Polymer 49 (2008) 4776–4783

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Preparation of ellipsoidal hematite/polymer hybrid materials and the corresponding hollow polymer ellipsoids

Guangyu Liu, Longyu Li, Xinlin Yang*

Key Laboratory of Functional Polymer Materials, The Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China

ARTICLE INFO

Article history:
Received 29 June 2008
Received in revised form 20 August 2008
Accepted 28 August 2008
Available online 3 September 2008

Keywords:
Inorganic-polymer hybrid
Hematite
Distillation precipitation polymerization

ABSTRACT

Ellipsoidal hematite/poly(ethyleneglycol dimethacrylate) core–shell hybrid materials were prepared by distillation precipitation polymerization of ethyleneglycol dimethacrylate (EGDMA) in the presence of 3-(methacryloxy)propyl trimethoxysilane (MPS)-modified hematite (α-Fe_2O_3) particles as the seeds. The polymerization of EGDMA was performed in neat acetonitrile with 2,2′-azobisisobutyronitrile (AIBN) as initiator to coat MPS-modified hematite seeds through the capture of EGDMA oligomer radicals with the aid of vinyl groups on the surface of the MPS-modified hematite particles in absence of any stabilizer or surfactant. The shell-thickness of the core–shell hybrid particles was controlled by the feed of EGDMA monomer during the polymerization. Other hematite/polymer core–shell hybrid particles, such as hematite/polydivinylbenzene (α-Fe_2O_3/PDVB) and hematite/poly(divinylbenzene-*co*- methacrylic acid) (α-Fe_2O_3/P(DVB-*co*-MAA)) were also prepared by this procedure. Hematite/poly(*N*,*N*′-methylenebisacrylamide-*co*-methacrylic acid) (α-Fe_2O_3/P(MBAAm-*co*-MAA)) were synthesized with unmodified hematite particles as the seeds. Hollow polymer ellipsoids were subsequently developed after the selective removal of the hematite core with hydrochloric acid (HCl) from hematite/polymer core–shell hybrids. The resultant core–shell hybrid particles and hollow polymer ellipsoids were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectra (FT-IR) and vibrating sample magnetometer (VSM).

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

During the last decade, the organic–inorganic hybrid materials, which combine the properties of inorganic and organic components within a single material, have attracted expanding interest for material scientists due to their advantages of the organic polymer matrix having facile process-abilities, flexibilities, and various functional groups, together with characteristics of the inorganic particles in terms of mechanical strength, modulus, and thermal stability [1,2]. The organic–inorganic hybrid materials can exhibit novel and excellent properties, such as mechanical, chemical, electrical, rheological, magnetic, optical, and catalytic, by varying the compositions, dimensions, and structures, which have proven diverse applications as drug-delivery system, diagnostic, coating and catalyst [3–8].

Hematite (α-Fe_2O_3), which is the most stable iron oxide under ambient conditions with *n*-type semiconducting properties, low cost and high resistance to corrosion, has been extensively utilized as the products for gas sensors, catalysts, pigments, magnetic recording media, anti-corrosive agents, and lithium-ion batteries with great scientific and technical importance [9–15]. Many efforts have been devoted towards the incorporation of magnetic particles into core–shell structures in order to control the particle shape, size, and magnetic properties [16–18]. For instance, the solvent-free atom transfer radical polymerization (ATRP) has been used for the synthesis of α-Fe_2O_3/polystyrene (PSt) core–shell nano particles with well-defined shape [19]. Zeolite capsule encapsulated with α-Fe_2O_3 have been afforded by a wet impregnation technique [20]. The colloidal polypyrrole–magnetite–silica nano particles have been synthesized by the aqueous deposition of silica onto ultrafine (15–20 nm) magnetite particles via controlled hydrolysis of sodium silicate with the subsequently oxidative polymerization of pyrrole using various oxidants in the presence of silica-coated magnetite particles [21]. The uniform coating of silica onto the ultrafine hematite particles has altered most properties of the iron oxide particles, such as the dispersibility in either aqueous or non-aqueous media [22], in which the anisometric shape of hematite cores was preserved with benefits via introduction of other functional materials on the particles. Hematite/silica/polypyrrole (α-Fe_2O_3/SiO_2/PPy) ellipsoidal sandwich composite spheres as well as SiO_2, SiO_2/PPy, PPy hollow capsules and PPy ellipsoidal hollow capsules with movable hematite cores have been successfully

* Corresponding author. Tel.: +86 22 23502023; fax: +86 22 23503510.
E-mail address: xlyang88@nankai.edu.cn (X. Yang).

0032-3861/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2008.08.043

afforded from hematite olivary particles through the oxidative polymerization of pyrrole in the presence of $FeCl_3$ as oxidant with subsequently selective removal of the inner cores, respectively [23].

In these years, polymer hollow microspheres have attracted much attention for their wide applications, such as encapsulation for controlled-release of drug and enzymes, fillers, pigments, catalysts, and adsorption materials for sound, which have been prepared by a variety of physical and chemical techniques [24–27]. However, non-spherical core–shell particles and the corresponding hollow particles have scarcely reported in the literature with the difficulty to get the suitable non-spherical template [23,28], which would be more attractive for their applications as ordered arrays due to the lower symmetries compared to the spherical particles. Most of the non-spherical particles and their ordered assembly structures have been forcibly obtained from original spherical ones under ion-irradiation or mechanical pressure [29]. It is still a challenge to get non-spherical polymer particles with well-defined shape and controllable size via the facile polymerization.

In our previous work, distillation precipitation polymerization has been successfully developed as a facile and powerful technique for the preparation of SiO_2/PMBAAm composite [30], SiO_2/PDVB and SiO_2/PEGDMA hybrid [31] core–shell microspheres. More recently, ellipsoidal tri-layer hematite/SiO_2/PDVB hybrid particles were prepared by distillation precipitation polymerization of divinylbenzene (DVB) in the presence of hematite/3-(methacryloxy) propyl trimethoxysilane (MPS)-modified silica (SiO_2) core–shell particles as the seeds [32]. Here, we introduce the distillation precipitation polymerization as a facile method for the synthesis of ellipsoidal hematite/polymer core–shell hybrid materials in absence of any stabilizer or additive, and the further development of the corresponding polymer hollow ellipsoidal particles by the removal of hematite cores in hydrochloric acid (HCl) aqueous solution.

2. Experimental

2.1. Chemicals

Ferric chloride ($FeCl_3 \cdot 6H_2O$) was purchased from Tianjin Guangfu Fine Chemical Engineering Institute. 3-(Methacryloxy)-propyl trimethoxysilane (MPS) was purchased from Aldrich and distilled under vacuum. Ethyleneglycol dimethacrylate (EGDMA) was purchased from Alfa Aesar and used without any purification. Divinylbenzene (DVB, 80% DVB isomers) was supplied as technical grade by Shengli Chemical Factory, Shandong, China, which was washed with 5% aqueous sodium hydroxide and water, then dried over anhydrous magnesium sulfate prior to utilization. Methacrylic acid (Tianjin Reagent Factory I, China) was purified by vacuum distillation before use. *N*,*N*′-Methylenebisacrylamide (MBAAm, chemical grade, Tianjin Bodi Chemical Engineering Co.) was recrystallized from acetone. 2,2′-Azobisisobutyronitrile (AIBN) was provided by Chemical Factory of Nankai University and recrystallized from methanol. Hydrochloric acid (HCl) was supplied by Tianjin Chemical Reagents II Co. as analytical grade. Acetonitrile (analytical grade, Tianjin Chemical Reagents II Co.) was dried over calcium hydride and purified by distillation before use. All the other reagents were of analytical grade and used without any further treatment.

2.1.1. Synthesis of shuttle-like MPS-modified hematite particles

Shuttle-like monodisperse hematite (α-Fe_2O_3) particles were synthesized according to the method in the literature [23]. Hematite particles were obtained via aging the aqueous solution of 2×10^{-2} M $FeCl_3$ and 4×10^{-4} M NaH_2PO_4 at 95 °C for three days. The formation of hematite particles was reflected by the appearance of a brick-red color in the hydrolysis system. The resultant hematite particles were centrifugated, decanted, and redispersed in acetone for three times, then dried at 50 °C under vacuum, till constant weight.

MPS (1.0 g, 4.0 mmol) was introduced into 20 mL of the ethanol suspension of hematite particles (0.5 g) under stirring in a 50-mL round-bottom flask. Coating of hematite particles with MPS was achieved by stirring the mixture of hematite particles and MPS for 8 h at 50 °C. The resultant MPS-modified hematite particles were purified by centrifugation, decantation, and resuspension in ethanol to remove the excessive MPS. The final MPS-modified hematite particles were dried in a vacuum oven at 50 °C till constant weight.

2.2. Preparation of ellipsoidal hematite/PEGDMA core–shell hybrids by distillation precipitation polymerization

A typical procedure for the distillation precipitation polymerization: In a dried 50-mL two-necked flask, 0.1 g of MPS-modified hematite particles were suspended in 40 mL of acetonitrile as a brick-red suspension. Then EGDMA (0.3 mL, total as 0.75 vol% of the reactive system) and AIBN (0.006 g, 2 wt% relative to the monomer) were dissolved in the suspension. The two-necked flask attached with a fractionating column, Liebig condenser and receiver was submerged in a heating mantle. The reaction mixture was heated from ambient temperature till the boiling state within 7 min and the reaction system was kept under refluxing state for further 5 min. Then the polymerization was carried out with distilling the solvent out of the reaction system and the reaction was ended after 20 mL of acetonitrile was distilled off the reaction mixture within 40 min. After the polymerization, the resultant hematite/PEGDMA core–shell hybrid materials were purified by repeating centrifugation, decantation, and resuspension in acetone with ultrasonication for three cycles. The hybrid particles were then dried in a vacuum oven at 50 °C till constant weight.

The other distillation precipitation polymerizations to prepare hematite/PEGDMA with different polymer thickness and hematite/PDVB, hematite/P(DVB-*co*-MAA) were much similar to that of the typical procedure by varying the mass ratio of EGDMA monomer to MPS-modified hematite particles, or comonomers, while the amount of AIBN initiator was maintained at 2 wt% relative to the monomer. The treatment of these core–shell hybrid particles was the same as that for the typical procedure. The reproducibility of the polymerizations was confirmed through several duplicate and triplicate experiments.

2.3. Preparation of ellipsoidal hematite/P(MBAAm-co-MAA) core–shell composites by distillation precipitation polymerization

The distillation precipitation polymerization to prepare hematite/P(MBAAm-*co*-MAA) core–shell composites was much similar to that of the typical procedure to prepare hematite/PEGDMA hybrids by varying the monomers from EGDMA to MBAAm (0.02 g) and MAA (0.08 mL) in the presence of unmodified hematite (0.1 g) as seeds, while the amount of AIBN initiator was maintained at 2 wt% relative to the comonomers and the amount of acetonitrile was maintained as 40 mL. The treatment of the core–shell composite particles was the same as that for the typical procedure to prepare hematite/PEGDMA hybrids. The reproducibility of the polymerizations was confirmed through several duplicate and triplicate experiments.

2.3.1. Synthesis of hollow polymer ellipsoids

The resultant hematite/polymer core–shell ellipsoidal particles were immersed in hydrochloric acid (HCl, 5 wt%) aqueous solution for 2 h. The hollow polymer ellipsoids were purified by several centrifugation/washing cycles in water till pH of 7. The resultant

Download English Version:

https://daneshyari.com/en/article/5188577

Download Persian Version:

https://daneshyari.com/article/5188577

Daneshyari.com