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Water-dispersible Fe_3O_4 nanoparticles stabilized with a biodegradable amphiphilic copolymer

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A B S T R A C T

In this work, we report a green synthetic method using water-dispersible magnetite nanoparticles containing oleic acid and poly(2-ethyl-2-oxazoline)-poly(ε-caprolactone) diblock copolymer as the magnetite nanoparticle dispersants. The Fe_3O_4 nanoparticles were prepared by co-precipitation and had a bilayer surface with a hydrophobic inner poly(ε-caprolactone) (PCL) layer and hydrophilic corona poly(2-ethyl-2-oxazoline) (POX) blocks. Also, the role of the ultrasonicating treatment's duration on the percent of magnetite in the complex and on its magnetic properties was investigated. Transmission electron microscopy (TEM) showed the average particle size to be about 10–20 nm in diameter for nanoparticles.

1. Introduction

Nanotechnology is now expanding very rapidly, as a result of the unique physical and chemical properties that nanoparticles exhibit compared to bulk materials. Magnetic Fe_3O_4 nanoparticles (Fe_3O_4–MNPs) have attracted much research interest over the recent years because of their inherent properties, such as large surface area and fast response under applied external magnetic field, superparamagnetism properties, high coercivity, and low Curie temperatures [1–8].

Magnetic nanoparticles are usually stabilized by the steric repulsion exerted by polymeric surfactants adsorbed on their surfaces, preventing them from being approached by the neighbouring nanoparticles [9,10]. Oleic acid has been used as a steric stabilizer to form Fe_3O_4 nanoparticles dispersed in organic medium [11,12]. To explain the stabilizing mechanism of the nanoparticles, it has been proposed that carboxylate groups partition on the surface of the nanoparticles and form a layer of hydrocarbon, sterically, stabilizing the nanoparticles in the dispersion [13,14].

Amphiphilic copolymers as block copolymers are one kind of excellent compounds for water-dispersible magnetite nanoparticles due to the nature of the micelles and their small size [15] Polymeric micelles formed in aqueous phase through the self-association of amphiphilic copolymers have attracted great interest. The micelles, based on amphiphilic block copolymers, are suitable for dispersing magnetite nanoparticles in water phase. An important new class of block copolymer is based on poly(2-alkyl-2-oxazoline) as a biodegradable copolymer. Block copolymers were synthesized based on poly(2-ethyl-2-oxazoline) as the hydrophilic block and poly(L-lactide) or poly(ε-caprolactone) as the hydrophobic block [16,17].

Recently, several works have been focused on the preparation of water-dispersible magnetite nanoparticles using polymeric micelles [18,19]. Adeli et al. [20] reported a new method to improve the functionality and water solubility of CNT/γ-Fe_2O_3 nanoparticles using linear-dendritic copolymers, and CNT/γ-Fe_2O_3 hybrid nanomaterials

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were obtained. In this research, poly(citric acid)–polyethylene glycol–poly(citric acid) linear-dendritic copolymers were used to improve the water solubility of CNT/γ-Fe_2O_3 nanoparticles. Non-covalent interactions between them and CNT/γ-Fe_2O_3 nanoparticles led to PCA–PEG–PCA/CNT/γ-Fe_2O_3 NP hybrid nanomaterials with improved water solubility and functionality.

In this work, water-dispersible magnetite nanoparticles are produced by the self-assembly of amphiphilic copolymers containing poly(2-ethyl-2-oxazoline) as the hydrophilic block; poly(ε-caprolactone), as the hydrophobic segment, could self-assemble into micelles with oleic acid modified Fe_3O_4 nanoparticles. Hydrophobic poly(ε-caprolactone) (PCL) segments can hypothetically adsorb onto the pre-synthesized Fe_3O_4 nanoparticles coated with oleic acid, and hydrophilic (poly(2-ethyl-2-oxazoline) POX) blocks can protrude outward from the particle surface to provide steric stabilization and enhance the solubility in water. The presence of Fe_3O_4 nanoparticles encapsulated by polymeric micelles is confirmed by TEM.

2. Results and discussion

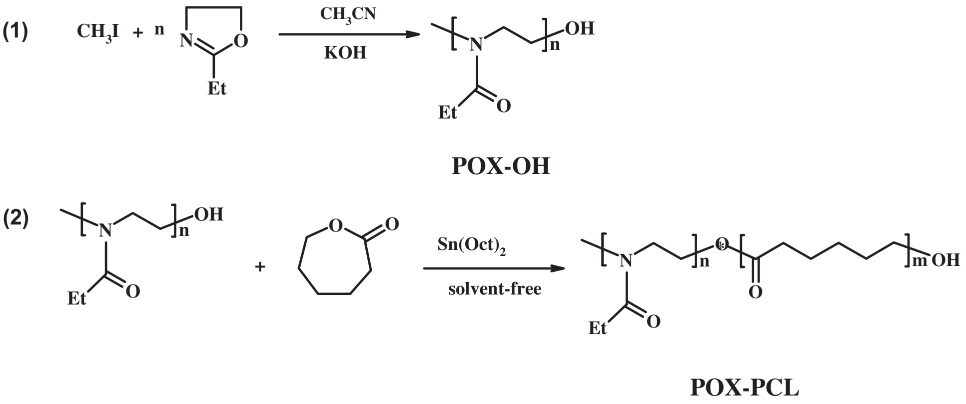
The synthesis and characterization of POX–PCL copolymers were performed following a literature procedure [21]. CH_3I was able to initiate the ring opening polymerization of oxazoline, and polymers poly(2-ethyl-2-oxazoline) (POX) were obtained. The polymerization process was quenched using 0.1 N methanolic KOH, and the polymers containing hydroxyl end functional groups (POX–OH) were obtained. ε-Caprolactone was then polymerized using the hydroxyl groups of POX, and amphiphilic diblock copolymers containing POX, and PCL blocks were synthesized (Scheme 1).

The molecular weights and block compositions of the amphiphilic copolymers were determined by the analysis of the ^1H NMR spectra in Fig. 1. The molar ratios of repeating units in POX were determined by the peak integration ratios of methyl protons CH_3I (3 ppm) and $COCH_2CH_3$ (1 ppm). The molecular weights of polymers were of 3000 (Fig. 1a). The molar ratios of the repeating units in POX and PCL blocks were determined by the peak integration ratios of methyl protons (1.1 ppm) in POX and CH_2OCO (4.05 ppm) in the PCL segment. Molecular weights of copolymers were of 4000 (Fig. 2a). The micelle formation of amphiphilic copolymers in an aqueous phase was confirmed by NMR spectroscopy. Fig. 1 shows the ^1H NMR spectra of POX–PCL micelles in $CDCl_3$ (a) and D_2O (c) solvents. While the resonance peaks from both POX segment and PCL block were clearly observed in $CDCl_3$, the peaks of the PCL segment disappeared in D_2O, which indicated the limited molecular motion of the PCL block surrounded by the hydrophilic POX. This result confirms the formation of a micelle of POX–PCL diblock copolymers in aqueous phase [21].

After co-precipitation of the Fe_3O_4 nanoparticles, they were stabilized with oleic acid and dispersed in hexane. To transfer oleic acid-coated Fe_3O_4 nanoparticles to the water phase, a copolymer aqueous solution with a certain concentration was introduced into the magnetite dispersion in hexane. The hexane–water mixture was phase-separated under ultrasound irradiation (Fig. 2). Fig. 2 also shows that the water-dispersible magnetite nanoparticles stayed in the water phase for a week without being released to the organic phase. Hydrophobic PCL blocks aggregated in water and formed a micellar core, while hydrophilic POX segments dispersed in water and formed a micellar corona. Once the hexane–water mixture had been sonicated, the hydrophobic particles were transferred from the hexane phase to the aqueous one and were trapped into the micellar core due to a physisorption interaction between oleic acid and the hydrophobic PCL block [23].

The magnetite nanoparticles' particle size was also investigated using transmission electron microscopy (TEM). A representative TEM image of a copolymer–magnetite complex dispersed in water with a 1.0 wt% copolymer concentration is displayed in Fig. 3. These nanoparticles with a diameter of 10–20 nm exhibit a spherical shape. However, the micelles formed by POX–PCL diblock copolymers could not be observed by TEM, a technique that was considered to be more sensitive to the electron-rich metal particles than copolymers. Similar phenomena were also observed in previous works [21].

The sonication duration of the water/hexane mixture of magnetite and copolymer also played a key role in the magnetic properties of the particles. Table 1 shows the



Scheme 1. Synthesis of the poly(2-ethyl-2-oxazoline)-poly(ε-caprolactone) diblock copolymers.