Micellar Peroxidase-Catalyzed Synthesis of Chiral Polyaniline

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Micellar peroxidase-catalyzed synthesis of chiral polyaniline (PANI) in the presence of dodecylbenzenesulfonic acid (DBSA) was developed. The effect of DBSA concentration on the catalytic efficiency of horseradish and palm tree peroxidases was examined. Favorable conditions for the enzymatic synthesis of chiral PANI, determined by a multiple factors design, demonstrated that the PANIs with the highest chirality were produced in the presence of low concentrations of optically active camphorsulphonic acid (CSA). Unexpectedly, the chiral PANI was also synthesized in the absence of CSA in feed. The favorable conditions for the enzymatic production of chiral and conducting PANIs were shown to be different. The morphology of the chiral PANI particles was examined by transmission and scanning electron microscopies.

Introduction

Natural polymers such as polysaccharides, proteins, and nucleic acids are chiral. The chirality allows the use of such polymers in the separation of enantiomers[1] and in the construction of chemical and biological sensors.[2−4] Besides natural chiral macromolecular compounds, a family of synthetic optically active polymers is known.[5] Chiral polyaniline (PANI) an example of such a polymer.[6−9]

Chiral PANI was synthesized first by electrochemical polymerization of aniline (ANI) in the presence of enantiomers of 10-camphorsulfonic acid (CSA).[10] The addition of either (*R*)- or (*S*)-CSA in the reaction mixture induced the formation of a helix conformation of PANI via "sergeants and soldiers" and supramolecular memory effects.[11] Chiral PANI was also produced by dissolving the emeraldine base form of chemically synthesized PANI in *N*-methyl-2-pyrrolidone containing (*R*)- or (*S*)-CSA.[12] The CD spectra of PANI doped by (*R*)- and (*S*)-CSA were mirror images. Each species had a band in the CD spectra at 300 nm typical of CSA and bands in the range of 350−700 nm, characteristic of PANI. After dedoping PANI with NH_4OH treatment, the bands in the visible range remained. This indicated that the dedoped PANI remained in the helix conformation.

Chiral PANI also can be obtained chemically upon the polymerization of aniline in the presence of one of the CSA enantiomers and ammonium persulfate.[13] Since CSA, persulfate, and sulfate, formed as polymerization byproduct, compete for the interaction with PANI and aniline, upon chiral PANI synthesis, highly concentrated CSA is used. Interestingly, the optically active PANI salts were shown to have different conformations for their polymeric chains depending on whether they were synthesized chemically or electrochemically.[14]

Despite much progress being made in the synthesis of chiral PANI, there remains a need for a large-scale facile procedure for the production of commercially available PANI with a high chirality. One of the known approaches used for the improvement of processability of PANI is micellar synthesis, where template micelles prevent the precipitation of PANI upon its synthesis.[15,16] Dodecylbenzenesulfonic acid (DBSA) is usually used in the micellar synthesis of PANI because this surfactant is able both to form micelles and concurrently to dope PANI. In this paper, we report the micellar synthesis of chiral PANI in the presence of DBSA using acid-stable palm tree peroxidase (PTP) as a catalyst for aniline polymerization.

Experimental Procedures

Materials. Aniline was purchased from the Sigma Chemical Co. and was purified by distillation before use. (*R*) and (*S*) enantiomers of 10-camphorsulfonic acid (CSA) were from Sigma Chemical Co., a 30% aqueous solution of H_2O_2 −was from Chemapol, and DBSA −was from TCI. All solutions were prepared using distilled water.

PTP was purified to homogeneity as described elsewhere.[17] The specific activity of PTP measured toward guaiacol was 6000 units/mg of protein. Isoenzyme C of horseradish peroxidase (HRP) (RZ 3.0, specific activity 1100 U/mg) was purchased from Merck.

Effect of DBSA on Catalytic Efficiency of Plant Peroxidases. The catalytic efficiency of the plant peroxidases was expressed by a second-order rate constant (k_{app}) calculated using eq 1.

$$k_{app} = \frac{\text{rate}}{[S]_0[E]_0} \quad (1)$$

where $[S]_0$ and $[E]_0$ are the total concentrations of substrate and peroxidase, respectively. Previously, this approach was successfully

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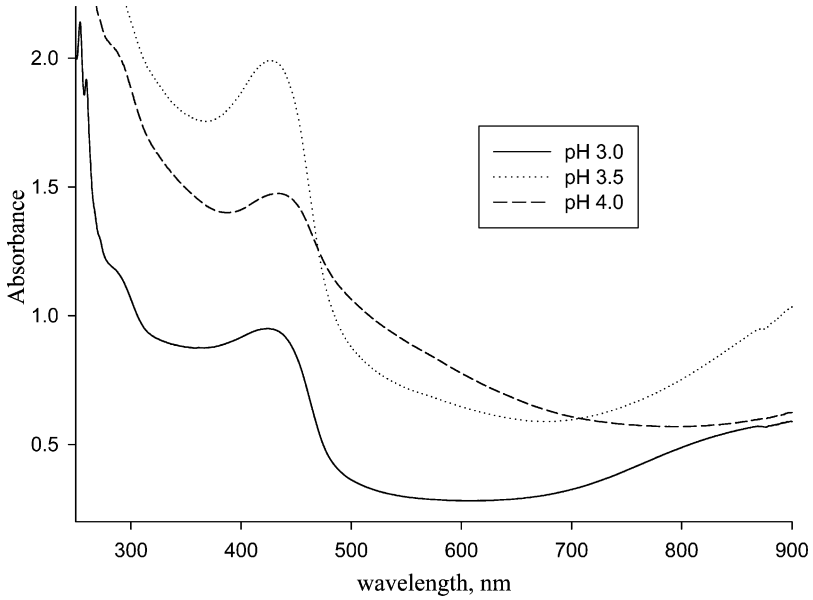

Figure 1. Effect of pH on the yield of aniline polymerization in the presence of DBSA micelles catalyzed by PTP at room temperature. The UV−vis spectra of PANI samples were recorded after 20-fold dilution by water. Experimental conditions of the synthesis: [aniline] = 100 mM, [DBSA] = 17 mM, [(*R*)-CSA] = 100 mM, and [PTP] = 1×10^{-7} M. Hydrogen peroxide was added 5 times with 10 min intervals, each time increasing the concentration of H_2O_2 in the reaction mixture up to 1 mM.

Table 1. Effect of DBSA on Catalytic Efficiency of Horseradish and Palm Tree Peroxidases

	favorable conditions for HRP and PTP catalysis			
enzyme	[DBSA] (mM)	[H_2O_2] (mM)	[*o*-dianizidine] (mM)	k_{app} (M^{-1} s^{-1})[a]
HRP		1.43	0.12	2.9×10^6
PTP		4.20	0.12	8.9×10^6
HRP	17	0.72	0.4	1.6×10^6
PTP	17	1.3	0.4	2.7×10^6

[a] Peroxidase activity was measured toward *o*-dianizidine in 90 mM citrate-phosphate buffer, pH 5.2

used to evaluate the catalytic efficiency of some plant peroxidases toward different substrates.[18−20]

The peroxidase activity was measured as follows: 1 mL of 90 mM citrate-phosphate buffer, pH 5.2, containing *o*-dianizidine, hydrogen peroxide, and DBSA (0 or 17 mM) was mixed with 10 μL of enzyme solution (final concentration 4.5×10^{-10} M). The optimal concentrations of substrates for each enzyme in the absence and presence of DBSA were determined in separate experiments (Table 1) as described previously.[18−20] The absorbance change at 420 nm was measured at 25 °C. The extinction coefficient for products formed upon *o*-dianizidine oxidation was 30 mM^{-1} cm^{-1}.

Enzymatic Synthesis of Chiral Polyaniline. The synthesis of chiral PANI was initiated by adding 15 μL of stock solution of PTP (2×10^{-5} M) in 3 mL of an aqueous solution of 75−150 mM aniline containing optically active CSA (0−150 mM) and DBSA (12−22 mM). The favorable conditions for the enzymatic synthesis of chiral PANI were determined by a multiple factors design.[21] Under experimental conditions, DBSA formed micelles because the critical micellar concentration for DBSA was 8.4 mM.[22] The pH value of the reaction mixture was justified using concentrated H_3PO_4 and 2 M NaOH. An aqueous solution of 0.2 M hydrogen peroxide (15 μL) was added incrementally in 10 separate portions (unless otherwise mentioned) at intervals of 10 min, each time adjusting the concentration of hydrogen peroxide up to 1 mM. The 10 min interval between hydrogen peroxide additions was used because for this period, the reaction stopped due to complete H_2O_2 consumption. The polymerization proceeded at 25 °C upon continuous agitation. The aniline polymerization was evaluated using visible spectroscopy.

Table 2. Variables Estimated at Optimization of Conditions of Enzymatic Synthesis of Chiral PANI in DBSA Micelles

	level		
variables	low (−1)	intermediate (0)	high (+1)
[ANI] (mM)	75	112.5	150
[(*R*)-CSA] (mM)	0	75.0	150
[DBSA] (mM)	12	17.0	22

Table 3. Experimental Conditions Used at Optimization of Enzymatic Synthesis of Chiral PANI in DBSA Micelles

	level		
no. of experiment	[ANI]	[(*R*)-CSA]	[DBSA]
1	−1	−1	−1
2	+1	−1	−1
3	−1	+1	−1
4	+1	+1	−1
5	−1	−1	+1
6	+1	−1	+1
7	−1	+1	+1
8	+1	+1	+1
9	−1	0	0
10	+1	0	0
11	0	−1	0
12	0	+1	0
13	0	0	−1
14	0	0	+1

Spectral Studies. UV−vis-NIR spectra of PANI samples were recorded on a Shimadzu UV-2401 PC spectrophotometer, and before measurement, the samples were diluted 20-fold with water to destruct DBSA micelles since the micelles with adsorbed aniline/PANI molecules were not optically transparent. In each measurement, distilled water was used as a control.

The chirality of as-synthesized PANIs was characterized by a Jasco 715 spectropolarimeter. The molar ellipticity (θ) (deg $decimol^{-1}$ cm^2) was calculated on the basis of the tetrameric repeat unit of the emeraldine form of PANI as described previously.[23] As in the case of UV−vis-NIR spectroscopy, before recording the CD spectra, the PANI

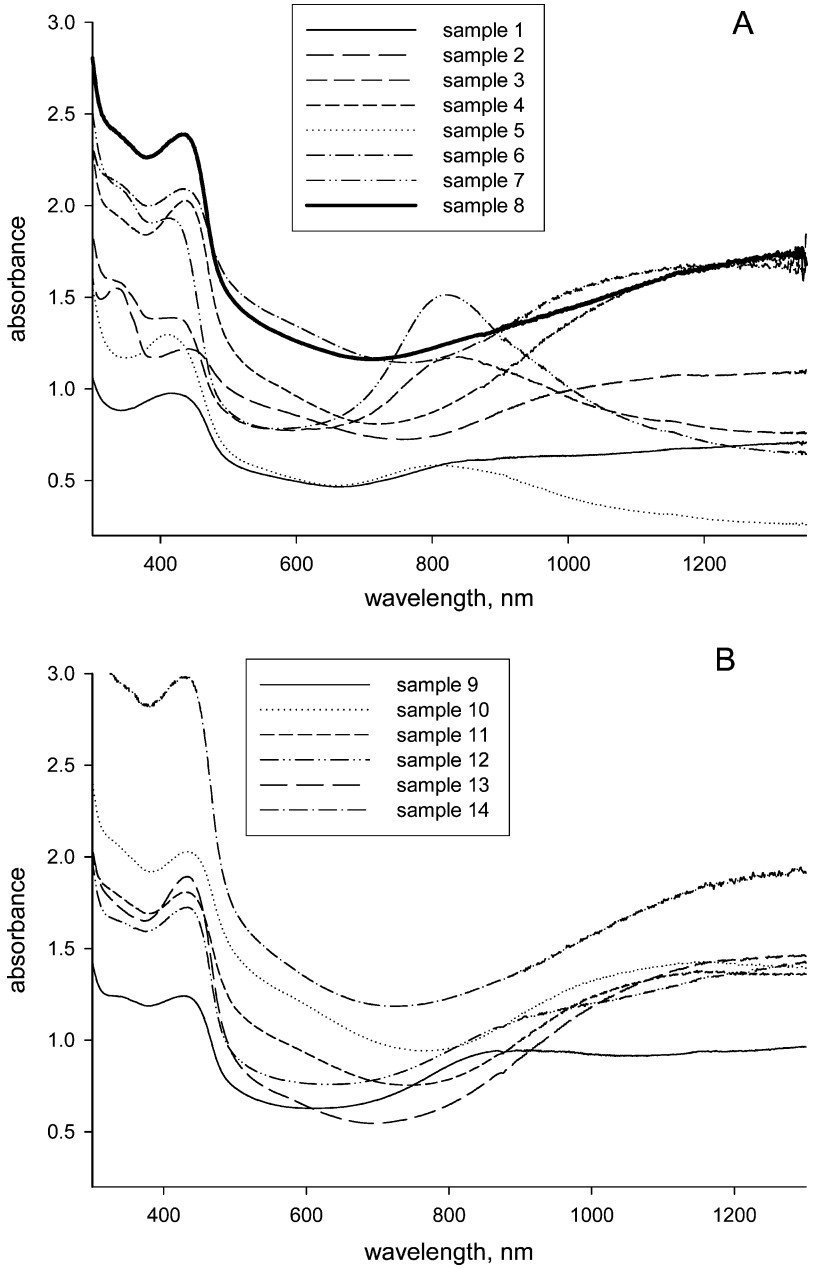

Figure 2. UV−vis-NIR spectra of PANI samples enzymatically synthesized in DBSA micelles. Spectra were recorded for the samples diluted 20-fold by water. Experimental conditions for PANI synthesis are presented in Tables 2 and 3.

samples were diluted 20-fold with water. The reaction mixture without hydrogen peroxide was used as a control.

EPR Studies. EPR spectra of as-synthesized PANI (150 μL aliquots in a quartz cuvette) were recorded on a Varian E-3 spectrometer using a microwave power of 4 mW and modulation amplitude of 0.5 G at a temperature of 293 K. For each PANI sample, the ratio EPR signal area/PANI concentration was calculated.

The PANI samples were purified by precipitation by adding 4 mL of water per each 1 mL of sample. Green precipitates obtained were collected by centrifugation (10 000 rpm for 5 min, 25 °C) and then washed 3 times with water. Finally, PANIs were dried at room temperature in a vacuo desiccator over $CaCl_2$. The quantity of the thus obtained PANI was determined gravimetrically.

A *g*-value was measured by conventional methods using the standard containing the signal of Mn(II) diluted by MgO and crystallized 2,2′-diphenyl-1-pycrylhydrazine.

Morphology. The morphology of the PANI samples was studied by TEM (Hitachi HU-11B) with an accelerating voltage of 75 kV and by SEM (JSM-6700 F JEOL) with an accelerating voltage of 10 kV. Prior to the morphological study, the solid PANI samples purified as described previously (EPR Studies section) were dispersed in water using ultrasonic treatment for 0.5 min (Branson Sonifier 250, power 200 W). Then, the obtained dispersions were adsorbed onto the Formvar film attached to 200-mesh copper TEM grids. The same dispersions were evaluated by SEM.

Results and Discussion

DBSA micelles are usually used in the polymerization of aniline to improve PANI processability because in the presence of this detergent, PANI is produced in a dispersed form, which is stable for a long time. However, when enzymes (peroxidases and laccases) are used as catalysts in PANI synthesis,[24−26] DBSA, like other detergents, can destroy their native 3-D structure and, hence, inactivate these biocatalysts. To evaluate

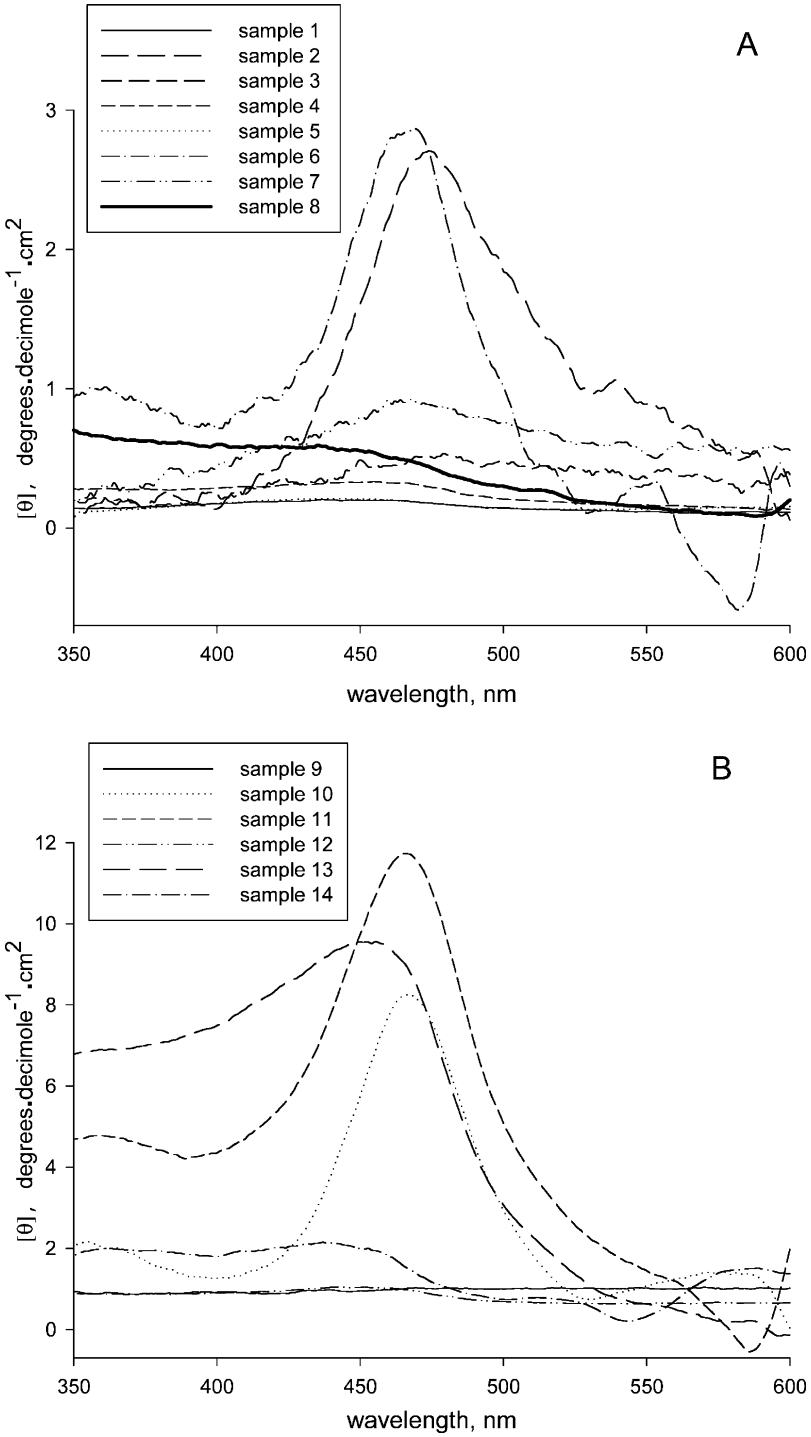

Figure 3. CD spectra of PANI samples enzymatically synthesized in DBSA micelles. Spectra were recorded for samples diluted 20-fold by water. Experimental conditions for PANI synthesis are presented in Tables 2 and 3.

the effect of DBSA on peroxidase catalysis, the second-order rate constant (k_{app}) values for horseradish peroxidase (HRP) and PTP were determined in the absence and presence of DBSA (17 mM).

As seen in Table 1, in the absence of DBSA, palm peroxidase was a more active biocatalyst than HRP. The DBSA presence in the reaction mixture resulted in a 2−3-fold decrease of the catalytic efficiency of both enzymes. The results obtained showed that although the enzymatic activity of PTP dropped in the presence of DBSA micelles, its catalytic efficiency in the presence of DBSA was similar to that of HRP without DBSA. Likewise, taking account of the fact that the stability of PTP under acidic conditions[27,28] as well as in the presence of H_2O_2[29] is higher than that of HRP, we used PTP as a biocatalyst in the PANI synthesis.

The study of PTP-catalyzed polymerization of aniline in the presence of sulfonated polystyrene (SPS) demonstrated that the maximum yield and highest rate of the reaction were observed when the reaction proceeded at pH 3.5.[25] As seen in Figure 1, the replacement of SPS with DBSA in the reaction mixture did not change the optimal pH value for PTP catalysis. Therefore, in this work, all synthetic experiments were carried out at pH 3.5.

The concentrations of aniline, CSA, and DBSA in feed can affect the efficiency of the micellar PTP-catalyzed synthesis of chiral PANI. To find favorable conditions, we used a multiple

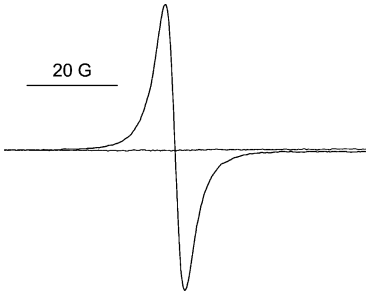

Figure 4. EPR spectrum of PANI enzymatically synthesized in DBSA micelles (sample 11). Conditions of the sample preparation are described in the EPR Studies section.

factors design with three independent variables. The variables and their concentrations are presented in Table 2. According to the theory of factorial design, for the optimization of conditions of chiral PANI synthesis, 14 different samples of PANI were obtained (Table 3).

As seen in Figure 2, the PANI samples obtained upon the enzymatic synthesis had UV−vis-NIR spectra typical of doped PANI. All spectra had a broad absorption band at 400−415 nm related to the doping level and formation of the polaron of PANI.[30,31] From the magnitudes of maxima of this peak, we showed that the highest yield of PANI was obtained when the reaction mixture contained 137 mM aniline and 22 mM DBSA and was in the absence of CSA (sample 14).

Some of the PANI samples obtained (1, 3, 5, 7, and 9) showed a band at 800 nm and a low absorption in the NIR range that indicated a formation of a compact coil conformation of the PANI chains.[32] Note that these samples were obtained when the lowest concentration of aniline (75 mM) in feed was used. Contrary to the samples mentioned previously, the others had a low adsorption at 800 nm and a free-carrier tail in the NIR range. The significant delocalization in the polaron band suggests the existence of an expanded coil type of conformation for chains of PANI samples of the latter group.[33,34]

Also note that both in the absence and in the presence of (*R*)-CSA, the spectra of enzymatically produced PANI were similar. Interestingly, the addition of CSA in feed significantly decreased both the rate of the enzymatic synthesis of PANI and the yield of the product.

A comparison of CD spectra of PANI samples obtained showed the chirality of PANI to strictly depend upon reaction conditions. Figure 3 shows that some of the samples had CD spectra in the visible range characteristic of chiral PANI.[14,35] CD spectra were recorded for the PANI preparations diluted with water to destruct DBSA micelles. Note that the control samples (the reaction mixtures without hydrogen peroxide) were achiral. Interestingly, the CD spectra of PANIs synthesized with (*R*)- and (*S*)-CSA were practically identical (data not shown). Previously, it was reported that the spatial configuration of CSA had no effect on the CD spectra of the polyelectrolyte complex of chiral PANI and poly(acrylic acid).[9]

PANI samples 2, 6, 10, 11, and 13 (Figure 3) had the highest chirality. Unexpectedly, all these chiral PANI samples were synthesized either in the absence or at low concentrations of (*R*)-CSA. Conversely, when the synthesis of the PANI samples proceeded at high concentrations of CSA, the obtained samples had a low chirality. Therefore, the addition of CSA in feed upon the peroxidase-catalyzed polymerization of aniline in the presence of DBSA micelles prevents the formation of an optically active conformation of PANI chains successfully formed in the absence of CSA.

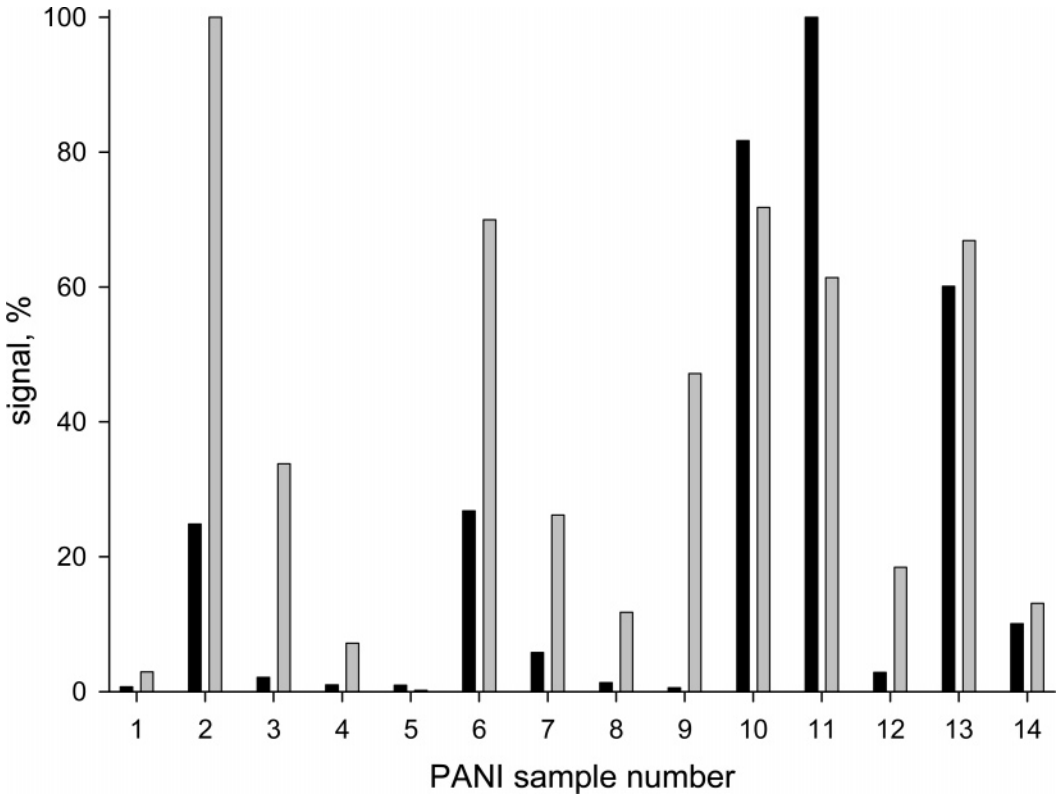

Figure 5. Dependence of values of molar ellipticity of PANI samples measured at 470 nm and area of their EPR signals as a function of the conditions of the enzymatic polymerization of aniline (compositions of the reaction media for each PANI sample are summarized in Table 3). Black bars: molar ellipticity and gray bars: ratio of EPR signal area/PANI concentration. Maximum values of molar ellipticity and ratio of EPR signal area/PANI concentration were taken as 100%.

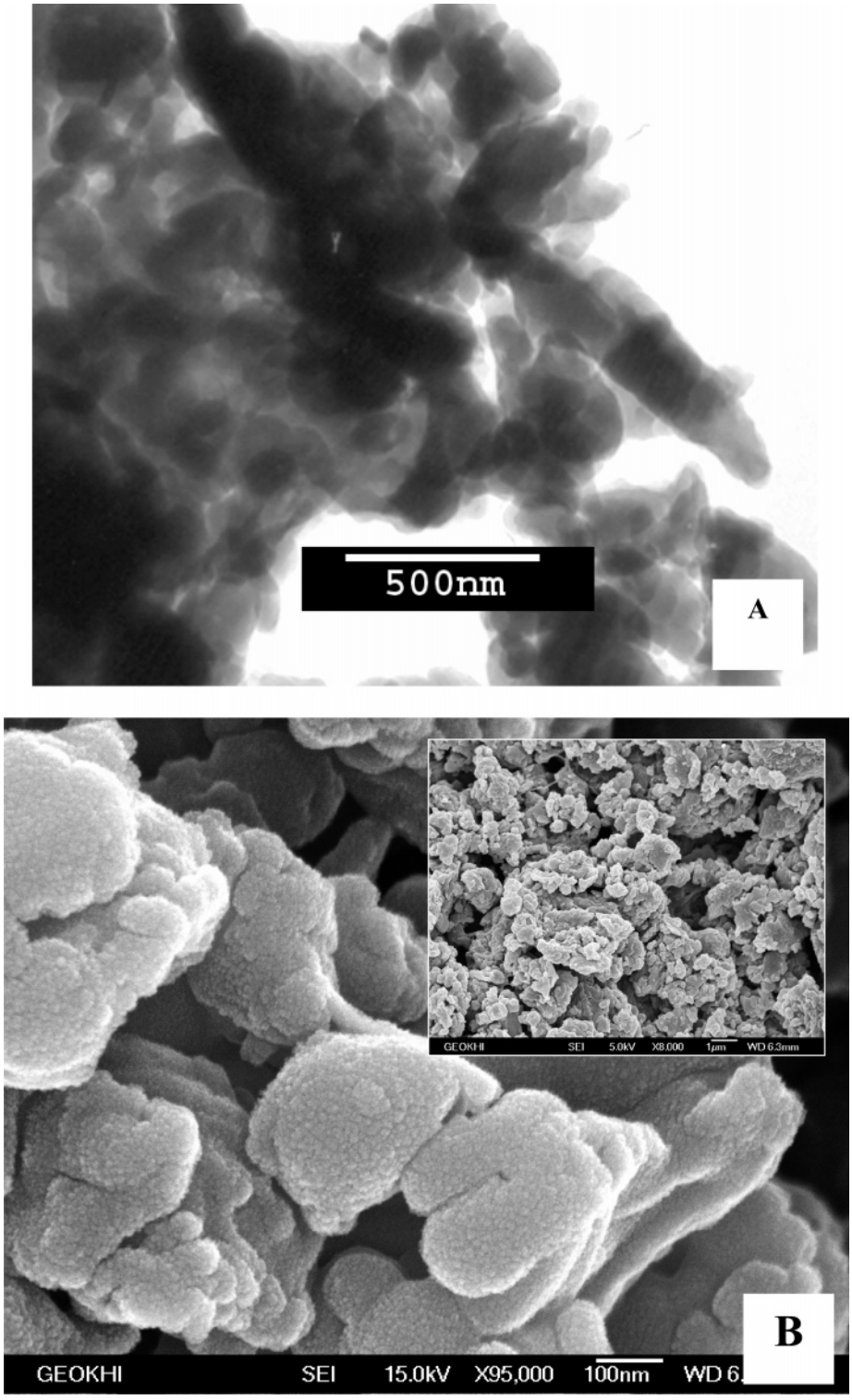

Figure 6. TEM (A) and SEM (B) images showing the morphology of chiral PANI particles (sample 11) enzymatically produced in DBSA micelles. Conditions of the sample preparation are described in the Morphology section.

Using factorial design, the dependence of molar ellipticity of PANIs as a function of the synthesis parameters was calculated (see Supporting Information)

$$[\theta]_{PANI} = -0.1[ANI]^2 - 0.01[ANI][CSA] - 0.02[CSA]^2 + 0.003[CSA][DBSA] + 5.8[DBSA]^2 + 0.005[ANI][DBSA] + 23[ANI] + 2.8[CSA] + 193[DBSA] - 2583 \quad (2)$$

Thus, all variables strictly affected PANI chirality. Note that contrary to the chemical and electrochemical syntheses, the enzymatic synthesis of chiral PANI did not demand high concentrations of CSA in feed. From eq 2, we determined the favorable conditions for the PTP-catalyzed synthesis of chiral PANI: 125 mM aniline, 17 mM DBSA, and 47 mM CSA.

The appearance of chiroptical effects for PANI likely can be explained by the formation of helical conformations of PANI chains, where chiral molecules of PTP can play a role as a chirality inductor. Yet, the intramolecular organization, a self-assembly of stiff, planar PANI molecules on the DBSA micelle surface, can also explain the optical activity of the resultant

PANI samples. Previously, a similar phenomenon was reported for chiral polythiophenes.[36]

The EPR method allowed a detection of unpaired or conducting electrons formed upon synthesis and doping of PANI. The EPR study showed that all PANI samples had similar spectra with a *g*-value typical of the EPR signal of free electrons (2.002)[37,38] (Figure 4). The absence of a hyperfine structure in the EPR spectra of the samples confirmed the existence of delocalized free radicals in the polymer backbone.

Comparison of the EPR signal area and molar ellipticity values for PANI samples demonstrated that no correlation existed between these parameters (Figure 5). This means that favorable conditions for the synthesis of PANI samples with chiroptical and conducting properties that are different should be taken in consideration upon the production of PANI with predominant properties.

The morphology of PANI samples was examined by TEM and SEM. It was shown that all PANI samples had the same morphology independently of the conditions of their synthesis. As seen in Figure 6A, the PANI aggregates consisted of individual rice-grain particles (average length ~140−180 nm and average width ~70−100 nm). A similar morphology for PANI particles was reported previously.[39] Moreover, the SEM image demonstrated that the surface of the PANI particles was porous (Figure 6B).

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Supporting Information Available. Calculation of the molar ellipticity of PANIs as a function of the synthesis parameters using the factoral design. This material is available free of charge via the Internet at http://pubs.acs.org.

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