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Polyaniline synthesis catalysed by glucose oxidase

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ABSTRACT

A novel method for synthesis of polyaniline (PANI) in aqueous media based on application of oxidizing-enzyme glucose oxidase (GOx) is reported. Hydrogen peroxide was produced during catalytic reaction of oxidizing-enzyme glucose oxidase from *Penicillium vitale* and initiated the polymerization of aniline. The increase in optical absorbance in the range of 340–700 nm was exploited for the monitoring of PANI polymerization process. The role of GOx in the formation of PANI, influence of the initial concentrations of GOx, and glucose and aniline monomer on the aniline polymerization rate was studied. The study of pH influence on polymerization rate showed that PANI polymerization was occurring in a broad pH range from the pH 2.0 to 9.0. Optimal polymerization/oligomerization temperature was found to be at 37 °C, which is also optimal for GOx-catalysed enzymatic reaction. After 10 days of continuous GOx-catalysed polymerization PANI appeared as colloid-microparticles visible by an optical microscope.

1. Introduction

Nanostructured conducting polymers [1] such as polyaniline, polythiophene or polypyrrole are very popular because of the numerous technological applications [2]. The advantages of conducting polymers compared to conducting inorganic materials are their diversity and sensitivity at room temperature [1,3]. PANI, among the other organic conjugated polymers, attracted attention due to its high conductivity in the doped state [4], its environmental [5,6], thermal [7] and electrochemical stability [8], and its interesting electrochemical, electronic, optical and electro-optical properties [9]. It has been found that PANI exhibits insulator–conductor transitions and multiple colour changes (pale yellow–green–blue–violet) depending on both: the oxidation state and pH. Due to its properties, PANI has numerous practical applications such as biosensors [10,11,12], rechargeable batteries, conducting paints, conducting glues, antistatic coatings, electronic devices, optical displays, light-emitting diodes, electromagnetic shielding [13,14], and thin film devices with molecular level control [15].

The PANI can be obtained by chemical or electrochemical polymerization of aniline in an aqueous or non-aqueous media in the form of powder or film [16–18]. Electrochemical polymerization of aniline and its derivatives typically is carried out in low-pH acidic aqueous solutions (e.g. HCl or H_2SO_4 aqueous solution) under a constant voltage or by cyclic voltammetry. Electrochemical polymerization can be used as coating of electrodes by conducting PANI layers. Furthermore, it enables coating of PANI on rather complex geometries. However, the electrochemical methods have some limitations. It is difficult to prepare a large amount of PANI because the polymerization is carried out only on the surface of the electrode; electrochemically synthesized PANI is often insoluble in common solvents. Chemical polymerization/oligomerization of aniline is performed using relatively strong chemical oxidants like ammonium peroxydisulfate [19,20], ferric [21], permanganate [22], bichromate [23,24] or hydrogen peroxide [25]. These oxidants are able to oxidize the monomers in the appropriate solution. This leads to chemically active cation radicals of the monomers used. The cation radicals formed react with monomer molecules, yielding oligomers or insoluble polymers. One of the key problems related to the potential application of PANI is that this polymer is non-soluble in typical solvents [26]. Some ways to eliminate this problem are to prepare PANI in forms of: either colloidal particles, fibers, thin films or sol–gels [27].

An alternative approach for synthesis of aniline oligomers and/or PANI is enzymatic polymerization/oligomerization [28]. This process does not require strong acidic media or additional purification steps [29,30]. In biocatalytic reactions oxidoreductases such as horseradish peroxidase [31–34], palm tree peroxidase [35], soybean peroxidase [36], bilirubin oxidase [37], laccase [38] were used as a catalyst for the aniline polymerization in an aqueous buffer. Biocatalytic polymerization using enzymes is advantageous in that it is a very simple one-step process. It is an environmentally friendly synthesis with high potential for industrial polymer production. Its high yield is due to the efficiency of the biocatalyst

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[39,40]. According to our knowledge, glucose oxidase has not been applied in the production of PANI as it has very recently been demonstrated for another conducting polymer – polypyrrole [41–44].

The aim of the current study was to demonstrate and investigate in detail the possibility to synthesize PANI by application of oxidizing-enzyme glucose oxidase. One of the advantages of this study is that oxidases usually utilize environmentally friendly substrates and produce environmentally friendly products. In this paper PANI enzymatic synthesis is induced by a redox enzyme (glucose oxidase). Some aspects characterizing this simple enzymatic synthesis of aniline oligomers and/or PANI are presented in this article.

2. Experimental procedures

Glucose oxidase (E.C. 1.1.3.4.) from *Penicillium vitale* (130 units/mg) was purchased from "Diagnosticum" Co. (Lviv, Ukraine). Aniline monomer and glucose were purchased from SIGMA (Berlin, Germany) and were used without any further purification. All other chemicals were of analytical grade or better, and all were used as received. All aqueous solutions were prepared in HPLC-grade water purified in a Purator-B Glas Keramic (Berlin, Germany). The solutions of glucose were prepared at least 24 h before use to allow glucose to mutarotate and to reach equilibrium between α- and β-forms. When needed the glucose oxidase solution was freshly prepared from powder of the enzyme. Aniline to remove all coloured components was purified by passing of 1.5 mL aliquots through a neutral Al_2O_3 column (5 cm length and 0.4 cm diameter).

Chemical synthesis of PANI was performed in 50 mM sodium acetate and sodium/potassium phosphate buffer solutions with a pH varying between 1.0 and 12.0 and containing 20 mM hydrogen peroxide and 200 mM aniline. Polymerization was carried out at room temperature in darkness. The UV–Vis spectra of solutions were recorded at different time intervals from the beginning of polymerization. This synthesis was performed in 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 6.0, containing 1 mg/ml of glucose oxidase, 20 mM of glucose and 200 mM of aniline if not otherwise stated. For determination of spectral characteristics of PANI synthesized at different pH, the synthesis of PANI was performed in buffer solutions with different pH, which varied between 1.0 and 12.0. Concentrated hydrochloric acid, glacial acetic acid and sodium hydroxide solutions were used to adjust the pH of buffer solutions.

UV–vis spectrophotometer Perkin-Elmer LAMBDA 25 (Shelton, USA) was used for monitoring PANI formation. Optical microscope OLYMPUS BX51 "Olympus Corporation" (Tokyo, Japan) and digital SLR camera Nikon D70S "Nikon Corporation" (Japan) were applied for optical imaging of the samples.

3. Results and discussion

The enzymatic polymerization of aniline solution was based on four major compounds: aniline – polymerisable monomer, glucose oxidase – hydrogen peroxide producing enzyme, glucose – reducing substrate of GOx, and dissolved oxygen – oxidizing substrate of GOx. In the presence of glucose and dissolved oxygen GOx started to generate hydrogen peroxide (reaction 1) and lactone of gluconic acid, which was hydrolyzed to gluconic acid (reaction 2):

$$\text{Glucose} + O_2 \xrightarrow{\text{GOx}} \text{Lactone of Gluconic Acid} + H_2O_2 \quad (1)$$

$$\text{Lactone of Gluconic Acid} + H_2O \rightarrow \text{Gluconic Acid} \quad (2)$$

It is known that oligomerization [28], and/or polymerization [19,21–25] of aniline can be performed using relatively strong chemical oxidants. This is due to these oxidants are able to oxidize the monomers in appropriate solution's, leading to chemically active cation radicals of the monomers, which are yield oligomers or polymers. In the presented work, a unique enzymatic approach has been developed wherein hydrogen peroxide produced during catalytic reaction of GOx (reaction 1) created conditions for the polymerization of aniline:

$$\text{Aniline} \xrightarrow{H_2O_2} \text{Polyaniline} \quad (3)$$

The research showed that under such conditions the enzymatic polymerization of aniline was initiated by H_2O_2 (reaction 3) produced by GOx (reaction 1). The progress of the polymerization reaction was monitored spectroscopically. The formation of PANI was performed in buffer solutions, with different pH, which ranged from 1.0 to 12.0. The absorption spectra prior to polymerization of aniline (dotted line) and the past 24 h at pH's ranging from 1.0 to 12.0 are given in Fig. 1B. The UV–Vis spectra show that at the start of polymerization all solutions have low absorption (dotted line) and no obvious absorption peaks are present in the spectra. After 24 h of polymerization the overall absorption of the solutions increased and one or two absorption peaks appeared in the 340–700 nm region, which is a characteristic of PANI [35]. Numerous control experiments were also carried out to confirm that enzymatic catalysis is responsible for the polymerization. When only aniline

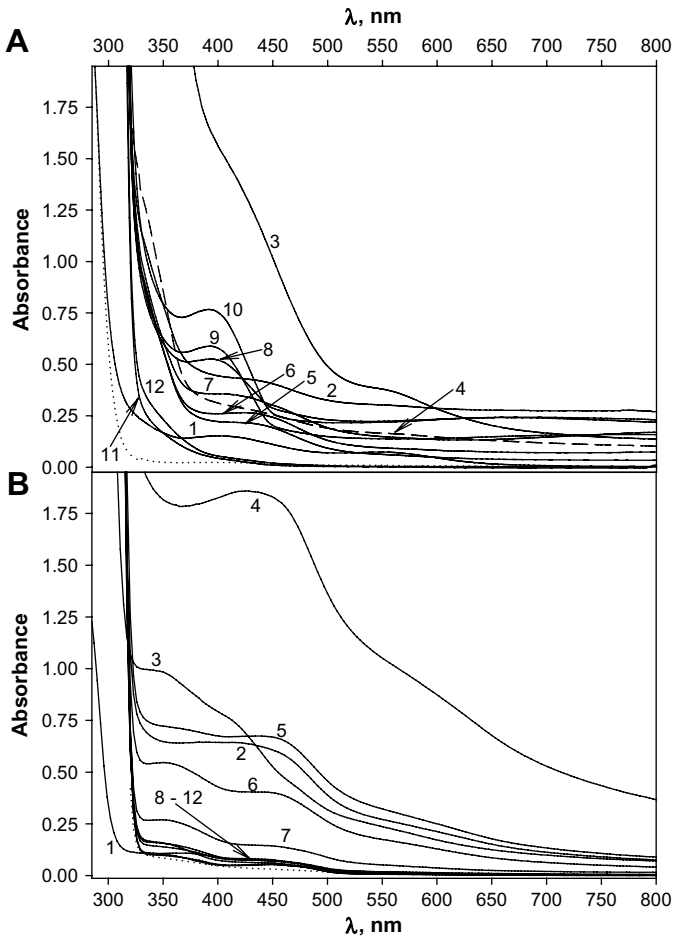

Fig. 1. Absorbance of polyaniline prepared in 50 mM sodium acetate and sodium/potassium phosphate buffers at different pH containing: (A) 20 mM of hydrogen peroxide and 200 mM of aniline; (B) 1 mg/ml of GOx, 20 mM of glucose and 200 mM of aniline. Polymerization time 24 h. Numbers correspond to pH of solutions.

or aniline and GOx were added to the buffer solution it was found that polymerization of aniline at such conditions is not detectable. When hydrogen peroxide was added to the monomer solution it was found that polymerization of aniline occurs (Figs. 1A and 2B), but the absorption spectrum of H_2O_2 initiated polymerization solutions is slightly different from the absorption spectra obtained by enzymatic polymerization (Figs. 1B and 2A). As shown in Fig. 1A PANI formed by chemical polymerization with hydrogen peroxide has one absorption peak in the 360–440 nm region and the other at approximately 550 nm. The main features in this absorption spectra are similar to that registered if optically active PANI was synthesized by Laccase-catalysed synthesis [45]. When aniline and glucose were added to the buffer solution it was found that under these conditions polymerization of aniline also occurred. Yet, the observed polymerization rate was insignificant in comparison to that observed in the presence of an enzyme. Therefore, these control experiments are the strong evidence that the polymerization of aniline is induced by H_2O_2 produced by GOx catalytic action.

It was found that PANI exhibits multiple colour changes in an aqueous media (pale yellow, green, blue and violet) depending on both oxidation state and pH [46,47]. A typical UV–Vis absorption spectrum of protonated PANI, polyemeraldine green form, has three absorption peaks in the regions 300–330, 400–430 and 780–826 nm [48–51]. The PANI base polyemeraldine blue shows two absorption peaks in the regions 300–325 and 550–585 nm [49]. The formation of PANI was performed at different pH, which ranged from 1.0 to 12.0, and in our case dark-red coloured solutions were formed which corresponds to the formation of non-conducting aniline oligomers [20]. The detected PANI absorbance spectrum was in agreement with that registered during horseradish peroxidase induced formation of aniline oligomers [28] and/or PANI [35]. The UV–Vis spectra of PANI solutions synthesized in the present study are presented in Figs. 1B and 2A. The polymerization solutions showed one, two, or three absorption peaks (Table 1). The first absorption peak was in the 345–365 nm region (peak 1). It can be associated with the π–π^* transition of the aromatic rings [36]. Furthermore, the optical absorption below 400 nm indicated the formation of low-molecular weight aromatic compounds produced by the hydrolysis of PANI [52]. The second one was in the range of 400–480 nm (peak 2). This peak can be attributed to the presence of multiple branched structures in the polymer or cross-linked polyaniline [13,53–55]. And the third absorption peak was in the range of 540–600 nm (peak 3). The following absorption peaks are due to the exciton transition of a quinoid ring in the undoped form of PANI [56–58]. Position of absorption peaks depends on the pH of polymerization solution and polymerization time. At pH 1.0 the polymerization solution shows an absorption peak of approximately 365 nm. At a higher pH (pH range from 2.0 to 11.0) a new peak emerges in the 400–480 nm region. At pH 12.0 the polymerization solution shows an absorption peak at approximately 345 nm. At pH 2.0, 11.0 and 12.0 a weak absorption peak emerges at approximately 540 nm, while at pH 4.0, 5.0, 6.0 and 7.0 at approximately 600 nm. Results show that the enzymatic polymerization of aniline is pH dependent [59].

Table 1
Absorption peaks attributed to PANI synthesized by enzymatic polymerization at different pH of polymerization solution.

pH	Peak 1, nm	Peak 2, nm	Peak 3, nm
1	365	–	–
2	–	400 and 475	540
3	345	415	–
4	–	440 and 480	600
5	360	440	–
6	360	445	600
7	360	445	600
8	360	450	–
9	360	450	–
10	360	445	–
11	360	450	540
12	345	–	540

In presence of GOx a significant increase in specific PANI absorption was registered within 365 h after the start of polymerization (Fig. 3). Almost linear dependence of PANI formation vs. polymerization period was detected for at least first 48 h of polymerization (Fig. 3A). The results show that enzymatic oxidation of aniline did not present an induction period which is observed in chemical polymerization of PANI [60]. The optimal pH for the GOx initiated PANI formation was in a broad pH region, which ranged from pH 2.0 up to pH 9.0 (Fig. 3A). At pH 1.0, 10.0, 11.0 and 12.0 the polymerization rate was significantly slower when compared with that registered in pH interval ranging from pH 2.0 up to pH 9.0. Within 23 h after the start of polymerization the maximal

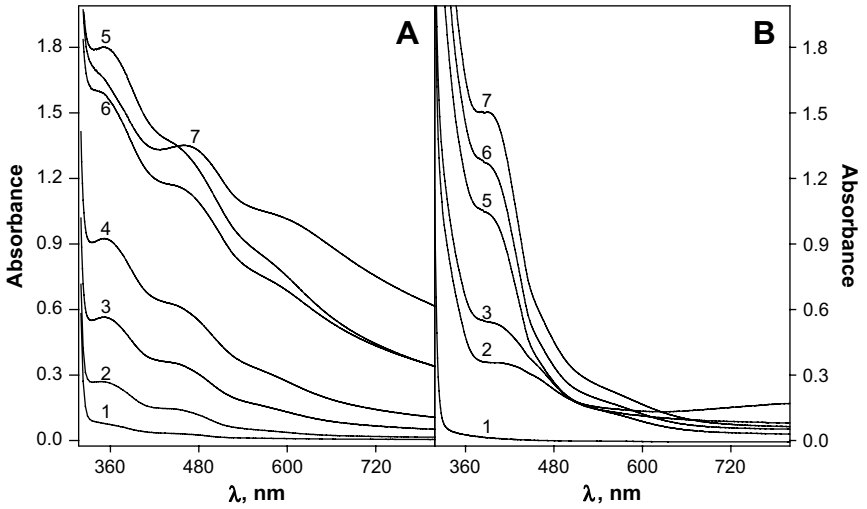

Fig. 2. Spectrophotometric study of polyaniline formation: (A) GOx initiated synthesis in 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 7.0, containing 1 mg/ml of GOx, 20 mM of glucose and 200 mM of aniline; (B) chemical synthesis in 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 7.0, containing 20 mM of hydrogen peroxide and 200 mM of aniline; 1 – start; 2 – 23 h; 3 – 47 h; 4 – 75 h; 5 – 143 h; 6 – 240 h; 7 – 365 h.

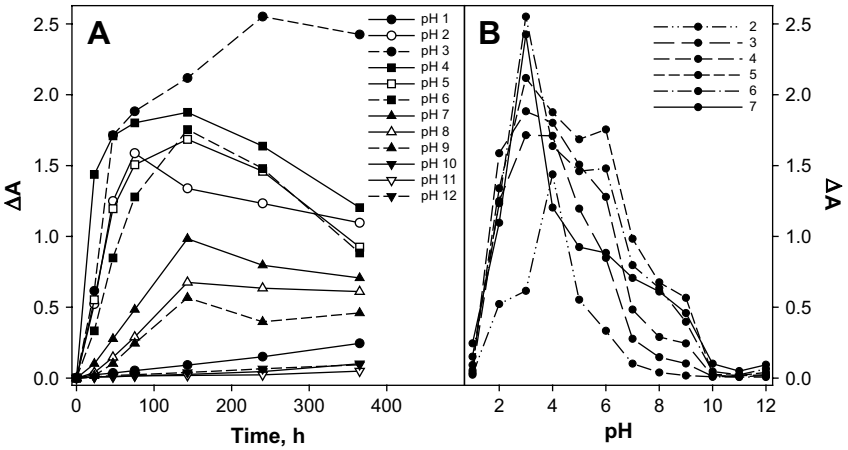

Fig. 3. Spectrophotometric study of polyaniline formation in 50 mM sodium acetate and sodium/potassium phosphate buffer containing 1 mg/ml of GOx, 20 mM of glucose and 200 mM of aniline: (A) optical absorbance vs. duration of polymerization, at different pH; (B) absorbance at $\lambda = 445$ vs. pH: 1 – start (corresponds to zero absorbance, not indicated); 2 – 23 h; 3 – 47 h; 4 – 75 h; 5 – 143 h; 6 – 240 h; 7 – 365 h. The segment related to light scattering is subtracted from all values presented in both (A and B) plots.

formation rate of aniline oligomers and/or PANI was registered at pH 4.0, while from 23 h to 365 h duration of polymerization the maximal PANI formation rate was registered at pH 3.0.

After 24 h aniline polymerization initiated by GOx an increase of PANI characteristic absorption in the range of 340–700 nm was 3–5 times higher when compared with that in the range of 700–800 nm (Fig. 2A). This phenomenon is related to significant increase in the light scattering and/or absorption determined by PANI nano-/microparticles formed during polymerization [41,61]. The formation of PANI particles from single PANI chains is determined by strong inter-chain interactions [62,63]. Moreover, the strong inter-chain interactions can contribute to increasing the conductivity of the system. The degree of cross-linking between polymer chains has been emphasized for the insulator–metal transition in conducting polymers [64]. The stabilization and decrease in polymerization reaction rate (Fig. 3) may be based on limited solubility of formed PANI particles and their precipitation from the reaction solution. After 240 h of polymerization, precipitate appeared in 1–3 μm diameter particles and/or clusters of PANI nanoparticles that were visible by an optical microscope (Fig. 4). The particles appeared ordinary shaped and similar in size because all visible particles were in the range near the optical resolution that was possible to achieve by the optical microscope used. It allowed us to make predictions that sub-micrometer-sized particles were suspended in the polymerization solution. From the results the researchers can conclude that chemically synthesized PANI might be soluble in polar solvents [29,59]. Moreover, no signs of formed PANI precipitation were detected before the 4–5th day of polymerization. Sub-micrometer-sized PANI particles can be potentially used as markers diagnostics assay [65]. It can be predicted that such biologically induced PANI synthesis makes this polymer even more attractive for biomedical applications [42] and/or for biosensor design [43,44].

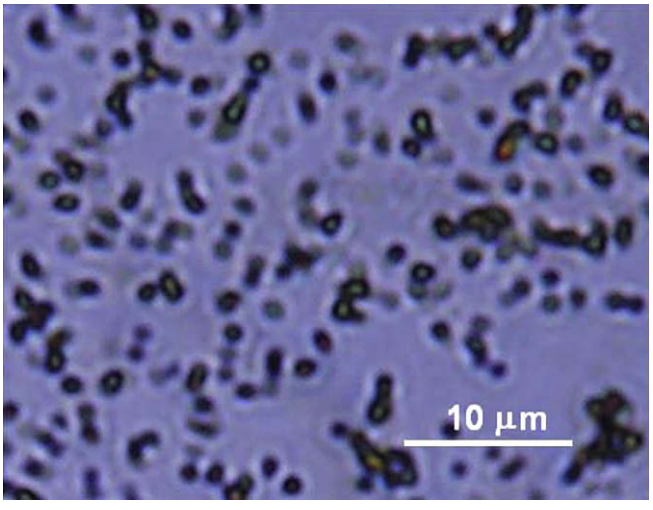

Fig. 4. Optical microscopy image of PANI particles formed after 240 h of polymerization in the presence of 1 mg/ml of GOx, 20 mM of glucose and 200 mM of aniline.

The study shows that PANI might be synthesized at conditions close to physiological ones (pH, salt concentration, and temperature) when the enzyme generating hydrogen peroxide is present in the reaction medium. Numerous experiments were carried out to confirm the initiating effect of GOx for aniline polymerization reaction. The investigations showed than PANI formation is dependent on aniline monomer concentration (Fig. 5A), which is a property of polymerization reaction [66]. In the presence of 20 mM of aniline the polymerization rate was 3.8 times slower (ratio calculated after 217 h polymerization period) compared with PANI formation registered in the presence of 200 mM of aniline. A similar effect occurs with different concentrations of glucose (Fig. 5B) and GOx (Fig. 5C). Polymerization rate was dependent on concentration of GOx and glucose, since both were crucial to produce hydrogen peroxide. Hydrogen peroxide is the initiator of this polymerization reaction, e.g. (i) in the presence of 200 mM glucose the polymerization rate was at least 20.6 times higher if compared with that registered in the presence of 2 mM glucose (the polymerization ratio calculated and compared after 217 h polymerization period); (ii) 2.4 times increase of polymerization rate was registered in the presence of 2 mg/ml of GOx compared with 0.1 mg/ml of GOx (the polymerization ratio calculated and compared after 168 h polymerization period).

It was found that some polymerization of aniline occurs in the buffer solution containing only aniline and glucose, although the polymerization rate was insignificant compared with that observed in presence of GOx (Fig. 5D, curves 3 and 2). Hence, in the absence of GOx the polymerization rate was 12.7 times slower (ratio calculated after 217 h of polymerization) compared with that in the presence of 1 mg/ml of GOx. Significant difference in polymerization rate, which was detected with and without GOx, demonstrated a large impact of GOx on aniline polymerization rate.

Results obtained (Fig. 5D, curve 1) illustrate that aniline polymerization occurs not only in buffer solution but also in distilled

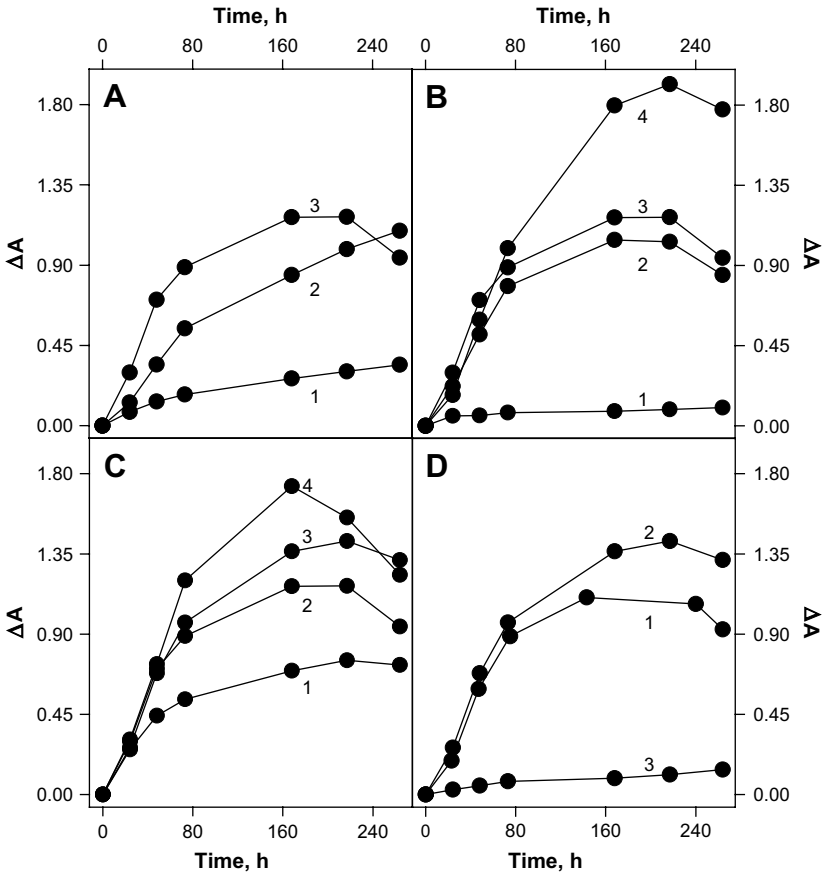

Fig. 5. Spectrophotometric study of polyaniline formation at different conditions: (A) in 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 6.0, containing 1 mg/ml GOx, 20 mM glucose and different concentrations of aniline 1 – 20 mM, 2 – 100 mM, 3 – 200 mM; (B) in 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 6.0, containing 1 mg/ml GOx, 200 mM aniline and different concentrations of glucose 1 – 2 mM, 2 – 10 mM, 3 – 20 mM, 4 – 200 mM; (C) in 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 6.0, containing 20 mM of glucose, 200 mM of aniline and different concentrations of GOx: 1 – 0.1 mg/ml, 2 – 0.5 mg/ml, 3 – 1.0 mg/ml, 4 – 2.0 mg/ml; (D) in distilled water (1) and 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 6.0 (2) containing 1 mg/ml of GOx, 20 mM of glucose and 200 mM of aniline, (3) in 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 6.0, containing 20 mM of glucose and 200 mM of aniline. Note: The segment related to light scattering is subtracted from all values presented in all four plots.

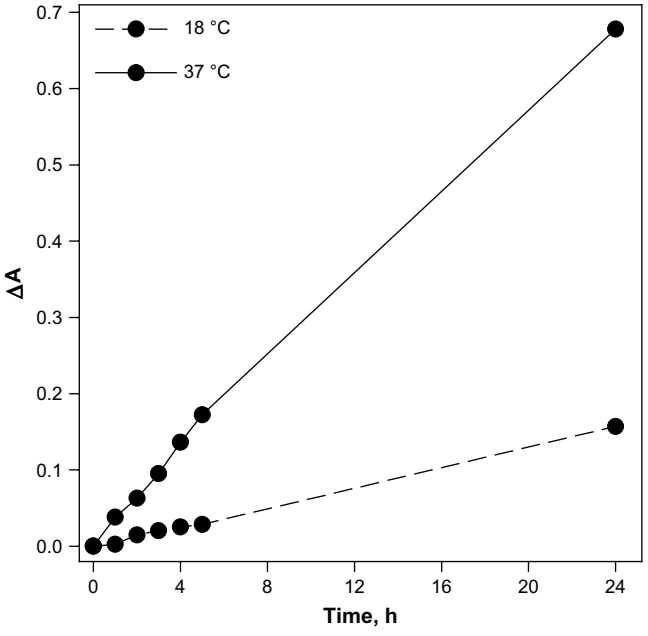

Fig. 6. Spectrophotometric study of polyaniline formation in 50 mM sodium acetate and sodium/potassium phosphate buffer, pH 7.0, containing 1 mg/ml of GOx, 20 mM of glucose and 200 mM of aniline at different temperatures. The segment related to light scattering is subtracted from all values presented in this figure.

water. It was found that the polymerization rate in distilled water was barely 1.2 times slower (ratio calculated after 217 h polymerization period) compared with that registered in buffer solution. Differences of PANI formation rate and temperature were detected and it was found that optimal temperature for PANI formation is 37 °C, which is optimal for GOx action. As shown in Fig. 6 at 37 °C the polymerization rate was 4.3 times faster (ratio calculated after 24 h polymerization period) than that registered at 18 °C.

Conducting polymers might be easily doped by low [67] and high [68] molecular weight organic molecules. PANI and other aniline based polymers/oligomers usually are doped by anionic materials that are present in polymerization solution [1,4]. From this we can predict that the described aniline oligomers were also doped by gluconic acid, which was formed during polymerization reaction described in this article.

4. Conclusions

New enzyme-based routes for the synthesis of aniline oligomers and/or PANI were demonstrated by this study. Action of GOx is principally different from other enzymes that were previously applied in synthesis of polyaniline, e.g. laccase [69,38] and HRP [69,31,32,33]. It was illustrated that polymerization of aniline in the presence of GOx and both substrates – glucose and dissolved oxygen is possible. For the initiation of polymerization reaction the

ability of GOx to generate the hydrogen peroxide was exploited. The optimal pH for PANI formation was detected in a broad pH range (from pH 2.0 up to pH 9.0). It was shown that optimal conditions for PANI polymerization are close to the physiological conditions. Formation of nanocomposite nanoparticles based on GOx enveloped within PANI as it was demonstrated in the case of GOx enveloped within polypyrrole [43,70]. It can be predicted that such GOx/PANI particles could have some anti-bacteriological effect because in the presence of glucose entrapped GOx will produce H_2O_2. In addition, another attractive property of PANI is the wiring of GOx in PANI doped hydrogels was reported [71]. It can be predicted that such biologically induced PANI synthesis will be utilized for new biomedical applications and for biofuel cells.

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