

Synthesis and characterization of poly(catechol) catalyzed by porphyrin and enzyme

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Abstract Catalytic polymerization of catechol was performed employing the cationic porphyrin and horseradish peroxidase (HRP) as catalysts. The obtained results demonstrate that the cationic metalloporphyrin is a more-efficient catalyst than the HRP in the catechol polymerization. The oxidative polymerization was carried out in the presence of polystyrene sulfonate (PSS) as a template. According to TGA data, poly(catechol) that is synthesized by porphyrin catalyst exhibits more thermal stability than the enzymatic catalyzed product. The GPC indicate higher molecular weight of polymer synthesized by porphyrin as a catalyst. Cyclic voltammetry measurements show that the synthesized polymers have convenient electroactivity. The poly(catechol) and its methyl and methoxy derivatives that are synthesized by porphyrin catalyst show low electrical conductivity.

Keywords Poly(catechol) · Catalytic polymerization · Tetrapyrroldiporphyrin · Water-soluble polymer

Introduction

The enormous interest in recent years for intensive research in the field of phenols and aromatic amine-based polymers is due to their wide applications [1]. These polymers have received considerable attention in industry and are employed for many purposes such as in adhesives, composites, and other applications [2]. These applications need a control on some properties such as molecular weight, degree of cross-linking, crystallinity, and so on [3]. Polymeric films of catechol have been exploited in a number of biosensors [4]. Also for some catechol copolymers an immunostimulating

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activity was detected [5]. Poly(catechol) with free hydroxyl groups have potent for applications in the immobilization of some species. The control of properties is difficult in oxidative coupling reactions that are carried out at extreme temperatures, pressures, and pHs employing inorganic catalysts [6]. Nevertheless, as an alternative method, considerable attention has been recently paid to enzymatic polymerization of certain compounds. This bioprocess possesses much potential to yield a polymer with a unique structure and desired properties at mild conditions [7].

Enzymatic polymerization has been studied as a promising, environmentally benign, and more efficient alternative method; this is within the context of the “green polymer chemistry” [8]. Recent efforts have resulted in the development of a unique enzymatic approach for the polymerization of aniline and its derivatives [9, 10]. This has been carried out in the presence of a polyelectrolyte such as polystyrene sulfonate (PSS) or poly(vinylphosphonic acid) (PVP) under mild conditions in phosphate buffer pH = 4.3 buffer [11–13]. Enzymatic polymerization of aromatic amines and phenols by the HRP in a mixture of water and 1,4-dioxane reported by Akkara et al. [14]. Also the polymerization of phenol and its derivatives by laccase [15, 16] and lipase [17] are reported. In this study, the polymerization of catechol was carried out by HRP in phosphate buffer 0.01 M at pH = 4.3.

Metalloporphyrin, which is an electron-rich compound, has been widely used in the catalytic oxygenation reactions [18]. Metalloporphyrins have a structure similar to the active site of the HRP and also have some advantages such as cheaper price and higher stability in comparison with the HRP. Recently, we have reported the polymerization of aniline synthesized by anionic and cationic metalloporphyrin [19, 20]. So, it can be applied as a catalyst for the polymerization of catechol. The synthesis of poly(catechol) and its 3-methyl and 3-methoxy derivatives were carried out by cationic metalloporphyrin as a catalyst and hydrogen peroxide as an oxidant in the presence of PSS as a template. The results of catechol polymerization by metalloporphyrins were compared with enzymatic polymerization of this monomer.

Experimental

Materials and reagents

Poly (sodium 4-styrene sulfonated) (MW of 70,000), which was used in this study, was purchased from the Aldrich Chemical Co. (Milwaukee, WI) and was applied without any further purification. HRP (EC 1.11.1.7) (about 170 units/mg), Hydrogen peroxide (30 wt%), catechol, and all other reagents were obtained from the Merck Company (Whitehouse Station, NJ). Fe^{III}TPyP was synthesized in our laboratory according to the Little method [21].

Instrumentation characterization

The FT-IR measurements were carried out with the help of a BOMEM MB-Series FT-IR spectrometer in the form of KBr pellets. Samples were analyzed by TGA (TGAQ50, TA Instruments) 20 °C/min for heating rate under air. Polymer mass was

pressed (~ 8 tons) to form a pellet and its conductivity was measured with a Keithley 213 electrometer. The cyclic voltammetry (CV) measurements were performed with a Metrohm Polarograph model 746 VA Trace Analyzer. The cyclic voltammograms were recorded at room temperature using a three electrode cell: platinum as an auxiliary electrode, Ag/AgCl as the reference electrode and Pt foil (0.2 cm^2 surface area) as the working electrode. The cyclic voltammograms were obtained in a 1.0 M HCl electrolyte and scanned from -0.1 to 0.9 V at various scan rates in the range of 100 – 500 mV/s . The molecular weight of poly (catechol)/SPS complexes catalyzed by porphyrin and enzyme were measured using gel permeation chromatography (GPC) with a Waters LC module I (Milford, MA) with two linear ultrahydrogel columns connected in series.

Catalyst synthesis

Tetrapyrroldiporphyrin (TPyP)

6.4 g (60 mmol) of 4-pyridylcarboxaldehyde and 4.04 g (60 mmol) of pyrrole were added to a mixture of 208 mL of propionic acid and 3 mL of acetic acid that was near boiling temperature according to the procedure of Little et al. [21] The reaction mixture was refluxed for 1 h and then dried under vacuum conditions by means of a rotary evaporator. The resulting black tar was briefly washed with water and subsequently with dilute ammonium hydroxide. The slightly wet material was triturated with minimum amount of methanol on a steam bath until the purple crystals of porphyrin were freed from tar. The slurry was then stored overnight in a freezer at $-5 \text{ }^\circ\text{C}$. The purple solid was filtered off and washed with minimal amount of methanol and dried. The material was dissolved in a minimal amount of chloroform and chromatographed on a column using chloroform as the eluant. The purity of H_2TPyP was confirmed by UV–vis [22] and IR spectroscopies. The UV–vis spectrum of H_2TPyP (H_2O , $\text{pH} = 2$) shows five peaks at 419 (soret), 516, 547, 582, and 643 nm. The IR spectrum of H_2TPyP (KBr) shows bands at 1592, 1486, 1402.8, 1351.6, 1066.6, 970.6, 879.4, and 799.82 cm^{-1} .

Tetrapyrroldiporphyrinated iron (III) ($\text{Fe}^{\text{III}}\text{TPyP}$)

Tetrapyrroldiporphyrin (TPyP) (0.5 g) and fourfold excess FeCl_2 were dissolved in 50 mL of dimethylformamide according to the procedure of Fleischer et al. [23] and the solution was heated at about $140 \text{ }^\circ\text{C}$ about 6 h. The completion of the reaction was checked spectrophotometrically. The reaction mixture was evaluated by UV–vis [22] and IR spectroscopies. The UV–vis spectrum of FeTPyP (H_2O , $\text{pH} = 2$) shows three peaks at 400 (soret), 500, and 628 nm. The IR spectrum of FeTPyP (KBr) shows bands at 1594, 1541, 1408, 1350, 1072.4, 922.6, and 792.9 cm^{-1} .

Polymer synthesis by HRP

The enzymatic polymerization of catechol was carried out in 0.01 M potassium phosphate buffer at $\text{pH} = 4.3$. The polymerization was performed by equimolar

amount of monomer and template (4.5 mmol). Typically, 0.009 g (4.5 mmol) PSS and 5 mg (4.5 mmol) catechol were added to 7.5 mL buffer solution under constant stirring, followed by the addition of catalytic amount of the enzyme (1 mg HRP). To initiate the reaction, a stoichiometric amount of diluted hydrogen peroxide (0.02 M) was added dropwise under vigorous stirring over a period of 1 h. The reddish-brown resulted solution was transferred to individual regenerated cellulose tube and was dialyzed (cut off molecular 3,000) overnight to remove any unreacted monomer and oligomers. The percentage yield of poly(catechol) was calculated on the basis of the concentration of unreacted catechol. The unreacted monomer concentration in the dialysis solution was determined by measuring the absorbance at 276 nm ($\epsilon = 2,280$) in 1 M HCl solution. The percentage yield of poly(catechol) that synthesized by porphyrin and HRP was calculated to be over 85 and 90%, respectively.

Polymer synthesis by porphyrin

The polymerization of catechol and its derivatives with hydrogen peroxide (catalyzed by water-soluble transition-metal tetrapyrroldiporphyrin) was carried out at pH = 2. To 10 mL of pH = 2 aqueous solution 0.009 g (0.045 mmol) of PSS (based on the molecular repeated unit) and 5 mg (0.045 mmol) of catechol were added under constant stirring. Then, 2.5 mL (3×10^{-5} M) of the iron (III) tetrapyrroldiporphyrin ($\text{Fe}^{\text{III}}\text{TPyP}$) (7.5×10^{-5} mmol) was added to the mixture. The reaction was initiated by adding 2.25 mL (0.02 M) of diluted hydrogen peroxide under vigorous stirring. The polymerization continued for 24 h. The final solution was dialyzed (molecular cutoff = 3,000) overnight to remove any unreacted monomers and oligomers. A homogeneous, reddish-brown, water-soluble poly(catechol) was obtained. Also, 3-methyl and 3-methoxy catechol were polymerized by the same procedure.

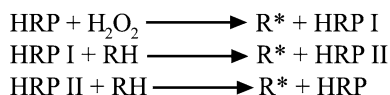
Results and discussion

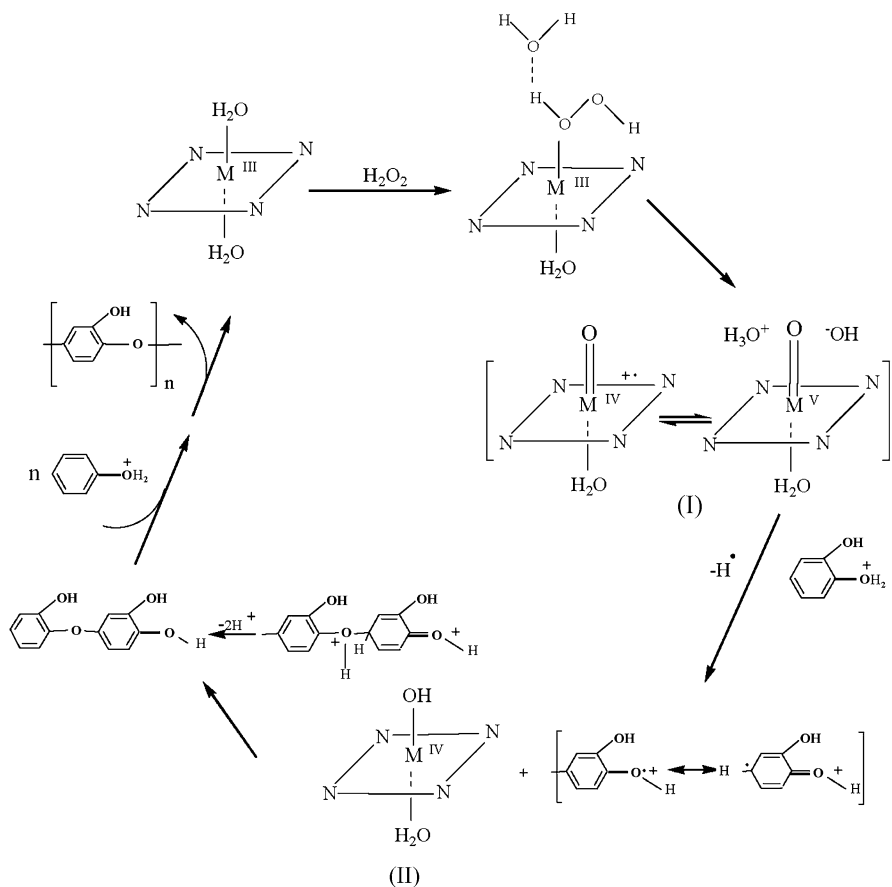
In the present investigation, horseradish peroxidase (HRP) and tetrapyrroldiporphyrin (TPyP) are used for oxidative polymerization of catechol. The polymerization of catechol was performed by metalloporphyrin at pH = 2 aqueous solution and by the HRP in the phosphate buffer 0.01 M pH = 4.3 and the water-soluble form of poly(catechol) were obtained.

Peroxidases are known to have high specificity for hydrogen peroxide to give an active enzyme substrate complex. This complex can oxidize hydrogen donors such as phenols and amines [7]. The catalytic cycle of the HRP for substrates can be schematically represented as Fig. 1 [24].

The mechanism of catechol polymerization by FeTPyP is shown in Scheme 1. Based on this mechanism, after the addition of hydrogen peroxide to the solution of

Fig. 1 Catalytic cycle of HRP





Scheme 1 Proposed mechanism for the polymerization of catechol with cationic metalloporphyrin (FeTPyP)

FeTPyP, iron (III) hydrogen peroxide porphyrin complex [(TPyP)Fe^{III}-OOH] was formed. This is due to the fact that Fe(TPyP)Cl complex tends to form high-valent iron (IV) oxo porphyrin cation radical intermediate [(TPyP)⁺Fe = O], via O–O bond heterolysis in the reaction of iron porphyrin complex with H₂O₂ [25–28]. Then, the intermediate reacts with catechol, resulting in the catechol cation radical. This radical cation attacks other cation radicals of the monomer to form a dimer, with elimination of two hydrogens. The reaction further propagates to give poly(catechol). Formation of poly(catechol) by these two methods were characterized by both FT-IR and cyclic voltammetry.

FT-IR Spectroscopy

FT-IR spectra of (a) enzyme, (b) cationic porphyrin-synthesized poly(catechol), and (c) catechol monomer are shown in Fig. 2. In Fig. 2c, reasonably broad doublet peaks at 3,451 and 3,326 cm⁻¹ belong to characteristic hydrogen-bonded phenolic

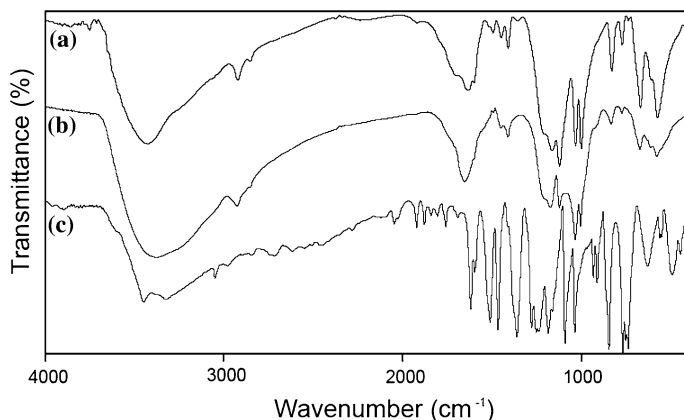
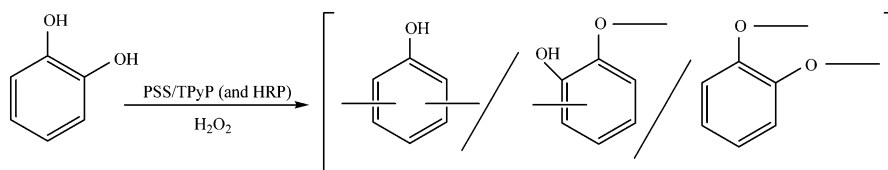


Fig. 2 FT-IR spectra of (a) enzyme-, (b) cationic porphyrin-synthesized poly(catechol) and (c) catechol monomer

O–H vibration bands of catechol [3]. In the synthesized polymers a broad peak centered at $3,300\text{ cm}^{-1}$ is due to phenolic O–H bond. The peaks between $1,470$ and $1,625\text{ cm}^{-1}$ are attributed to the aromatic ring C=C vibration bands. The C–O–C stretching frequency of phenyl ether is also seen at $1,250$ and $1,100\text{ cm}^{-1}$ [7]. Also, the peak at $1,487\text{ cm}^{-1}$ belongs to the ortho disubstitute benzene ring. The band at $2,922\text{ cm}^{-1}$ can be attributed to the C–H stretching in the aliphatic group of the dopant molecules [24]. The peaks at 800 and 750 cm^{-1} belong to the out-of plane bending of =C–H bonds of an aromatic ring. These data indicate that the polymer structure is composed of oxyphenylene units and there are still a high amount of phenolic O–H functional groups on the poly(catechol). In addition, the presence of asymmetric and symmetric S=O stretching bands at $1,006$ and $1,037\text{ cm}^{-1}$ confirms the presence of the PSS in the complex [29].

The FT-IR absorption bands of the polymeric structure were limited compared to the catechol absorption bands. This is due to the more rigid structure of the polymer compared to that of the catechol molecule. The results are compatible with poly(catechol) structure that shown in Scheme 2.

FT-IR spectra of (a) poly(catechol), (b) poly(methyl catechol), and (c) poly(methoxy catechol) synthesized by cationic porphyrin catalyst (FeTPyP) are also presented in Fig. 3. The comparison of these spectra shows similar bands characteristic of poly(catechol) and its derivatives.



Scheme 2 Mechanism of the catalytic polymerization of catechol with the presence of PSS

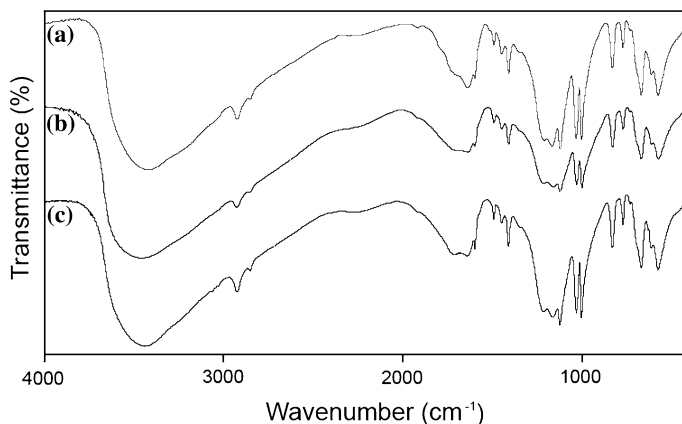


Fig. 3 FT-IR spectra of (a) poly(catechol), (b) poly(methyl catechol) and (c) poly(methoxy catechol) synthesized by cationic porphyrin catalyst (FeTPyP)

Electrical properties

It is already known that polymer conductivity depends on various factors such as the method of synthesis, isolation and purification techniques, etc. [7]. In the present study, the conductivity of the poly(catechol) and its derivatives synthesized by HRP and cationic porphyrin are in the range of 10^{-7} – 10^{-9} S cm⁻¹. The low conductivity of the synthesized polymers may be due to the presence of ether linkage in the chain.

Thermal analysis

The thermal properties of the synthesized polymers were investigated by thermogravimetric analysis. With regard to presence of the PSS as a template, its thermal behavior was studied. Figure 4 shows the TGA thermogram of the PSS. There appears a weight loss (less than 10%) of the polymer below 200 °C which may possibly be due to the evolution of moisture from the polymer matrix. There is a mass loss near 400 °C which may be due to the degradation of sulfonic group. As shown in Fig. 4, the maximum weight loss of the PSS is at 550 °C. By this point, 40% residual was remained up to 800 °C.

The TGA thermogram for poly(catechol) synthesized by (a) HRP enzyme and (b) cationic porphyrin are shown in Fig. 5.

The thermal behavior of poly(catechol), catalyzed by porphyrin, is different from enzymatically synthesized polymer. In the first step, there is a slight weight loss ($\sim 5\%$ for porphyrin- and $\sim 10\%$ for HRP-synthesized polymers) up to 150 °C which may be due to evolution of moisture from the polymer. After 200 °C, however, degradation of the HRP-synthesized poly(catechol) starts and the mass loss occurs very rapidly. A weight loss about 400 °C is observed in both synthesized poly(catechol) by porphyrin and the HRP that may be due to removing of sulfonic group of the PSS that is in complex with polymer. The mass loss of the HRP-catalyzed poly(catechol) at 520 °C is about 10% of the initial poly(catechol),

Fig. 4 TGA thermogram of PSS

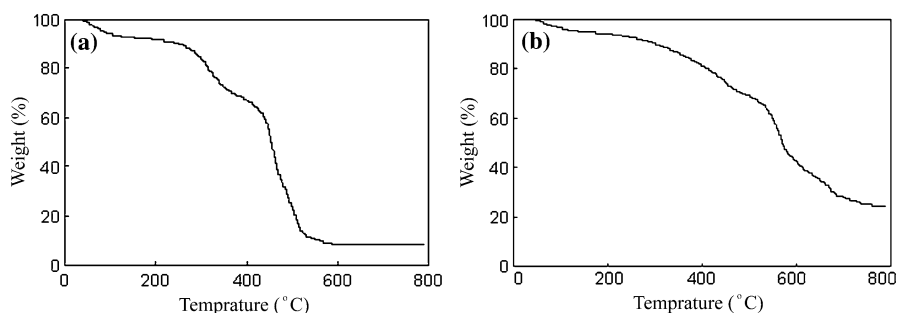
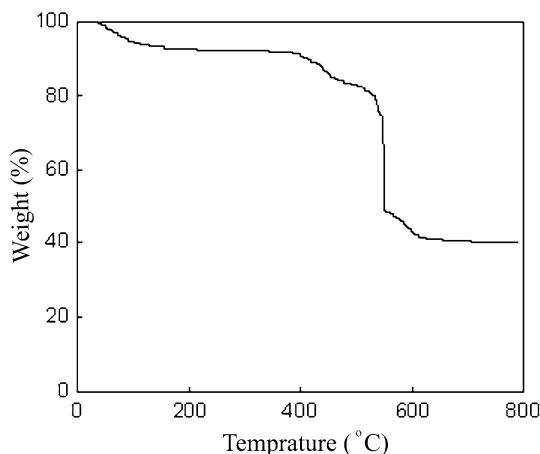


Fig. 5 TGA thermogram **a** HRP catalyzed and **b** cationic porphyrin catalyzed poly(catechol)

while for the porphyrin-catalyzed one at 650 °C is more than 20%. The degradation rate for porphyrin-catalyzed poly(catechol) is very low in comparison to the HRP-catalyzed one. Therefore, the TGA data confirm that the porphyrin-catalyzed poly(catechol) has more thermal stability compared to the HRP-catalyzed one. Previously is reported TGA data for catechol monomer [3]. It is observed that the degradation starts about 110 °C and the degradation peak maximum is reached at 155 °C. The comparison of monomer and polymer TGA data confirms that the poly(catechol) is formed.

This result confirms the high thermal stability of the synthesized poly(catechol) that is very convenient for high-temperature applications.

Cyclic voltammetry

Figure 6 shows the cyclic voltammograms of poly(catechol)/PSS complexes recorded at different scan rates which were synthesized with (a) HRP and (b) Fe^{III}TPyP. One anodic peak at $E_{1/2} = 0.48$ V is observed for the HRP-synthesized polymer and one cathodic peak at 0.33 V. For the porphyrin synthesized polymer, the anodic peak appears at 0.55 V and the corresponding reversible cathodic peak at

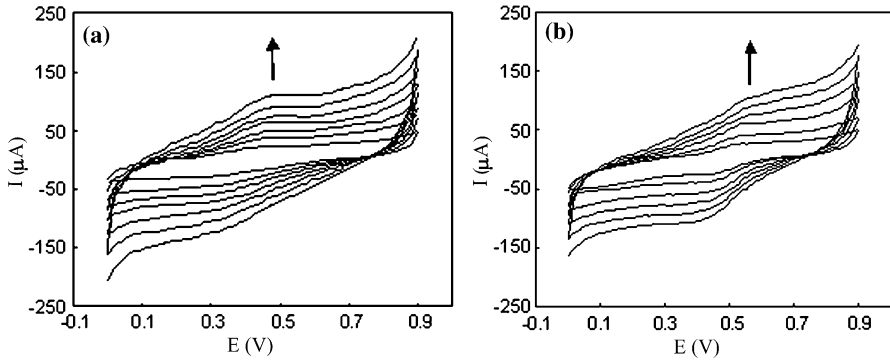


Fig. 6 Cyclic voltammetry of a solution of **a** HRP and **b** $\text{Fe}^{\text{III}}\text{TPyP}$ poly(catechol)/PSS complexes in 1.0 M HCl at different scan rates between 50 and 500 mV/s

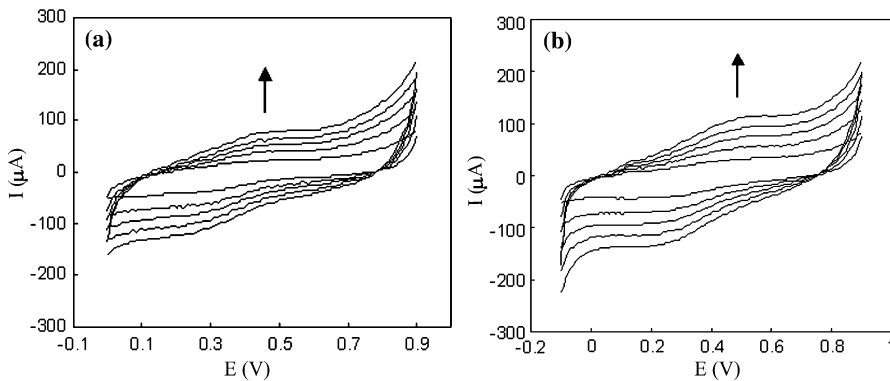


Fig. 7 Cyclic voltammetry of a solution of **a** poly(methyl catechol) and **b** poly(methoxy catechol) complex with PSS catalyzed by FeTPyP in 1.0 M HCl at different scan rates between 100 and 500 mV/s

0.42 V vs. Ag/AgCl. The cyclic voltammograms are recorded over a potential window of 0.0–0.9 V by different scan rates. Figure 5 also shows the voltammograms of (a) poly(methyl catechol) and (b) poly(methoxy catechol) synthesized by cationic porphyrin. In Fig. 7, the anodic peaks for methyl and methoxy catechol are about 0.5 V. As is observed in these figures, the poly(methoxy catechol) has a better electroactivity.

The CV curves suggest that poly(catechol) and its derivatives synthesized by metalloporphyrin are electrochemically active.

Gel permeation chromatography

The gel permeation chromatograms (GPC) of the polymer solutions were studied. To eliminate the aggregation of molecules, 1% (W/V) LiBr was added to the sample before GPC analysis. The results are shown in Fig. 8a–c. Because of the formation

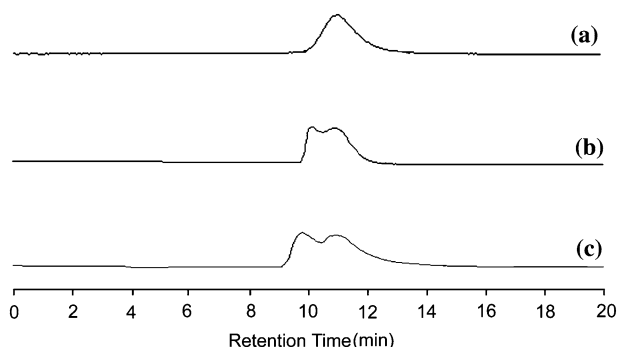


Fig. 8 The gel permeation chromatographs of PSS (a), poly(catechol)/PSS synthesized by HRP (b) and porphyrin (c)

of poly(catechol)/PSS complexes, we cannot determine the molecular weight of poly(catechol) alone, but the GPC results confirmed progress in polymerization. As it can be seen in Fig. 8a, one peak observed with retention time at 11 min related to PSS. After polymerization of catechol in the presence of PSS another peak emerges at shorter retention time than PSS. This is evidence that complexes are formed and that higher molecular weight species obtained [9]. The observed peaks in Fig. 8b, c at 10 and 9.8 min are related to poly(catechol) synthesized by enzyme and porphyrin catalysts, respectively. Comparison of Fig. 8b, c has shown that the polymerization with porphyrin generated higher molecular weight poly(catechol).

Conclusion

The poly(catechol) was successfully synthesized by the HRP and cationic porphyrin. Also, 3-methyl and 3-methoxy catechol derivatives were synthesized by the porphyrin catalyst. The structure and properties of the synthesized polymers were investigated by spectroscopic methods. FT-IR indicates that ether form of poly(catechol) was synthesized with $\text{Fe}^{\text{III}}\text{TPyP}$ and HRP. TGA data shows that the thermal stability of synthesized poly(catechol) by porphyrin is more than HRP-catalyzed one. Both poly(catechol) synthesized by HRP and cationic porphyrin show low electrical conductivity. The cyclic voltammograms of the synthesized poly(catechol) and its derivatives with $\text{Fe}^{\text{III}}\text{TPyP}$ confirm the electroactivity of these polymers.

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