ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

Materials Letters 61 (2007) 949 – 952

materials letters

www.elsevier.com/locate/matlet

Synthesis of thermoresponsive silica nanoparticle/PNIPAM hybrids by aqueous surface-initiated atom transfer radical polymerization

Kai Zhang [a], Jia Ma [b], Bao Zhang [a], Shuang Zhao [a], Yapeng Li [a],
Yaxin Xu [a], Wenzhi Yu [a], Jingyuan Wang [a,*]

[a] *College of Chemistry, Alan G. MacDiarmid Institute, Jilin University, Qianwei Road 10#, Changchun 130012, PR China*
[b] *Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, PR China*

Received 19 February 2006; accepted 10 June 2006
Available online 30 June 2006

Abstract

This paper described the synthesis of a novel kind of thermoresponsive silica nanoparticle/PNIPAM hybrids by aqueous surface-initiated atom transfer radical polymerization at room temperature. These resulting hybrid particles were characterized by FT-IR, XPS, TEM, TGA and variable temperature DLS which indicated that they owned both core/shell structures and thermoresponsiveness.

Keywords: ATRP; Silica nanoparticles/PNIPAM hybrids; Core/shell structure; Ambient temperature; Thermoresponsiveness

1. Introduction

During the past decade, nanoparticle/polymer (core/shell) hybrids have attracted strong interest [1,2] because of the combination of both the properties of the inorganic nanoparticles (optical, electronic, or mechanical) and those of the polymer (solubility, film formation, and chemical activity). Among the polymers employed in the formation of the core/shell hybrid structures, a stimuli-responsive polymer has gained much attention because the polymeric layer would endow the hybrid structure with an additional function/property on the top of the cores [3]. Thermoresponsive polymers are a class of the environmentally switchable materials and poly(*N*-isopropylacrylamide) (PNIPAM) has most intensively been studied [4]. The lower critical solution temperature (LCST) of PNIPAM is about 32 °C: the polymer is in the chain-extended, highly hydrated form below the LCST (hydrophilic state) and the polymer chains collapse above the LCST (hydrophobic state) in water [5]. Because of this unusual property, PNIPAM has been grafted from various substrates widely used in synthesizing thermoresponsive materials [6,7]. It was also reported that the LCST of PNIPAM grafted from the surface of solid substrates [8], cross-linked hydrogels [9], and block polymers [10] was nearly identical to the LCST of a homopolymer in aqueous solution.

Covalent attachment of polymer chains to solid substrates is an effective method for tailoring surface properties [11]. As one of the most effective methods, surface-initiated atom transfer radical polymerization (ATRP) method has gained more and more attention recently [12] because it is a suitable method for the controllable preparation of polymer layers covalently bound to the surface of different surfaces such as SiO_2 [13], Au [14], and Fe_3O_4 [15]. Although it is difficult to polymerize substituted acrylamides by ATRP in organic media, Brooks and coworkers have succeeded in polymerizing substituted acrylamides including *N*,*N*-dimethylacrylamide and NIPAM from polystyrene latex by aqueous surface-initiated ATRP [16,17]. Water can always act not only as solvent but also as accelerator in the ATRP process and enable the polymerization to be carried out under very moderate conditions [18].

In this letter, we report the preparation of a kind of thermoresponsive silica nanoparticle/PNIPAM hybrid particles by aqueous surface-initiated ATRP at room temperature.

2. Experimental

N-isopropylacrylamide (NIPAM: Acros, 97%) was purified by crystallization from hexane and stored under argon at −20 °C

---

* Corresponding author.
E-mail address: wangjingyuan_jlu@yahoo.com.cn (J. Wang).

0167-577X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2006.06.021

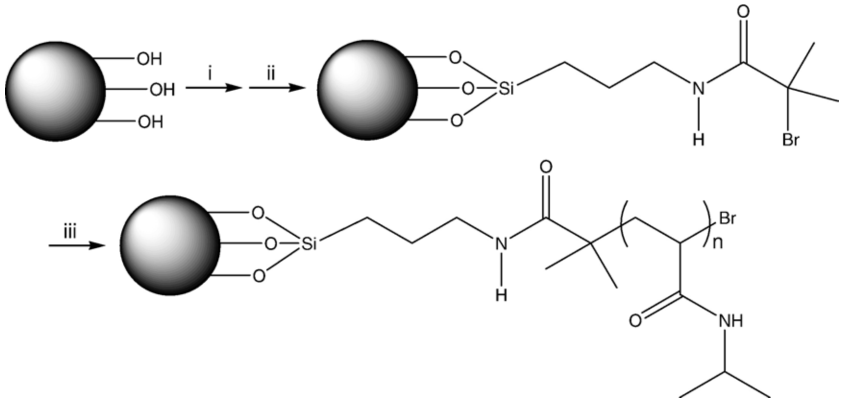

Fig. 1. Scheme of the synthesis of silica nanoparticle/PNIPAM hybrids. Conditions: (i) APTES, toluene; (ii) α-bromoisobutyryl bromide, TEA, toluene; (iii) NIPAM, CuCl, 2,2′-bipyridine, H_2O, MeOH.

until used. CuCl purchased from Shanghai Chemical Co. (A.R., 97.0%) was purified according to the literature [19]. 2,2′-bipyridine (bpy) (A.R., 97.0%) provided by Beijing Chemical Co. was recrystallized twice from acetone. 3-aminopropyl triethoxysilane (99.0%) (Aldrich) and α-bromoisobutyryl bromide (97.0%) (Fluka) were all used as received. Triethylamine (A.R., 99.0%) and toluene were all dried by CaH_2 overnight, then distilled under reduced pressure before use. The water used throughout these experiments was either demineralised or purified using a Millipore Simplicity 185 system at 18.2 MΩ. Methanol (MeOH) (G.R.) purchased from Beijing Chemical Co. was used as supplied. Silica nanoparticles were prepared in ethanol according to the Stöber method [20,21].

Fourier transform infrared spectra (FT-IR) was carried out using a Nicolet FT/IR-410 instrument. The X-ray photoelectron spectroscopy (XPS) was recorded on a VG ESCA LAB MKII x-probe spectrometer with Mg Kα X-ray radiation to determine the surface composition of the substrates. Thermogravimetric analysis (TGA) was carried out using a Pyris Diamond TG-DTA (PerkinElmer) apparatus. The morphology of the initiator and polymer modified silica nanoparticles was observed by using transmission electron microscope (TEM) (Hitachi H 8100). The hydrodynamic diameter of silica nanoparticle/PNIPAM hybrids was determined by variable temperature dynamic light scattering (DLS) (Wyatt Technology).

3. Results and discussion

To prepare the polymer/silica hybrids from the surface of silica nanoparticles, a uniform and densely initiator-modified substrate is indispensable. Fig. 1 schematically outlines the procedure used for the preparation of initiator-modified silica nanoparticles and synthesizing the thermoresponsive hybrid particles. First, the α-bromoester initiator [22] on the silica nanoparticles was prepared by the self-assembly of aminopropyl triethoxysilane (APTES), followed by amidization with α-bromoisobutyryl bromide using triethylamine (TEA) as the catalyst. Then surface-initiated ATRP of NIPAM [23] in aqueous media at room temperature was carried out from the above initiator-modified particles as soon as the initiator-modified silica nanoparticles were obtained. Water was used as one of the solvents because it can act as a kind of

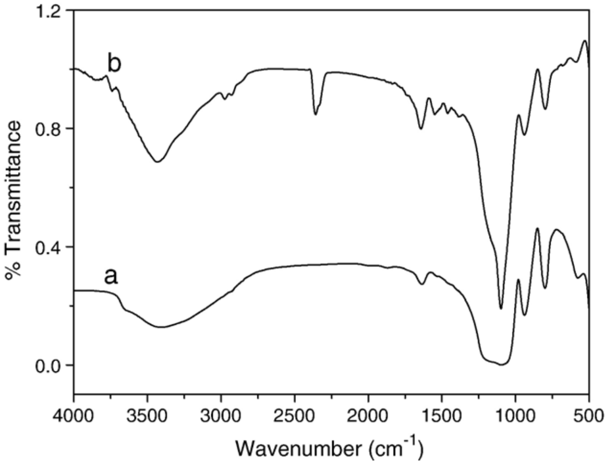

Fig. 2. FT-IR spectra of initiator (a) and PNIPAM (b) modified silica nanoparticles.

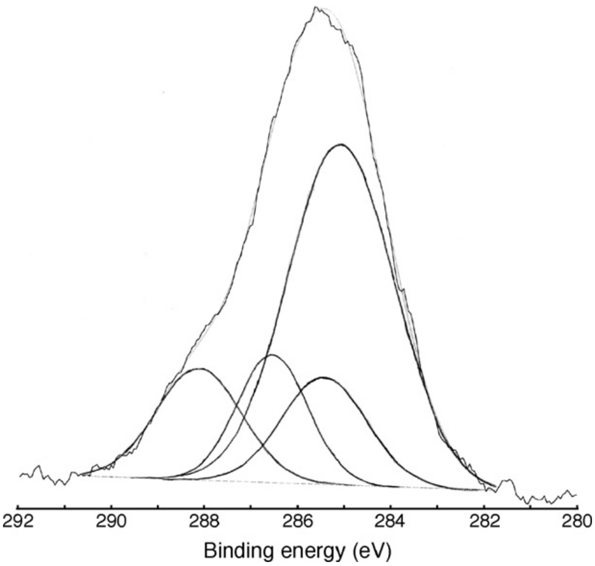

Fig. 3. C1s XPS spectra of PNIPAM modified silica nanoparticles.