

Research paper

Stimuli-responsive behavior of smart copolymers-grafted magnetic nanoparticles: Effect of sequence of copolymer blocks

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ARTICLE INFO

Article history:

Received 26 December 2017
 Received in revised form 11 February 2018
 Accepted 20 February 2018
 Available online 21 February 2018

Keywords:

Magnetic nanoparticles
 Smart polymers
 Thermoresponsiveness
 pH-sensitivity
 Sequence of copolymer blocks

ABSTRACT

In this work, surface-initiated atom transfer radical polymerization (SI-ATRP) is used to synthesize smart copolymer-grafted Fe_3O_4 magnetic nanoparticles (MNPs). To do this, MNPs is modified with (3-aminopropyl)triethoxysilane (ATPES) and α -bromoisobutyryl bromide (BIBB) to yield MNPs@ATPES and MNPs@BIBB nanoparticles. Then, ATRP-initiator-grafted nanoparticles are used in polymerization of 2-(dimethylamino)ethyl methacrylate (DMAEMA) and *N*-isopropylacrylamide (NIPAAm) as stimuli-responsive monomers to obtain MNPs@PDMAEMA and MNPs@PNIPAAm respectively. Homopolymer-grafted MNPs are used as macroinitiators to produce smart copolymers-grafted MNPs named MNPs@P(DMAEMA-*b*-NIPAAm) and MNPs@P(NIPAAm-*b*-DMAEMA) those have different sequences of copolymer blocks. Successful synthesis of different structures is proved by means of different methods including FT-IR, TGA, VSM, XRD, FE-SEM, and TEM. All homopolymer- and copolymer-grafted MNPs are subjected to variation of pH and temperature to investigate stimuli-responsive behavior of hybrid structures. Although no surprising result is investigated for MNPs@PDMAEMA and MNPs@PNIPAAm nanoparticles, copolymer-grafted MNPs showed a dual pH- and temperature-sensitive behavior where copolymer sequence is important to define smart characteristic of hybrid MNPs.

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1. Introduction

Iron oxide nanoparticles as magnetic nanoparticles (MNPs) are ideal candidates for applications need combination of high specific surface area and superparamagnetism [1–2]. They have been utilized for magnetic resonance imaging (MRI) [3], targeted drug delivery [4], diagnostic medical devices [5], etc. However, because of stability problems, MNPs should be modified using different compounds such as polymers [6]. Among methods for preparing polymer-coated nanoparticles, surface functionalization by grafting of polymers is the most effective method as the surface properties can be widely changed by choosing a variety of functional monomers [7–8]. In this field, grafting from approach via surface-initiated atom transfer radical polymerization (SI-ATRP) is the most powerful method due to simple experimental conditions and yields polymers with narrow molecular weight distributions [9,10].

Stimuli-responsive polymers as an interesting class of polymers show variable physical and chemical properties adjusted by external stimuli such as temperature [11], pH [12], ionic strength [13],

etc. They undergo a phase transition from soluble to insoluble state in water at lower critical solution temperature (LCST) or upper critical solution temperature (UCST) [14,15]. Besides temperature, pH is another important triggering signal for phase transitions in polymer aqueous solutions where protonation/deprotonation of structure induces a responsive behavior on polymer [16]. Savoji et al. [17] studied thermo-responsive behavior of random copolymers of poly(*N,N*-propylacrylamide-*co*-2-(diethylamino)ethyl methacrylate) and found that cloud point (T_{cp}) in the range of 13–68 °C strongly depends on solution pH. Matsumoto et al. [18] reported a pH-tunable thermo-responsive aggregation behavior of a poly(*N*-isopropylacrylamide-*co*-acrylic acid) conjugated protein nanoparticles as a useful system in drug delivery. Dong et al. [19] studied the solution behavior of weak polyelectrolyte spherical brushes under different modes of confinement. Three types of models with different degrees of confinement were designed and prepared based on PDMAEMA spherical brushes, namely, PDMAEMA brushes, shell cross-linked PDMAEMA brushes and hollow PDMAEMA nanocapsules. They found that by varying pH from 6.0 to 8.0, the conformational change is predominated by hydrophobic interactions rather than electrostatic repulsions and hydrogen bonding interactions and by increase of ionic strength of aqueous solution, an evident decrease in R_h was observed. Wang et al. [20] reported core-shell

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magnetic nanoparticles as separators to destabilize water-in-oil inverse emulsion and separate water from oil. Chakraborty et al. [21] reported that PNIPAAm-grafted gold nanoparticles present slower aggregation kinetics compared to bulk PNIPAAm.

Although different works have been reported stimuli-responsive behavior of homo- and copolymers even grafted on different nanoparticles, no mentionable research has been performed on the effect of sequence of copolymer blocks on such a behavior. In this work, two stimuli-responsive polymers including PDMAEMA and PNIPAAm are used to coat Fe_3O_4 MNPs via SI-ATRP. PDMAEMA is a pH dependent thermo-responsive polymer and PNIPAAm has an LCST around 32 [22]. So, it is expected that hybrid nanoparticles show a stimuli-responsive behavior. Furthermore, SI-ATRP is utilized to graft P(DMAEMA-*b*-NIPAAm) and P(NIPAAm-*b*-DMAEMA) block copolymers onto surface of MNPs. All samples are characterized via different analysis methods to prove formation of core-shell hybrid nanoparticles. Also, pH-sensitive and thermoresponsive behaviors of synthesized structures are investigated. Additionally, effect of sequence of copolymer blocks on stimuli-responsive behavior of hybrid nanoparticles is studied.

2. Experimental section

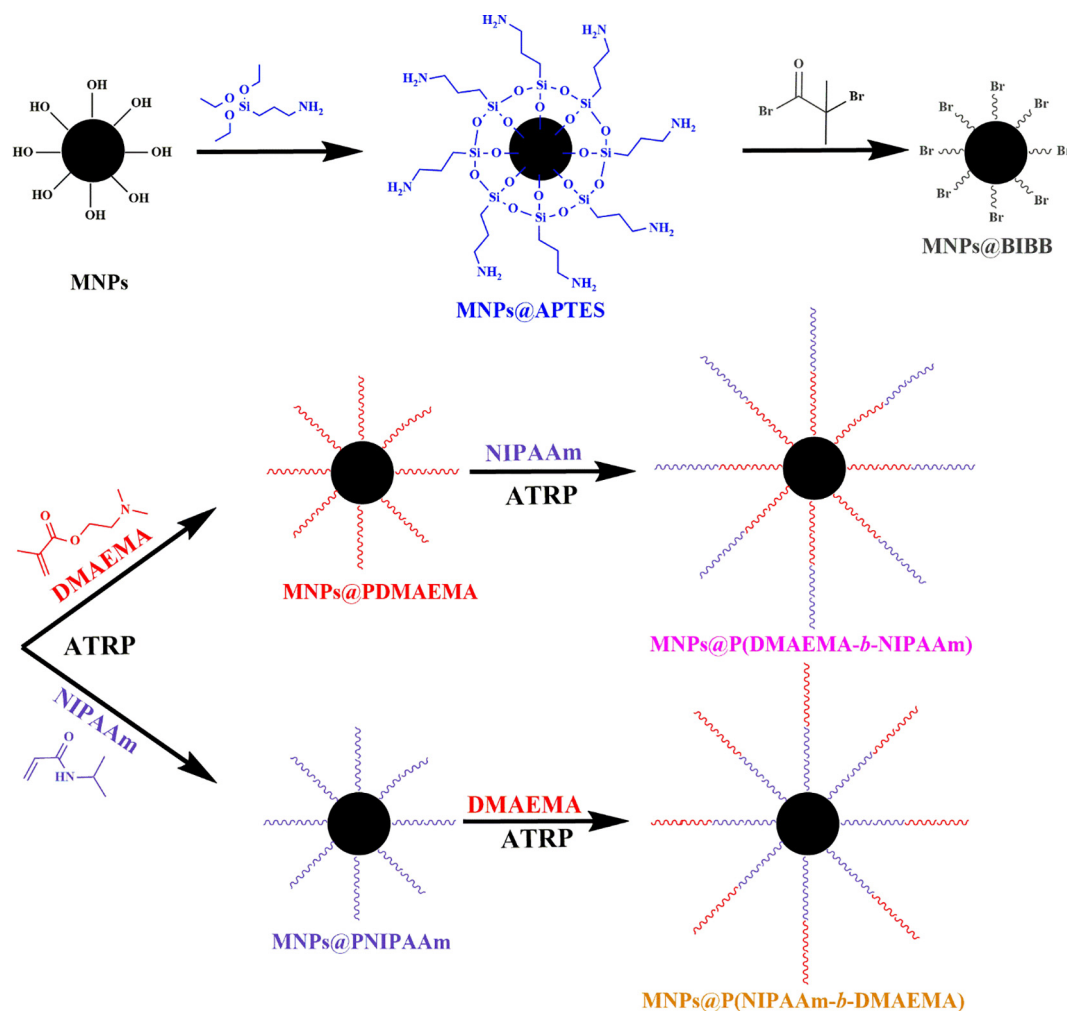
2.1. Materials

Fe_3O_4 MNPs nanoparticles (specific surface area: $81.98 \text{ m}^2/\text{g}$, >99.5%) were purchased from US Research Nanomaterials and

stirred in deionized water for a day. Then, they were separated by centrifugation, filtered, dried, and finally stored in a vacuum oven (50°C , 40 mm Hg). 2-(Dimethylamino)ethyl methacrylate (DMAEMA, 99%, Merck) was passed through a basic alumina column to remove polymerization inhibitor. *N*-Isopropylacrylamide (NIPAAm, 99%, Merck), Cu(I)Br (98%, Sigma-Aldrich), 2,2'-bipyridine (bpy, Sigma-Aldrich, 99%), (3-aminopropyl)triethoxysilane (APTES, 98%, Merck), triethylamine (TEA, 99.5%, Sigma-Aldrich), toluene (99%, Merck), tetrahydrofuran (THF, 99%, Merck), methanol (99%, Merck), and α -bromoisobutyryl bromide (BIBB, 98%, Sigma-Aldrich) were used as received.

2.2. Synthesis of initiator-modified magnetic nanoparticles (MNPs@BIBB)

Initiator-grafted magnetic nanoparticles were synthesized via a two-step simple route. Firstly, in a 200-mL flask, MNPs (1.000 g) were dispersed in a solution of deionized water/ethanol (20 mL/80 mL) by ultrasonication (45 min) at room temperature. Then, pH was adjusted to 4 and APTES (4 mL, 0.017 mol) was added dropwise under vigorous stirring and reaction was continued for 24 h at room temperature. Obtained nanoparticles (MNPs@APTES) were washed with a solution of ethanol/deionized water several times and dried for 24 h at 40°C in vacuum oven. To obtain ATRP-initiator-grafted nanoparticles, MNPs@APTES nanoparticles (0.5 g) were dispersed in 50 mL toluene via ultrasonication (10 min). Then, BIBB (1 mL, 0.008 mol) and triethylamine (1.2 mL,



Scheme 1. Synthetic route for preparation of (co)polymers-grafted MNPs.

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