with the design of structured multilayered hybrid spherical particles composed of an ordered mesoporous silica component and a grafted polymer. In the present work, we reported the synthesis of the well-defined structurally silica–nonlinear polymer brush core–shell nanoparticles by the surface-initiated atom transfer radical polymerization (SI-ATRP) (Scheme 1). At first, 3-(2-bromoisobutyramido)propyl(triethoxy)-silane (BIBAPTES, the ATRP initiator) was prepared by the reaction of 3-aminopropyltriethoxysilane with 2-bromoisobutyryl bromide in the presence of triethylamine. The ATRP initiator (BIBAPTES) was covalently attached onto the nanosilica surface via the reaction between hydroxyl and triethoxysilane groups. The subsequent ATRP of HEMA from the initiator-attached SiO_2 surface was carried out in the presence of $CuBr/CuBr_2$/1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) as the catalyst system in order to afforded functional nanoparticles bearing a hydroxyl moiety at the chain end, SiO_2-g-PHEMA-Br. The esterification reaction of pendent hydroxyl moieties of PHEMA segment with 2-bromoisobutyryl bromide afforded the SiO_2-based multifunctional initiator, SiO_2-g-PHEMA(-Br)-Br, bearing one bromine moiety on each monomer repeating unit within the PHEMA segment. Finally, the synthesis of SiO_2-g-PHEMA(-g-PSt)-b-PSt was accomplished by the ATRP of styrene (St) monomer using SiO_2-g-PHEMA(-Br)-Br as multifunctional initiator.

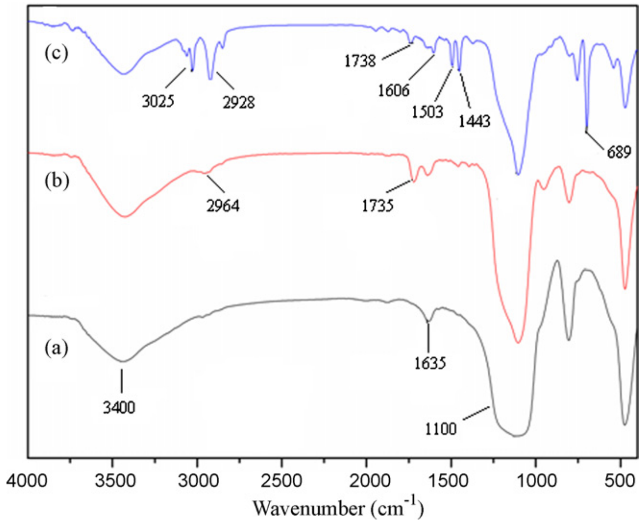

Fig. 1. FT-IR spectra of (a) bare SiO_2, (b) SiO_2-g-PHEMA-Br and (c) SiO_2-g-PHEMA(-g-PSt)-b-PSt particles.

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA, 97%, Aldrich), N,N,N′,N′′,N′′-pentamethyl diethylenetriamine (PMDETA, 99%, Aldrich), 3-aminopropyltriethoxysilane (APTES, 99%, Aldrich), 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA, 99%, Aldrich), 2-bromoisobutyryl bromide (BIBB, 98%, Aldrich), tetraethyl orthosilicate (TEOS, 99%, Aldrich), copper(I) bromide (CuBr, 98%, Aldrich) and copper(II) bromide ($CuBr_2$, 98%, Aldrich), were used as received. HEMA were passed through the ready-to-use inhibitor-removing column (Aldrich Chemical Co.) and stored under an argon atmosphere at −10 °C. Styrene (St) (AR, Shanghai Chemical Reagent Plant) were washed with 5% NaOH and ion-free water, stirred over CaH_2 overnight, and distilled before