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Enzymatic synthesis of colloidal polyaniline particles

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Abstract

Polyaniline colloidal particles were enzymatically synthesized in aqueous media using poly(vinyl alcohol) as steric stabilizer. Hydrochloric acid, toluenesulfonic acid, and camphorsulfonic acid were used as doping agents during polymerization. Polyaniline showed chemical redox reversibility as demonstrated by changes in its electronic absorption spectra. Fourier transform infrared and UV–visible spectroscopic studies indicate a linear chemical structure of the synthesized polymer, whereas the results from X-ray photoelectron spectroscopy indicate the adsorption of poly(vinyl alcohol) at the surface of the particles. The doping agent used during the enzymatic polymerization of aniline influenced morphology and thermal stability of the synthesized particles. Polyaniline colloids prepared using *p*-toluenesulfonic acid showed spherical morphology and a narrow size distribution as shown by scanning electron microscopy and dynamic light scattering.

Keywords: Polyaniline colloids; Enzymatic synthesis; Dispersion polymerization

1. Introduction

Polyaniline (PANI), an intrinsically conducting polymer, has received great attention because of its wide potential for many technological applications, such as sensors, anticorrosion coatings, and electrorheological fluids [1,2]. This is due to its good environmental stability, adjustable electrical conductivity, and because it can be easily synthesized in large quantities from a readily available and inexpensive monomer. However, the development of the aforesaid applications has been limited by the infusible character and low solubility of this conductive polymer. Water solubility of PANI can be improved by sulfonation with fuming sulfuric acid [3], whereas doping with functionalized counter-ions has been used to dissolve PANI in cresol, xylene, and other organic solvents [4]. However, either the use of toxic organic solvents or the harsh functionalization conditions make those processes disadvantageous for commercial purposes and raise concerns about their safety in use or their potential impact for the environment. An alternative approach to improve PANI processability is its preparation in the form of water dispersible colloids. This is usually done by polymerization of aniline in an aqueous acidic solution containing a steric stabilizer, for example a water-soluble polymer [5–8]. A wide range of steric stabilizers have been studied and stable dispersions have been obtained using poly(vinyl alcohol) [5], polyvinylpyrrolidone [6], and poly (vinyl pyridine) [7], among others. Electrochemical polymerization in dispersed media has been also employed to synthesize PANI colloids [8], but large surface area electrodes are needed, making this synthetic route less attractive than chemical polymerization.

Peroxidase-mediated polymerization of aniline is a recently developed synthetic route, compared to chemical or electrochemical oxidation [9,10]. This method is carried out in milder conditions and has been mainly used to obtain water soluble complexes of PANI with polyanionic templates [11,12], although recently, PANI nanowires were obtained in peroxidase catalyzed interfacial polymerization of aniline [13]. Template-assisted enzymatic polymerization of aniline represents a great advantage in PANI processability, and stable solutions of doped PANI can be obtained in this way [10–12,14,15], however, the PANI thus synthesized is highly complexed with the template that behaves also as counterion, and consequently, isolation of the PANI in its undoped form is impeded. Unlike the anionic polyelectrolyte used in the

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template-assisted approach, steric stabilizers used in dispersion polymerization are commonly non-ionic, therefore they are adsorbed on the PANI particles in a low amount, and most of the stabilizer can be eliminated by centrifugation–redispersion cycles. The use of low molecular weight doping agents during synthesis also allows to freely change the doping agent of the synthesized PANI particles by undoping–redoping process. In enzymatic catalyzed polymerization, the oxidation rate is mainly dependent of the amount and activity of the enzyme [15,16], and unlike chemical oxidation, is a non-autocatalytic reaction [17]. For these reasons, it may be useful to prepare PANI colloids in dispersed media, because during chemical polymerization of aniline, aggregation of the particles takes place during the autoacceleration period [18], and thus, the oxidation rate is seemingly one of the key parameters to control the morphology of the colloidal particles. In addition, during enzymatic oxidation no by-products are generated, avoiding contamination of the reaction media with salts [19,20] and limiting the increase in acidity observed in chemical polymerizations of aniline [21]. Nevertheless, in spite of the potential advantage of this environmentally friendly oxidation route, enzymatic oxidation of aniline has not been carried out in dispersed media to prepare sterically stabilized PANI colloids.

In this study, water dispersible colloidal particles of PANI were obtained by enzymatic polymerization of aniline in aqueous media using poly(vinyl alcohol) as steric stabilizer. The PANI morphology was observed by scanning electron microscopy (SEM) and dynamic light scattering (DLS), whereas its chemical structure and oxidation degree were investigated by FTIR, UV–vis, and X-ray photoelectron spectroscopy.

2. Experimental

2.1. Materials

Aniline (Química dinámica, Mex.) was distilled under reduced pressure over a mixture of stannous chloride and potassium hydroxide. The middle fraction was collected and stored at −28 °C prior to use. Hydrogen peroxide (30 wt% solution), ammonium persulfate and horseradish peroxidase (HRP, Type II, 240 U/mg, RZ = 1.9) were acquired from Sigma. *p*-Toluenesulfonic acid monohydrate (TSA, +99%) was acquired from Merck. Poly(vinyl alcohol) (PVAL, hydrolyzed 99+%, M_w 89,000–98,000), aniline hydrochloride (+97%), and (±)-camphor-10-sulfonic acid (β) (CSA, +99%) were purchased from Aldrich. All reagents, except aniline, were used without further purification.

2.2. Enzymatic polymerization in dispersed media

Enzymatic dispersion polymerization was carried as follows: 18 mL of a PVAL solution (5.6 wt%), 0.002 M of aniline, and 0.002 M of doping acid (CSA or TSA) were added in a three neck 50 mL reactor and kept under vigorous magnetic stirring in a water/ice bath. When hydrochloric acid (HCl) was studied as doping agent, 0.002 M of aniline hydrochloride was added instead of the aniline and the doping acid. Then, 2 mL of a freshly prepared HRP solution in distilled water (2.5 mg/mL) were added to the reaction media. The reaction was initiated by adding 26 μL of hydrogen peroxide (30 wt%) in step additions every 3 min until equimolar ratio to aniline was achieved (8 additions). This procedure avoids inactivation of the enzyme by excess of hydrogen peroxide in the reaction media. After 2.5 h of reaction time, the obtained dark green PANI dispersion was collected by centrifugation.

2.3. Characterization

The UV–vis spectra of the PANI dispersions were obtained on a Shimadzu 2410 spectrophotometer. An aliquot was withdrawn from the reaction media and diluted in hydrochloric acid (1.0 N) or ammonia aqueous solution (0.25 N), to obtain the spectrum of the doped or undoped form, respectively. PANI particles were isolated from the steric stabilizer solution by several centrifugation–redispersion cycles using deionized water and dedoped by treatment with ammonia solution. FTIR spectra were obtained using KBr pellets on a Nicolet Magna 550 FTIR spectrophotometer. Thermogravimetric analyses were performed in a TA Instruments 2920 equipment under a 40 mL/min nitrogen flow, at a 20 °C/min heating rate. SEM images were obtained on a Leo VP1450 scanning electron microscope. X-ray photoelectron spectroscopy analysis was carried out on a modified laser ablation system, Riber LDM-32. The X-ray Al Kα line at 1486.6 eV was used as X-ray source. The binding energies were calibrated with reference to Cu $2p_{3/2}$ at 932.67 eV and Ag $3d_{5/2}$ at 368.26 eV, respectively. The base pressure in the analysis chamber was approximately 10^{-10} Torr. Survey spectra were gathered by acquiring data every 1.0 eV with an energy resolution of 3 eV. Dynamic light scattering (DLS) measurements were carried accordingly to the technique described by Riede et al. [22], using a Malvern PCS 4700 instrument equipped with a 15.3 mW argon laser operating at 488 nm and a Multi-8 7032 correlator. Prior to the measurements, PANI dispersions were diluted in 0.005 M sulfuric acid and the scattered light was detected at 90° to the incident beam. Hydrodynamic radius of the particles were calculated using the CONTIN program.

3. Results and discussion

3.1. UV–vis spectroscopy

Enzymatic reactions must be carried out at higher pH values than those employed in chemical synthesis of PANI to preserve peroxidase activity. Under these reaction conditions, branching and *ortho*-coupling reactions are favoured, and enzymatically synthesized PANI is not always structurally similar to that chemically synthesized [23]. For this reason, we carried out an UV–vis spectroscopic study of the synthesized colloids. After the first addition of hydrogen peroxide, the color of the reaction medium changed immediately to blue, regardless of the acid used as doping agent. After a few minutes, the reaction medium

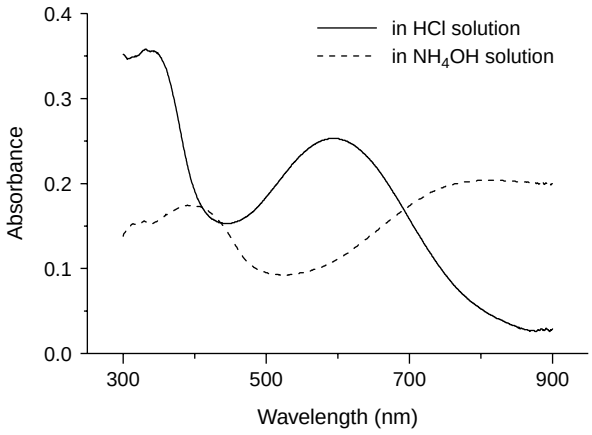

Fig. 1. UV–visible spectra of enzymatically synthesized PANI dispersion using *p*-toluenesulfonic acid (TSA) as doping agent.

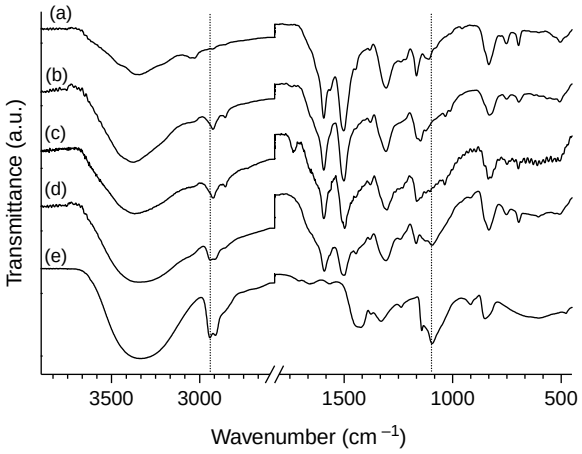

Fig. 2. Fourier transform infrared spectra of dedoped PANI particles enzymatically synthesized using: (a) HCl without steric stabilizer, (b) TSA, (c) CSA, (d) HCl, and (e) spectrum of the PVAL used as steric stabilizer. Dotted lines indicate the CH_2 and C–O stretching bands at 2950 and 1100 cm^{-1}, respectively.

showed a dark green color, which is associated to the emeraldine salt state of PANI [20]. The rate of color change is larger than that of chemical oxidation, due to absence of induction period in enzymatic oxidation [17]. The UV–vis spectrum in acidic medium of the PANI obtained using TSA as doping agent is shown in Fig. 1. The presence of a peak at 400 nm and a broad peak at 800 nm evidence the formation of a polaron [2,18]. The latter peak appears shifted to 840 nm for PANI synthesized using CSA and to 760 nm for PANI synthesized using HCl (spectra not shown), indicating differences in the polaron delocalization degree [24]. When the PANI dispersion was diluted in NH_4OH solution, a blue color was developed and the spectrum was the characteristic of the emeraldine base state of PANI, indicating that dedoping took place. Two absorption bands were observed at 330 and 600 nm, the former corresponds to the π–π^* transition of the benzenoid rings and the latter is due to the exciton absorption of the quinoid rings [24,25]. The position of the second band is dependent on the doping acid used during synthesis, appearing at 565 nm for dedoped PANI synthesized using HCl and 635 when using CSA (spectra not shown). This shift has been associated to differences in the conjugation extent [24] of the base form of PANI, which in turn, originates the different delocalization degree of the polaron observed in acidic media.

3.2. Fourier transform infrared spectroscopy

Fig. 2 shows the FTIR spectra of the isolated samples of PANI (curves a–d), and the spectrum of the PVAL used as stabilizer (curve e). Enzymatically synthesized PANI using HCl as doping agent in absence of PVAL (Fig. 2(a)) was prepared as control. The spectrum of this sample shows the main peaks characteristics of the emeraldine base form of PANI, such as the C–C stretching for quinoid and benzenoid rings at 1598 and 1504 cm^{-1}, respectively [17], the C–N– stretching at 1303 cm^{-1}, the C–N= stretching between a benzenoid and quinoid units at 1375 cm^{-1} [25], and the C–H out-of-plane bending at 830 cm^{-1} and in-plane bending at 1170 cm^{-1}, characteristics of 1,4-substituted aromatic rings [17,26]. These signals are also observed in the samples synthesized using PVAL as steric stabilizer regardless of the acid used as doping agent (curves b–d in Fig. 2) and are consistent with a predominantly linear structure of the polymer.

The presence of PVAL in the particles of PANI synthesized using HCl (Fig. 2(d)) is confirmed by the peaks marked with a dotted line at 2910 and 1110 cm^{-1}. These peaks correspond to the C–H and C–O stretching of the PVAL molecules, respectively. FTIR spectra of the PANI synthesized using TSA or CSA as doping agent (Fig. 2(b) and (c), respectively) show a lower contribution from the stabilizer, and the signal at 2910 cm^{-1} attributed to PVAL is less intense in both samples as compared to the signal at the same wavenumber in the spectrum of the PANI particles synthesized using HCl (Fig. 2(d)). The PVAL is strongly attached to the PANI particles and additional purification, i.e. further washing with hot water under ultrasonic stirring, had no effect on the PVAL signals on these spectra. A weak band at 1735 cm^{-1}, due to carbonyl stretching is observed in PANI synthesized using CSA (Fig. 2(c)), and is attributed to traces of CSA that were not eliminated during dedoping treatment of PANI [27].

3.3. Thermal stability of the colloids

The thermogravimetric analyses of the synthesized PANI colloids are shown in Fig. 3. The PANI synthesized as control in absence of stabilizer (Fig. 3(a)) shows a degradation temperature above 300 °C. The thermal stability of enzymatically synthesized PANI is lower than that of chemically synthesized PANI [17,26], most likely due to some chain defect sites that promote thermal degradation [28,29]. These chain defects are produced because of the higher pH conditions employed during the enzymatic synthesis. Since PVAL (Fig. 3(e)) has a considerably lower thermal stability than PANI (Fig. 3(a)), it is expected that adsorption of PVAL would reduce the thermal stability of the PANI colloidal particles. Accordingly, the PANI synthesized using HCl (Fig. 3(d)), the sample that showed higher amount of adsorbed PVAL in the

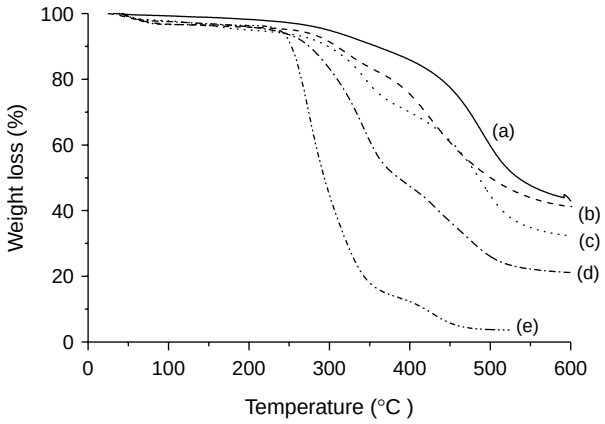

Fig. 3. Themogravimetric scans of dedoped PANI particles enzymatically synthesized using: (a) HCl without steric stabilizer; (b) CSA, (c) TSA, (d) HCl, and (e) scan of the PVAL used as steric stabilizer.

FTIR spectroscopic study, had lower thermal stability than PANI particles synthesized using TSA (Fig. 3(c)) or CSA (Fig. 3(b)) as doping agent. The weight loss below 100 °C in the PVAL (Fig. 3(e)) and in the PANI particles stabilized with PVAL (Fig. 3, curves b–d), is attributed to loss of water adsorbed, and is not shown in the control sample of PANI synthesized in absence of PVAL (Fig. 3(a)), also supporting the adsorption of PVAL on the PANI colloids.

3.4. Particle morphology and colloidal stability

The morphology of the dried colloidal particles was studied by SEM, and representative images are shown in Fig. 4. The spherical shape and the narrow size distribution of the particles, with an average diameter of 240 nm, is observed when TSA was used as doping agent (Fig. 4(a)). The particles synthesized using HCl formed chain-like structures that might result from aggregation of smaller primary particles (Fig. 4(b)) whereas those synthesized using CSA as doping agent produced flake-shaped and some needle-like particles (Fig. 4(c)). The shape and higher particle size of this sample may be the cause of the low colloidal stability of its aqueous dispersion. However, the morphology of dried PANI colloids cast as films is usually different from that observed in aqueous environment. Both PANI and the steric stabilizer might be solvated in aqueous media, and after drying the dispersion, both the shape and size is not always preserved. For this reason, a dynamic light scattering study of the colloidal particles was done. This technique has been successfully employed to determine the hydrodynamic radius of PANI colloidal particles synthesized using either inorganic [22,30] or polymeric [31] steric stabilizers. In the Fig. 5(a) the intensity-weighed size distribution for PANI colloidal particles synthesized enzymatically using TSA is shown. The average particle diameter measured was of 303 nm. The hydrodynamic radii measured by DLS is commonly higher than that observed by SEM, due to the contribution of an overlayer of the solvated steric stabilizer. In addition, swelling of the PANI colloid with water is also possible [22], particularly because the particles contain

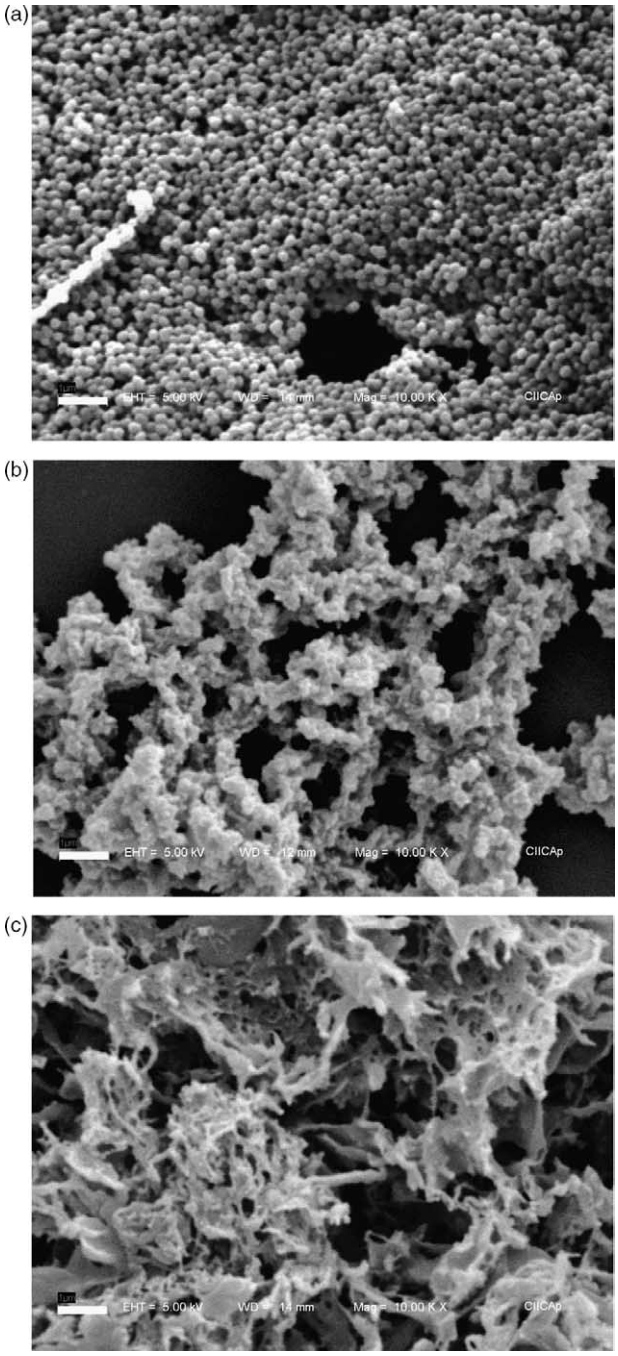

Fig. 4. SEM images of dedoped PANI particles synthesized using PVAL as steric stabilizer and different doping acid during synthesis: (a) TSA, (b) HCl and (c) CSA. The white bar on the images corresponds to 1 μm.

a certain amount of the highly hydrophilic PVAL, as indicated by FTIR. The PANI particles synthesized using HCl (Fig. 5(b)) show a multipeak distribution, most likely due to particle aggregation. The peak corresponding to particles of smaller size has an intensity-average diameter of 272 nm, and might be representative of the primary particles present in the dispersion. Two more peaks with larger intensity-average diameters (740 and 2000 nm) were observed and might correspond to aggregates of the primary particles, since SEM observation did not show individual particles of these dimensions. On the

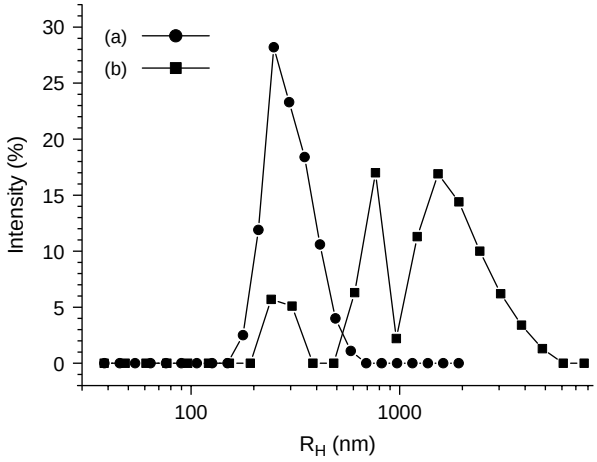

Fig. 5. Intensity-weighed size distribution for PANI colloidal dispersions recorded at 90° and synthesized using (a) TSA and (b) HCl.

other hand, DLS measurements of PANI colloids synthesized using CSA were not reproducible due to lack of colloidal stability. This might be due to several reasons, such as their high-aspect ratio shape, the formation of large aggregates or insufficient adsorption of PVAL to provide steric stabilization.

Surface composition of the dedoped PANI particles was analyzed by means of XPS. The spectra (Fig. 6) showed three peaks corresponding to the C 1s, N 1s and O 1s core-level signals. The oxygen presence is consistent with the adsorption of PVAL, although adsorption of atmospheric oxygen and incorporation of oxygen in the polymer due to overoxidation is not ruled out [32]. In fact, bulk enzymatically synthesized polyaniline in absence of PVAL also showed an O 1s peak [29]. The PANI colloidal particles displayed a higher C/N ratio as compared to enzymatically synthesized PANI reported by our group [29], indicating that adsorption of PVAL took place on the surface of the colloids. PANI synthesized using TSA has a C/N ratio of 10.8 (Fig. 6(a)), whereas that synthesized using HCl has a ratio of 29.4 (Fig. 6(b)), indicating that adsorption of

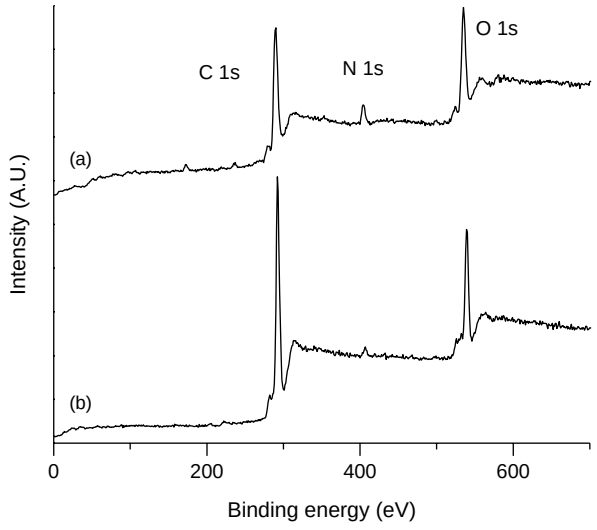

Fig. 6. XPS wide-scan of dedoped PANI particles synthesized using (a) TSA and (b) HCl.

a higher amount of PVAL on the surface was promoted by using HCl as doping agent. When the FTIR spectra of the PANI samples are compared with their corresponding XPS spectra, a large difference in the observed composition is observed. FTIR indicates that particles consist mainly of PANI, whereas the lower amount of nitrogen detected by XPS indicates a higher PVAL concentration on the surface. These results can be explained by a 'hairy-like' particle morphology, common in PANI colloids obtained by dispersion polymerization [18], that consists of a PANI core surrounded by a thin layer of adsorbed PVAL, which provides the steric stabilization.

3.5. Further discussion

PANI colloids have been commonly synthesized by chemical oxidation using HCl as doping agent [5–7,19–22,30–32], and often using CSA [8,33]. PANI doped with organic acids such as TSA or CSA is more hydrophobic, and this is supported by its increased solubility in organic solvents [4]. This factor can reduce both solvation of the colloid and adsorption of PVAL. We have attributed the differences in size and shape of the particles between the three samples discussed here, mainly to the change of the acid used as doping agent, because PANI doped either with CSA, TSA or HCl adsorbed different amounts of PVAL during their synthesis, whereas the amount of the enzyme (the oxidation catalyst) was kept constant. Adsorption of PVAL in the PANI particles occurs mainly due to hydrogen bonding, but also entanglement [6] and grafting of PVAL is possible [7]. In addition, aniline/CSA salts may self-assemble in solution producing some nanostructured materials during polymerization [13,34]. It is also noteworthy that enzymatic reactions carried out without stirring, as used extensively in chemically synthesized PANI dispersions, produced chain like agglomerates in all cases. It is possible that despite the oxidation rate of the aniline is controlled, is excessively high for dispersion polymerization, leading to aggregation of the particles, therefore additional stabilization must be provided by stirring the reaction medium [18]. Although the mechanism of colloid formation using enzymatic oxidation of aniline is still not completely understood, it must be different from the mechanism of the chemical route. For example, in dispersion polymerization of aniline through the chemical oxidation approach, after the primary PANI particles are formed and precipitated from the monomer solution, the particles coalesce and grow due to polymerization of aniline on their surfaces, while no new primary particles are formed in the autoacceleration stage [18]. This mechanism is promoted by the autocatalytic nature of the chemical oxidation. On the other hand, in the enzymatic oxidation of aniline, is possible that PANI particles grow mainly by aggregation of very small primary particles that are continuously formed during the polymerization. Further experiments, such as particle size monitoring during the reaction, are being conducted to clarify the mechanism of colloid formation using this method.

4. Conclusions

PANI colloidal particles were prepared by enzymatic polymerization of aniline in dispersed media using PVAL as steric stabilizer. Different doping agents influence the morphology and chemical properties of the synthesized particles. PANI colloids were obtained using TSA or HCl, whereas CSA led to high aspect ratio particles. Higher PVAL adsorption and lower thermal stability was obtained when HCl was used as doping agent. UV–vis spectroscopic studies showed a doping–dedoping transition, indicating switching ability between electrically conductive to insulating states of PANI. Enzymatic polymerization of aniline in dispersed media appears to be an attractive route to synthesize colloidal particles due to the lower release of by-products than traditional chemical polymerization and absence of autoacceleration stage during oxidation of the aniline.

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