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Enzymatic synthesis of pH-responsive polyaniline colloids by using chitosan as steric stabilizer

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Abstract

Polyaniline colloidal particles were prepared by enzymatic polymerization of aniline using chitosan as steric stabilizer and toluenesulfonic or camphorsulfonic acids as doping agents. Fourier transform infrared and UV–vis spectroscopic studies indicate that enzymatic polymerization of aniline in dispersed media results in the emeraldine salt form of polyaniline. The morphology of the colloids was studied by transmission electron microscopy. Toluenesulfonic acid produced mainly oblong particles whereas rod-like shaped particles were obtained using camphorsulfonic acid. Polyaniline particles with good colloidal stability and size below 200 nm were obtained using 1.0 wt% of chitosan in the reaction media, indicating that this polymer was highly efficient as a steric stabilizer. The content of chitosan attached to the polyaniline colloids was approximately 20 wt% as indicated by elemental analysis. The colloids synthesized either with toluenesulfonic or camphorsulfonic acid showed a strong pH-dependent colloidal stability and underwent rapid flocculation in near neutral or alkaline media. This interesting behavior could be exploited in separation technology applications.

Keywords: Enzymatic polymerization; pH-sensitive; Smart flocculation; Conductive polymers

1. Introduction

Polyaniline (PANI) is one of the most promising conducting polymers because of its good chemical stability, facile synthetic route and relatively high electrical conductivity [1]. However, its application has been limited due to its infusible character and low solubility in most organic solvents. To overcome these problems, dispersion polymerization of aniline has been widely used to obtain water-dispersible colloidal particles that can be cast as films or blended with other materials to prepare composites. The synthesis of water dispersible PANI colloids is considered a "green technology" due to the reduction in the use of organic solvents during the processing of this conductive polymer. Besides

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several synthetic water-soluble polymers, such as poly(vinyl alcohol) [2,3] and polyvinylpyrrolidone [4], a few biological macromolecules, such as cellulose derivatives [5,6] or proteins [7] have been used as steric stabilizers for aniline polymerization in dispersed media. One of the most interesting biological macromolecules is chitosan, an inexpensive and renewable biopolymer, which is increasingly being employed as surfactant or stabilizer [8–10]. Even though it is a naturally occurring polymer, large-scale production of chitosan is realized mainly through partial *N*-deacetylation of chitin, which is among the three most abundant biopolymers [11]. Chitosan is a soluble cationic polyelectrolyte in acidic media, and it has been previously used in PANI chemical polymerization [12]. Although to the best of our knowledge, the morphological characterization of the synthesized PANI has not been reported.

On the other hand, during the last decade, enzymatic polymerization of aniline has attracted great attention as an alternative synthetic route with lower environmental impact as compared with classical chemical oxidations because it is carried out under milder conditions and reduces the oxidation by-products to water [13–15]. One great advancement in the enzymatic polymerization of aniline was the development of the template-assisted enzymatic polymerization approach [16]. This method comprises the use of an anionic polymeric template to promote the head-to-tail coupling of aniline radicals in order to obtain a water-soluble complex of electrically conductive PANI. The template-assisted polymerization of aniline can also be performed enzymatically in a two-phase system [17], or by chemical oxidation using both synthetic [18] and biological polymers [19] yielding water-soluble polyelectrolyte complexes. However, regardless of the oxidation method employed in this approach, the separation of the PANI from the polyanion is impeded by the high degree of complexation between them.

Besides the preparation of water-soluble PANI complexes using sulfonic or phosphonic based polyelectrolytes as templates, the preparation of polymer colloids by enzymatic synthesis has attracted a great deal of attention as well. The use of a weaker anionic polyelectrolyte, such as polyacrylic acid, during enzymatic oxidation of aniline has resulted in PANI colloids [20,21]. On the other hand, the enzymatic synthesis of PANI in micellar solutions has been reported, although the morphology of the product was not characterized [22]. Enzymatic polymerization in dispersed media has been employed to obtain polyphenol particles by using poly(vinyl methyl ether) as stabilizer in partially organic media [23]. We have shown that enzymatic polymerization of aniline using poly(vinyl alcohol) as steric stabilizer results in stable dispersions of PANI colloidal particles, with physicochemical properties similar to those synthesized by chemical oxidation [24]. Recently, we reported the "smart behavior" of polyaniline colloids prepared enzymatically by using chitosan or poly(*N*-isopropylacrylamide) as steric stabilizer [25]. In this work, we focused on the use of chitosan as steric stabilizer during the enzymatic polymerization of aniline in aqueous media to understand in a more comprehensive way the formation of these colloids. It was found that the morphology is dependent on the sulfonic acid used as doping agent. The physicochemical properties of the PANI colloids were studied by different characterization techniques whereas their morphology was analyzed by transmission electron microscopy. Water-dispersible PANI colloidal particles were obtained by a fully environmentally friendly process, which combines a biopolymer as steric stabilizer, and a biocatalytic oxidation pathway. In addition, by using an environmentally sensitive polymer as steric stabilizer, a pH-responsive colloidal stability is given to the particles.

2. Experimental section

2.1. Materials

Aniline was acquired from Baker and purified by distillation at reduced pressure over a mixture of potassium hydroxide and stannous chloride. The middle fraction was collected and stored at −28 °C in the dark prior to use. Chitosan was purchased from *Carbomer*, the deacetylation degree (87%) was calculated by FTIR spectroscopy, according to the method described by Brugnerotto et al. [26], whereas the viscosimetric molecular weight ($M_v = 9.70 \times 10^6$) was determined by the Mark–Howink equation using the procedure reported by Rinaudo et al. [27]. 4-Toluenesulfonic acid (TSA), (±)-camphor-10-sulfonic acid (β) (CSA), ammonium hydroxide (28 wt%), *N*-methyl-2-pyrrolidinone (NMP), and hydrogen peroxide (30 wt%) were acquired from Aldrich. Soybean peroxidase (RZ = 1.3, Activity 56 U/mg) was purchased from *Sigma Chemical Co*. All reagents were of analytical