



Macromolecular Nanotechnology

Surface initiated ATRP in the synthesis of iron oxide/polystyrene core/shell nanoparticles

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Abstract

A method to prepare magnetic nanoparticles with a covalently bonded polystyrene shell by surface initiated atom transfer radical polymerization (ATRP) was reported. First, the initiator for ATRP was covalently bonded onto the surface of magnetic nanoparticles through our novel method, which was the combination of ligand exchange reaction and condensation of triethoxysilane having an ATRP initiating site, 2-bromo-2-methyl-*N*-(3-(triethoxysilyl)propyl) propanamide. Then the surface initiated ATRP of styrene mediated by a copper complex was carried out and exhibited the characteristics of a controlled/“living” polymerization. The as-synthesized nanoparticles were coated with well-defined PS of a target molecular weight up to 45 K. These hybrid nanoparticles had an exceptionally good dispersibility in organic solvents and were subjected to detailed characterization using DLS, GPC, FTIR, XPS, UV–vis, TEM and TGA.

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Keywords: Polymer composite materials; Atom transfer radical polymerization; Magnetic nanoparticles**1. Introduction**

As a result of anisotropic dipolar attraction, pristine nanoparticles of iron oxides tend to aggregate into large clusters and thus lose the specific properties associated with single-domain, magnetic nanostructures. Therefore, surface modification of magnetic nanoparticles (MNPs) is an essential and challenging step for most of their applications and fundamental

studies. Polymeric shells have some unique advantages because of the flexibility in the controls of chemical compositions and functions of the polymers. Among many approaches for coating the surface of nanoparticles with a shell of organic polymers, the surface initiated atom transfer radical polymerization (ATRP) has become a method of choice recently [1]. Several groups have reported the synthesis of the polymeric core/shell nanoparticles such as SiO₂ [2], Au [3], MnFe₂O₄ [4], and Fe₂O₃ [5] via ATRP. ATRP can offer polymeric shells with low polydispersity and this method is easy to control the molecular weight, thereby, the thickness of the polymeric shell [6].

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However, as far as we know, previous ATRP studies for the synthesis of core/shell MNPs usually yield a carboxylates bonded shell of polymeric molecules protecting iron oxide cores. The linear polymeric molecules attach to the surface of iron oxide cores through the initiator via the –COOH group. For instance, Wang et al. [5] has utilized a solvent-free ATRP approach for the synthesis of the core/shell nanoparticles in which iron oxide cores are protected with a layer of carboxylates bonded polystyrene shell. A simple carboxylates linkage between the iron oxide core and the polymeric chain is not sufficient to achieve a permanent linkage. Instead, a dynamic exchange between the polymeric chains and other competing molecules possessing a –COOH group can lead to the dissociation of the polymeric chains from the core surfaces. To solve the problem, Li et al. [7] use divinylbenzene (DVB) as a crosslinker copolymerized with styrene through ATRP. But the disadvantage of this method is that the introduction of DVB into the polymerization mixture leads to the crosslinking among particles.

Recently, some groups have reported the trialkyloxysilane or trichlorosilane with initiating site for ATRP to be covalently bonded on the surface of MNPs through sol–gel method [8]. However, most of them can not avoid any silica encapsulated small aggregates of several MNPs due to the trialkyloxysilane or trichlorosilane's high trend to self-condensation.

In the present paper, we would like to report our synthesis of the iron oxide/polystyrene core/shell nanoparticles via surface initiated ATRP. First our novel method was employed to covalently bond initiators onto the surface of MNPs, which was the combination of ligands exchange reaction and condensation of triethoxysilane having an ATRP initiating site, 2-bromo-2-methyl-*N*-(3-(triethoxysilyl)propyl) propanamide [9]. Then the polystyrene shell was grafted from the initiating sites on the surface of MNPs through ATRP. The covalently bonded polymeric shell could prevent the undesired site exchange of the MNPs surface functionalities.

2. Experimental section

2.1. Materials

Ferrous sulfate heptahydrate, ferric chloride hexahydrate, oleic acid (OA), 2-bromoisobutyryl bromide, γ -aminopropyl triethoxysilane (APS), cop-

per bromide (CuBr, 99.0%), *N,N,N',N''*-pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich Chemical Co. and used as received. Styrene was washed with aqueous NaOH to remove inhibitors, then dried for several hours with MgSO₄ and distilled under reduced pressure. Toluene was purified by distillation from CaH₂. Triethylamine (TEA) was dried over potassium hydroxide and distilled from CaH₂ before use. All other reagents were used as received from commercial sources.

2.2. Synthesis of OA coated MNPs

OA coated MNPs were synthesized via a two-step method (Scheme 1). First step: 2.35 g ferrous sulfate heptahydrate (FeSO₄·7H₂O > 99%) and 4.1 g ferric chloride hexahydrate (FeCl₃·6H₂O > 99%) were dissolved into 100 mL deionized water in a flask. This solution was stirred, followed by adding 25 mL 25% (w/w) NH₃·H₂O quickly at room temperature. The solution color changed from orange to black, leading to a black precipitate. Then under vigorous stirring, 1 mL OA was dropped into the dispersion slowly at 80 °C in 1 h. The whole process was carried out under nitrogen atmosphere. The as-synthesized MNPs could be well dispersed into water by the protection of the double layers of OA.

Second step was to extract MNPs from water into toluene. In a typical procedure, 50 mL MNPs' water dispersion and 50 mL toluene were mixed together in a 250 mL extractor. By adding small amount of sodium chloride, MNPs transferred into toluene phase and under the protection of single layer of OA, they had good dispersibility in toluene. Finally, the toluene dispersion was refluxed to remove most of the water under nitrogen atmosphere and the content of MNPs was diluted with toluene to 10 mg/mL.

2.3. Synthesis of 2-bromo-2-methyl-*N*-(3-(triethoxysilyl)propyl) propanamide (BTPAm)

BTPAm was synthesized as follows: toluene (10 mL) with 2-bromoisobutyryl bromide (0.1 mL, 0.8 mmol) was added dropwise to a cold solution of γ -aminopropyl triethoxysilane (APS) (0.18 mL, 0.8 mmol) in dry toluene (10 mL) with TEA (0.12 mL, 0.8 mmol) at 0 °C. The mixture was magnetically stirred for 3 h at 0 °C and then for another

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