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# Laccase-mediated synthesis of conducting polyaniline

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ABSTRACT

Laccase-mediated system based on potassium octocyanomolybdate (4+) was first used for acceleration of the enzymatic aniline polymerization. The enzymatic reaction yielded oxidized octocyanomolybdate (5+) which can oxidize the aniline monomer to the aniline radical cation. This resulted in the formation of conducting polyaniline with the concomitant regeneration of the redox mediator. The proposed method is environmentally benign, permits a higher degree of control over the kinetics of the reaction and, hence, the synthesis of a conducting polymer with improved physicochemical properties. The optimal conditions for the laccase-mediated synthesis have been found. The redox mediator does not modify the backbone of conducting polyaniline (PANI). The characterization of the polymer obtained by either a laccase-catalyzed method or a laccase-mediator method was carried out using UV–vis, FTIR spectroscopy, TEM investigation and the MALDI-TOF mass spectrometry. The advantage of a laccase-mediated synthesis of PANI compared with the synthesis catalyzed by laccase alone has been shown.



## 1. Introduction

Laccases (benzenediol: oxygen oxidoreductase, EC 1.10.3.2) are the multicopper oxidases which catalyze the oxidation of a wide range of organic and inorganic substrates with the concomitant four-electron and four-proton reduction of molecular oxygen to water [1,2]. The natural substrate of laccase is monolignol which upon oxidation polymerizes into lignins [3]. In addition, laccase catalyses the in vitro polymerization of aniline and a number of phenol derivates [4–7]. The enzymatic oxidation of organic substrates occurs with specificity of laccases depending on the structure and redox potential of the T1 copper site ($E_{T1}$), the first electron acceptor of the enzyme [8]. According to $E_{T1}$, laccases can also be classified as low- and high-redox potential enzymes [9–11]. It is believed that only compounds with the ionization potentials below $E_{T1}$ can be efficiently oxidized by laccase [12].

Since 1990 when the ABTS was found to serve as a substrate mediating the enzyme action, [13] the range of compounds that can be converted by laccases has dramatically increased. Mediators were considered to represent mean low molecular weight laccase substrates whose enzymatic oxidation gives rise to stable high redox potential intermediates. The latter take part in chemical (nonenzymatic) reactions with another compound, not oxidizable by laccase alone, following the diffusion-controlled kinetics. The oxidized mediator is reduced to the initial form by the component to be oxidized [14,15], thereby closing the cycle. Laccase-mediator systems are employed in different biotechnological processes, such as green biodegradation of xenobiotics including pulp bleaching [16,17] and green organic synthesis including polymer synthesis [18,19].

Polyaniline (PANI) is an important member in the class of intrinsically conducting polymers due to an easy doping–dedoping process and its thermal and environmental stability. The conjugation mechanism of PANI is unique among other conducting polymers owing to a combination of benzenoid and quinoid rings leading to three different oxidation states [20]. PANI has many potentialities for practical applications: rechargeable batteries [21]; energy-storage devices [22]; anticorrosion protection [23]; antistatic coating [24], biosensors [25] and so on. A common method for aniline polymerization is chemical oxidation under harsh conditions using as oxidant ammonium peroxydisulfate, potassium dichromate or ferric chloride in highly acidic solutions [26–29]. The reaction proceeds with an induction period due to

*Abbreviations:* PANI, polyaniline; FTIR, Fourier transform infrared spectroscopy; TEM, transmission electron microscopy; MALDI TOF, matrix assisted laser desorption/ionization coupled to time-of-flight mass spectrometry; SDBS, sodium dodecylbenzenesulfonate; PAMPS, poly(2-acrylamido-3-methyl-1-propanesulfonic acid); NHE, normal hydrogen electrode; ABTS, –2,2′-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt; PEDOT, poly(3,4-ethylenedioxythiophene).

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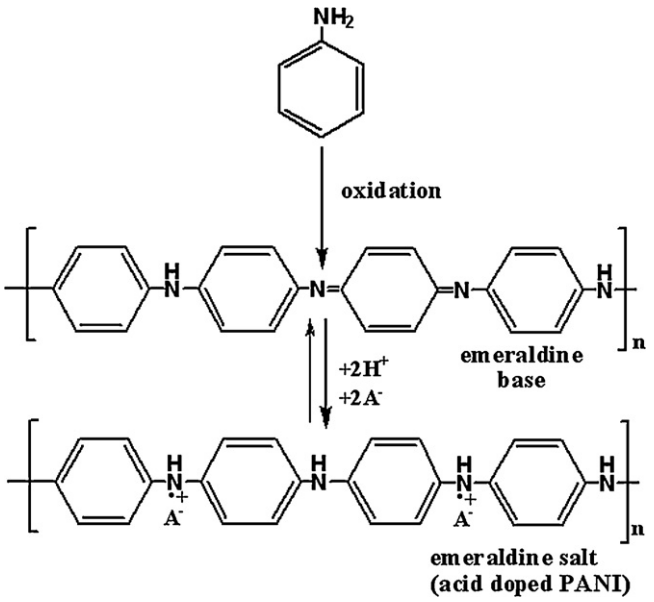


**Fig. 1.** Chemical structure of polyaniline forms.

the autocatalytic mechanism of the chemical oxidation of aniline [30]. The emeraldine base of polyaniline is formed in the course of the monomer oxidation (Fig. 1). Emeraldine salt is usually obtained from the emeraldine base via protonation of its imine sites with sufficiently strong acids. This process is referred to as "doping".

It has been shown over the past decade that enzymatic catalysis is more attractive as an alternative route for the synthesis of conducting PANI because it is carried out under milder conditions compared with the chemical aniline polymerization [31–33]. The enzymes used in this method are mainly peroxidases, for example, horseradish peroxidase, soybean peroxidase, palm tree peroxidase or other oxidoreductases, e.g. glucose oxidase [34]. In contrast to a chemical synthesis, an enzymatic reaction of the monomer polymerization occurs without an induction period as observed in chemical reactions [35,36].

The use of laccase as a catalyst in aniline polymerization has attracted a great interest as an alternative route as compared to both chemical and peroxidase-based synthesis. In contrast to the peroxidase-based oxidative polymerization, the laccase catalyzed production of PANI is not only environmentally friendly but also does not require a stepwise addition of diluted hydrogen peroxide to the reaction medium. The atmospheric oxygen in laccase-catalyzed reactions serves as oxidant. It is worth mentioning that peroxidases are very sensitive to the hydrogen peroxide concentration and at above 1 mM they start to loose their catalytic activity. Moreover, some peroxidases (e.g. horseradish peroxidase) show a low stability at pH below 4 due to acidic dissociation of holoenzyme.

The polymerization rate of aniline with laccase alone is relatively low due to its high oxidation potential. Redox mediators for laccase can accelerate the polymerization reaction of the monomer and make it possible to obtain the PANI with different molecular weight and solubility.

It is of interest in this context to study into the properties of both the PANI synthesized by various methods and its complexes with other components such as a polymeric acid or an anionic surfactant. The use of the template-assisted method of the enzyme-catalyzed PANI synthesis enables the formation of water-dispersible PANI/template complexes and investigation of the polymerization reaction. The aim of this work is to study the effect of the redox potential of the T1 center of various laccases and the redox mediator of this enzyme on the oxidative polymerization of aniline, as well as a comparison of the physical and chemical properties of the PANI obtained by laccase-catalyzed and laccase-mediator methods.

## 2. Materials and methods

### 2.1. Materials

Aniline (Labtech, Russia) was distilled under a reduced pressure before using. Potassium octacyanomolybdate (4+), poly(2-acrylamido-2-methyl-1-propanesulfonic acid), PAMPS (MW ca. 2,000,000 Da, Aldrich, USA), dodecylbenzenesulsonic acid sodium salt, sodium hydroxide (Fluka, Italy), $Na_2HPO_4$, citric acid anhydrous (Riedel-deHaën, Germany), tetrahydrofurane (VWR, Austria), potassium ferrocyanide trihydrate (ICN, USA) were used without further purification. Fungal laccase from *Trametes hirsuta* (Wulfen) Pilát CF-28 was purified to homogeneity as described previously [37]. The specific activity of the enzyme preparation was ca. 200 units/mg of protein using catechol as substrate. Partly purified *Rhus vernicifera* laccase from the latex of the lacquer tree was kindly provided by Prof. B. Reinhammar (University of Gothenburg, Sweden). The final purification for the laccase was performed by mean of HPLC on TSK DEAE-2SW column (LKB, Sweden) using a Stayer HPLC system (Acvilon, Russia). The enzyme was homogeneous as judged from SDS-PAGE. All the solutions were prepared using water purified with Milli Q system (Millipore, USA).

### 2.2. Methods

#### 2.2.1. Polymerization

In the case of laccase-catalyzed polymerization, equimolar quantities (typically 10 mM) of the surfactant template SDBS and aniline were dissolved into 10 mL of 50 mM $Na_2HPO_4$–citric acid buffered solution (maintained at pH 3.5) at room temperature with constant stirring. The pH was then adjusted to 3.8 with $H_3PO_4$. Micelles formed spontaneously when the concentration of the surfactant in the solution was higher than the critical micellar concentration (CMC). The known CMC of SDBS is 1.6 mM [38]. The reaction was initiated by the addition of 16 μL of the stock laccase solution under vigorous magnetic stirring. The final activity of laccase in the reaction medium was about 60 units. It is noteworthy that in the case of aniline enzymatic polymerization atmospheric oxygen serves as oxidation agent and laccase is the catalyst.

After initiation, the reactions were left under stirring for more than 24 h to complete the polymerization process, and UV–vis spectra of the reaction products were constantly being recorded at certain intervals.

Depending on the purpose of the experiment, either the initial aqueous PANI/SDBS dispersion obtained by both laccase-catalyzed synthesis and laccase-mediated synthesis or the surfactant-free product was used. To do this, the product of the enzymatic synthesis was first treated with 3% aqueous ammonia for 3 h and then diluted with the equal volume of ethanol. The precipitate was separated by centrifugation, washed with deionized water, and dried for 48 h at 70 °C.

The guided-template method of the laccase-catalyzed aniline polymerization with PAMPS as a template was carried out as follows.

A reaction solution containing both freshly double distilled aniline (25 mM) and PAMPS (25 mM, based on the monomeric repeat unit) in 0.1 M Na-citrate-phosphate buffer (pH 3.5) was stirred for 1.5 h. Polymerization in the enzymatic syntheses was initiated by the addition of the laccase from *T. hirsuta* or *R. vernicifera* with the final specific activities of the enzymes in the reaction medium

1.2 U/ml. The syntheses of PANI/PAMPS complexes were carried out in a humidity chamber at 20 °C under the air saturated conditions at continuous stirring for 24 h to complete the reaction of polymerization. The obtained complexes were purified several times by dialysis against deionized water in order to remove excess low molecular weight compounds. The final products were monitored using UV–vis spectroscopy.

The laccase-mediated synthesis of conducting PANI based on the guided-template method using SDBS or PAMPS as templates was carried out as described above but in the presence of the redox-potassium octocyanomolybdate (4+) in the concentration range of 0.01–0.1 mM.

#### 2.2.2. Characterization

FTIR-spectra of dedoped products of the enzymatic aniline polymerization in KBr pellets were recorded with a Nicolet Magna-750 spectrophotometer. The morphology of the product was studied by transmission electron microscopy using JEM-100 CX/SEG ("Jeon", Japan). The sample of the aqueous dispersion was preliminary dialyzed against deionized water to separate excess salt whose crystals could cause the image distortion and then spotted onto templates. MALDI-TOF spectra of the dedoped products were obtained on a Brucker Daltonics Microflex mass spectrometer. The spectra were recorded in the reflection mode. The instruments were calibrated against peptides with the known molecular mass from 700 Da to 3500 Da.

Conductivity measurements of the PANI product were carried out by a two-probe method.

## 3. Results and discussion

### 3.1. The influence of the redox potential of the T1 copper site of laccase on the rate of aniline polymerization

One of the objectives of this study was to define the efficiency of polymerization of aniline by laccases with different redox potentials of the T1 centers. The polymerization products of the monomer are water-insoluble, which hampers the investigation process into this reaction. Therefore, this study utilized a template method of the enzymatic synthesis of PANI which makes it possible to yield water dispersible complexes of polyaniline with the template and to study the reaction of oxidative polymerization of aniline. Aqueous solutions of micelles of SDBS and PAMPS were used as templates. These templates have the two main functions: (1) they bind and align the aniline cation, thus resulting in a preferential head-to-tail coupling and therefore leading to the formation of mainly a linear structure of PANI; (2) the template molecules are attached to the backbone of PANI and play the role of a dopant which leads to an increase in the conductivity of a polymer.

Electrooxidation of aniline at a glassy carbon electrode at pH values appropriate for the conditions of the laccase-catalyzed synthesis starts at a potential of ~950 mV (vs. NHE). The redox potential of the T1 center of a high redox potential fungal laccase *T. hirsuta* is 780 mV (vs. NHE) [39]. The oxidation reaction of aniline involving laccase *T. hirsuta* can occur at a sufficiently high rate due to a small difference in redox potentials. The result is the formation of an conducting PANI/PAMPS complex (see Fig. 2(1)). Laccase *R. vernicifera* has a redox potential of the T1 center (the primary electron acceptor) of the enzyme ~420 mV (vs. NHE) [40]. The difference in the oxidation potentials of aniline and the T1 center of this enzyme is ~530 mV, which makes the reaction of the oxidative polymerization of aniline impossible (Fig. 2(2)).

The conductivity of the sample of the PANI/PAMPS complex synthesized using laccase *T. hirsuta* was ~1 mS/cm. Thus, the polymerization of aniline can be achieved only using high redox potential laccases.

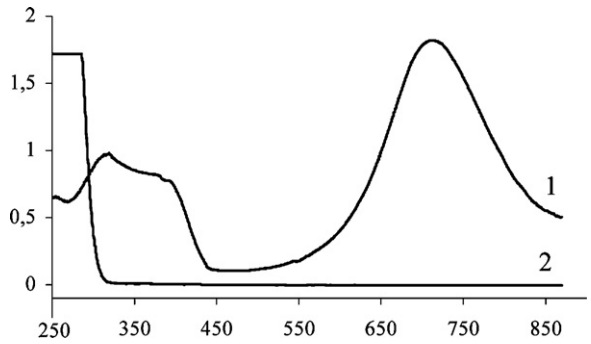


**Fig. 2.** UV–vis absorption spectra of laccase-catalyzed aniline polymerization with different laccases: 1, high redox potential *T. hirsuta* laccase; 2, low redox potential *R. vernicifera* laccase. Experimental conditions: 0.1 M Na-citrate-phosphate buffer, pH 3.5; [laccase *R. vernicifera*] = [laccase *T. hirsuta*] = 0.6 U/ml; [aniline] = [PAMPS] = 25 mM; reaction time = 100 h. The product of aniline polymerization with laccase *T. hirsuta* was diluted with buffer (1:10).

### 3.2. Enzymatic synthesis of the PANI/PAMPS complex using laccase-mediator system

The reaction of the enzymatic polymerization of aniline involving laccase proceeds, in contrast to the chemical polymerization of the monomer, in the kinetic mode, its rate depending on the concentration of the enzyme [36]. However, given the high cost of the biocatalyst and a quite low rate of polymerization of the monomer, there is another way of accelerating this reaction which is based on the usage of laccase enhancers. The scheme of reactions occurring in the laccase-mediator system of the polyaniline synthesis is presented below (Fig. 3). Potassium octocyanomolybdate (4+) was used as a redox mediator. The laccase-mediator synthesis of PANI was carried out following the investigation into the correlation between the rate of enzymatic oxidation of the redox mediator involving a high redox potential laccase from the fungus *T. hirsuta* and the pH of the reaction medium. This study is needed since the synthesis of the electrically conductive PANI with a linear structure is possible only in acidic conditions. Therefore, the enzymatic transformation of the redox mediator should proceed under acidic conditions. Fig. 4 shows the profile of the pH dependence of the enzymatic oxidation of the redox mediator $K_4Mo(CN)_6$ involving a fungal laccase. The reaction is seen to occur at acidic values of the reaction solution (pH 2.5–3.5). Thus, the redox mediator can be used for the synthesis of an electrically conductive polyaniline.

The laccase-mediator system accelerates the rate of polymerization of aniline compared with the usage of the laccase only under the same experimental conditions (Fig. 5(1 and 2)). The change of the electronic spectra of PANI/PAMPS complexes during the laccase-mediator synthesis with time is shown in Fig. 6. It is seen that the polaron absorption maximum is shifted to the long wavelength part of the spectrum with the increased time course of polymerization of the monomer. This may indicate both the alignment of the structure of the resulting polymer or the increase in

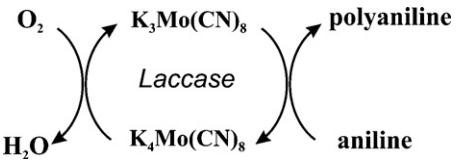


**Fig. 3.** Scheme representing the role of the redox mediator for laccase-catalyzed oxidation of aniline.

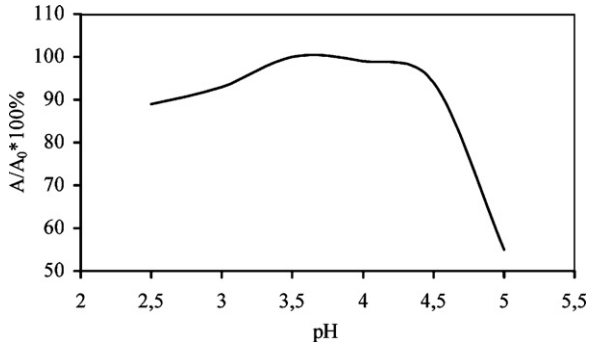


**Fig. 4.** Effect of pH on the rate of $K_4Mo(CN)_8$ oxidation in the presence of *T. hirsuta* laccase.

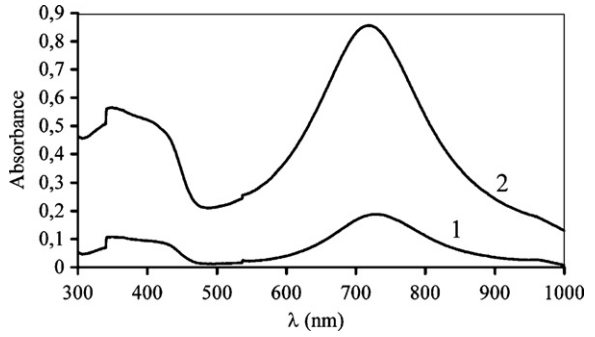


**Fig. 5.** UV–vis spectra of PANI/PAMPS complexes obtained after 3 h. 1, laccase-catalyzed aniline polymerization; 2, laccase-mediated aniline polymerization. Experimental conditions: 0.1 M Na-citrate-phosphate buffer (pH 3.5); [aniline] = [PAMPS] = 25 mM; [laccase *T. hirsuta*] = 1.6 U/ml; $[K_4Mo(CN)_8]$ = 0.1 mM; $t$ = 20 °C. The samples were diluted with buffer (1:20).

the degree of its polymerization. The rate of polymerization measured by the changes in the optical absorption at λ = 760 nm for the same time depends on the concentration of a redox mediator (data not shown). The acceleration of the conducting PANI formation in the PANI/SDBS complex using the laccase-mediator system compared with the laccase only is also observed when applying another template for the polymerization of aniline–sodium dodecylbenzenesulfonate (Fig. 7(1 and 2)). The shift of the absorption in the polaron longer wavelength spectrum was also observed with the increased reaction time (data not shown).

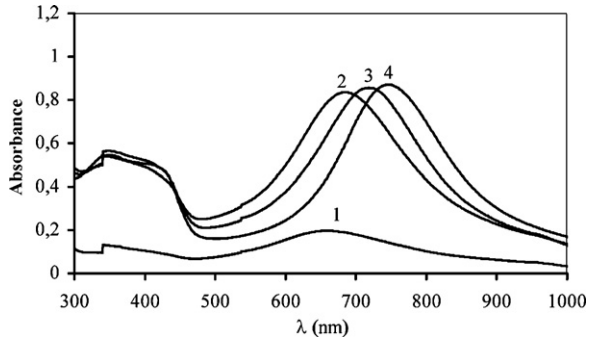


**Fig. 6.** Evolution of UV–vis absorption spectra of the product at laccase-mediated aniline/PAMPS complex oxidation with the reaction time: 1–5 min, (dilution, 1:10); 2–1 h, (dilution, 1:10); 3–3 h, (dilution, 1:20); 4–24 h, (dilution, 1:70). Experimental conditions: 0.1 M Na-citrate-phosphate buffer (pH 3.5); [aniline] = [PAMPS] = 25 mM; [laccase *T. hirsuta*] = 1.2 U/ml; $[K_4Mo(CN)_8]$ = 0.1 mM; $t$ = 20 °C.

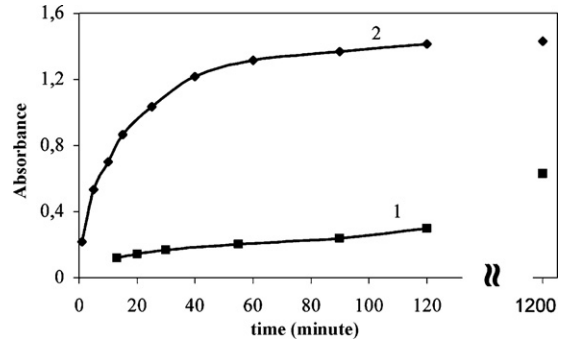


**Fig. 7.** Kinetics of the polymerization reaction of aniline in the presence of SDBS: 1, laccase alone; 2, laccase-mediator system. Experimental conditions: 0.1 M Na-citrate-phosphate buffer (pH 3.8); [aniline] = [SDBS] = 10 mM; [laccase *T. hirsuta*] = 6.0 U/ml; $[K_4Mo(CN)_8]$ = 0.1 mM; $t$ = 20 °C.

### 3.3. Characterization of the PANI synthesized by laccase and laccase-mediated methods

#### 3.3.1. FTIR investigation

The FTIR absorption spectrum of the PANI/SDBS complex synthesized by laccase alone is quite similar to that obtained with laccase-mediator system (Fig. 8(a and b)). The spectra of PANI/SDBS complexes exhibit the characteristic absorption bands arising from the vibration mode of the quinonoid diimine unit near

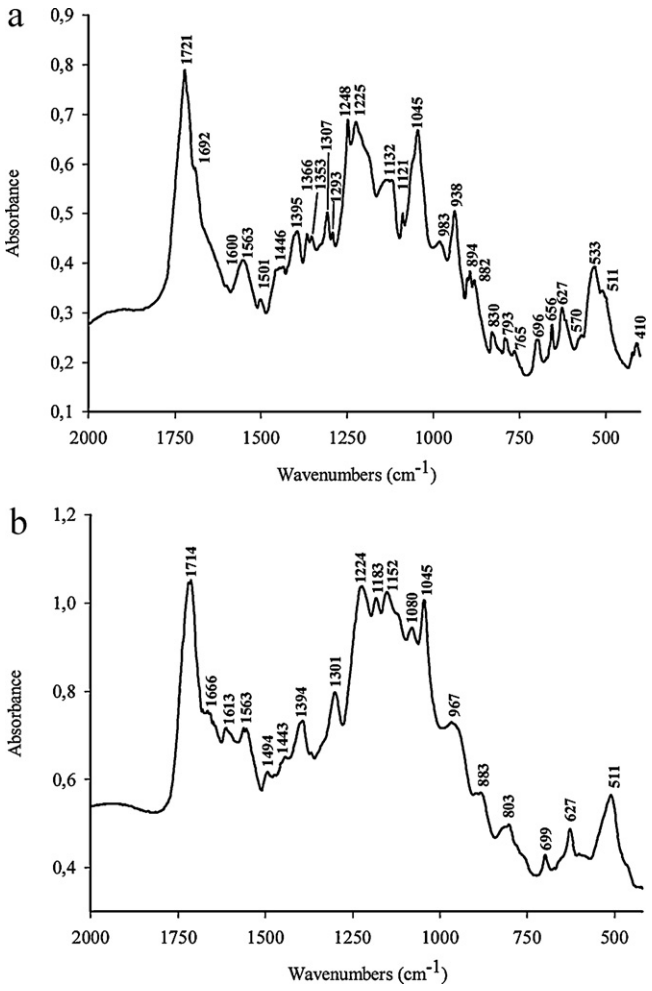


**Fig. 8.** FTIR spectra of dedoped PANI/SDBS complexes prepared by laccase-catalyzed (a) and laccase-mediated (b) methods.

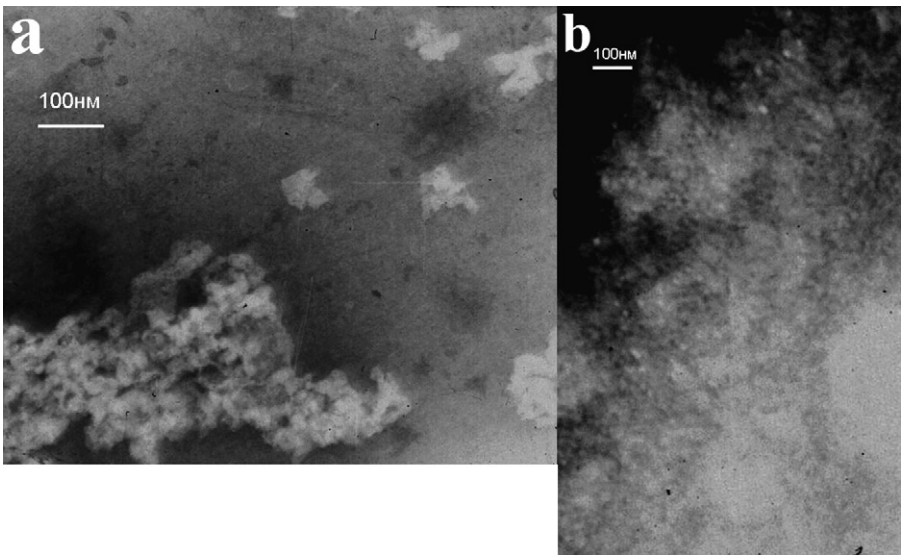


**Fig. 9.** TEM micrographs of PANI/PAMPS complexes: laccase-catalyzed (a) and laccase-mediated syntheses (b).

1560 $cm^{-1}$, while the band near 1500 $cm^{-1}$ is attributed to the C–C aromatic ring stretching of the benzenoid diamine unit [41]. The 1,2,3-trisubstituted aromatic ring absorbs between 750 $cm^{-1}$ and 700 $cm^{-1}$, while the 1,4-disubstituted aromatic ring absorbs between 880 $cm^{-1}$ and 800 $cm^{-1}$ [42].

*3.3.2. Electrical conductivity and the yield of PANI*

The conductivity values of the PANI/PAMPS complexes measured by the two-point probe method were in the ranges of 0.95–1.5 mS/cm and 4.8–5.9 mS/cm for polyaniline prepared by laccase alone and laccase-mediator methods, respectively. The yield of PANI in the composition of PANI/PAMPS complexes synthesized using laccase alone and laccase-mediator methods was 61% and 78%, respectively.

When micelles of anionic surfactant SDBS were used as a template, the yield of PANI was 35% and 70% for each method, respectively.

*3.3.3. Transmission electron microscopy*

TEM investigation of both PANI/PAMPS samples prepared by laccase alone and laccase-mediator methods indicates the morphological similarity of the prepared particles. Fig. 9(a and b) shows the TEM images of such PANI/PAMPS samples deposited on a substrate by absorption from water. The samples of the aqueous dispersion of PANI/PAMPS complexes were preliminary sonificated for 20 min before investigation. The samples of the complexes prepared by both methods formed aggregates containing globular particles.

However, the size of individual particles synthesized by laccase-mediator method is substantially smaller than in the case of the laccase catalyzed method of synthesis, with the complex having a high degree of surface coverage of the substrate.

*3.3.4. MALDI-TOF mass spectrometry of low molecular weight fraction of polyaniline*

A MALDI–TOF mass spectrometry of the PANI obtained at the end of both laccase-mediator reaction and reaction with laccase alone was not possible since the polymers were too long and PANI is insoluble in most polar and nonpolar common solvents. The products of various syntheses of PANI might differ in their polydispersity index or a cross-linked level, and, hence, in their conducting properties, solubility and ability to mix with other polymers. The presence of low molecular weight byproducts of the oxidative polymerization of aniline in the final product of polymerization strongly influences its microscopic properties. The low molecular weight compounds were extracted from the final products of aniline polymerization with tetrahydrofuran. To obtain samples for the MALDI–TOF analysis, the guided template method of the enzymatic aniline polymerization with SDBS as template was carried out as described in Section 2.

Before the mass spectral analysis, the PANI/SDBS complexes synthesized by both methods were dedoped with the aqueous ammonia solution to remove SDBS, repeatedly washed with deionized water and dried. Since molecules are activated with the UV laser and both PANI and oligoanilines are strong absorbents of the UV radiation, they may absorb a sufficient energy for

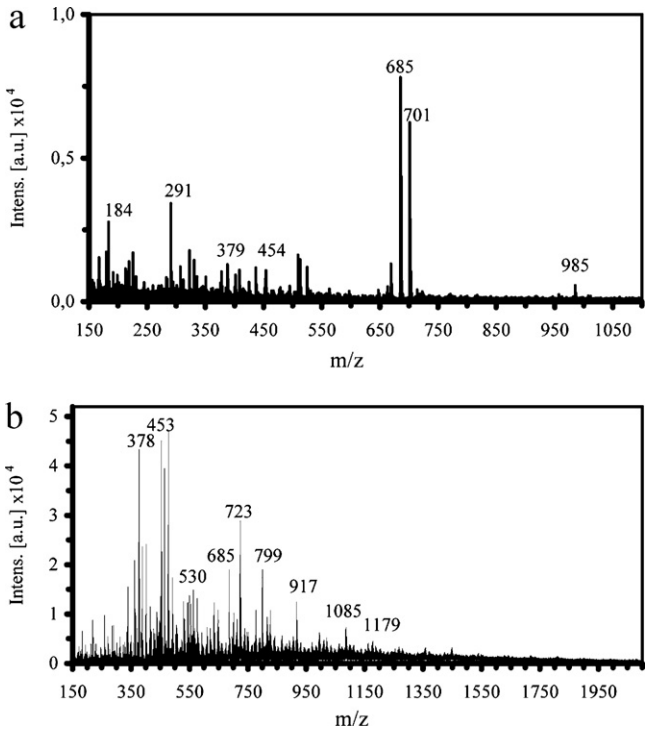


**Fig. 10.** MALDI-TOF spectra of the low molecular weight product extracted from dedoped PANI/SDBS samples with tetrohydrofuran: prepared by laccase-mediated (a) and laccase-catalyzed (b) methods.

desorption and ionization without an additional matrix. Mass spectra of the PANI fractions processed from tetrahydrofurane are shown in Fig. 10(a and b). The measurements for the given fractions were taken for the two samples of the PANI prepared by laccase alone and laccase-mediator methods. The spectra of aniline oligomers extracted from the samples after the laccase-mediator synthesis of the polymer (Fig. 10a) have intense peaks with $m/z$ 378; 453, 530; 647, 723, 799, 917, 1985, which can be attributed to 3-12-dimensional fragments of PANI. The maximum mass of the aniline oligomers in the extracts from a sample of the PANI synthesized with the involvement of laccase in the absence of the mediator of the enzymatic reaction corresponds to 8-mer with the presence in the sample of 3 and 5-mers (Fig. 10b).

The peaks of the mass spectra of all the samples of aniline oligomers studied are grouped in multiplets, which implies the presence in the extracts of the segments of PANI structures having not only $-C_6H_4-NH-$ or $-C_6H_4=N-$ but also other oxidation states of terminal groups such as $-NO_2$ and NO. It is important to note that the yield of PANI after rinsing the obtained samples with tetrahydrofuran drops for the laccase catalyzed and laccase-mediator syntheses by 16%, 58%, respectively. This indirectly suggests that the degree of PANI polymerization in the presence of the redox mediator of laccase is significantly higher than in the presence of laccase alone.

## 4. Conclusion

It is proposed that a high redox potential laccase and inorganic redox mediator potassium octocyanomolybdate (4+) can be used for the synthesis of conducting polyaniline. Comparison of reactions of the aniline oxidative polymerization with laccase and laccase-mediator system has shown that the presence of the mediator accelerates the polymerization of the monomer. Conducting polyaniline synthesized by the laccase-mediator method has the conductivity approximately five times as great as that in the case of the laccase-catalyzed method and is obtained in a higher yield. PANI/SDBS complexes synthesized by the both methods have a granular structure but differ in the particle size. The MALDI-TOF mass spectrometry identified the low molecular by products extracted with tetrahydrofuran from the PANI samples synthesized with laccase alone and laccase-mediator methods. MALDI-TOF studies have shown that the laccase-mediator synthesis leads to the formation of PANI with a higher molecular weight as compared with the laccase-catalyzed reaction. Laccase-mediated method with potassium octocyanomolybdate (4+) may be used for the synthesis of another conducting polymers e.g. polypyrrole or PEDOT.

## Acknowledgements

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