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Enzymatic polymerization of hydroxy-functionalized carbazole monomer

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ABSTRACT

Up to date, enzymatic polymerization of phenolic compounds bearing different moieties such as ferrocene, sugar, furamide, and male-imide have been reported. In this study, horseradish peroxidase (HRP)-catalyzed polymerization of another hydroxy substituted aromatic compound, 2-hydroxycarbazole (HC), was firstly presented. The structure of the polymer (PHC) was verified by using nuclear magnetic resonance and infrared techniques. Further characterization was carried out by means of TG, DSC, CV (cyclic voltammetry), SEM (scanning electron microscopy), fluorescence analyses, and solid state conductivity measurements. Average molecular weight of the polymer was determined by gel permeation chromatography and was around two thousands. The optical and electrochemical band gaps of PHC were dramatically lower than those of HC. The photochemical behaviors of HC and PHC were investigated by recording the fluorescence spectra in two different solvents. Solid state conductivity measurement showed that the electrical conductivity value of hydroxyl-functionalized carbazole polymer is relatively higher than those of the previously reported phenol polymers in the literature. Moreover, the conductivity of PHC increased by doping with iodine vapour.

1. Introduction

Enzymatic polymerization has gained much attention to prepare phenolic polymers. This process has been developed by Dordick, Kobayashi, and Uyama [1–10]. Oxireductases are used to catalyze the polymerization of a wide variety of –OH, –NH_2 functionalized aromatic compounds. Among the oxireductases, horseradish peroxidase (HRP) has been used extensively by several research groups [11–12]. HPR is isolated from horseradish which is a hardy herb for many years that is cultivated in temperate regions of the world mainly for the culinary value of its roots. There is rich source of the heme-containing enzyme, which utilizes hydrogen peroxide to oxidize many kinds of the organic compounds [13,14]. HRP catalyzes phenolic monomers in the presence of hydrogen peroxide, forming phenoxy radicals which couple spontaneously at various positions to form dimers, oligomers, and polymers [11]. Enzymatic polymerization of phenol derivates gives polymers constituted of units A and B as shown in Scheme 1 [14].

Typical monomers used for the peroxidase-catalyzed polymerization are phenol, aniline, and their substituted derivatives [15–19]. Phenol and aniline derived polymers have found many applications in mechanical, electrical, and optical uses [20]. The enzymatic polymerization of phenol monomers bearing different moieties such as ferrocene [14], flavonol [15], sugar [16], furamide [17], and male-imide [18] have been reported so far. Liu et al. reported that the phenol monomer having azophenol group offered interesting optical properties [21].

Yamaguchi and Yamamoto presented the enzymatic synthesis of phenol polymer containing ferrocenophane pendant groups. The obtained polymer, whose M_n and M_w values were 5000 and 5400 g mol^{-1}, was soluble in some organic solvents like chloroform, N,N-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) [14]. Tawaki et al. have studied HRP-catalyzed polymerization of sugar-based phenols [22]. Wang and Dordick studied the nucleoside-based polyphenols using soybean peroxidase (SBP) [23]. Nakano et al. studied the polymerization of arbutin using HRP in aqueous buffer [24]. Peroxidase-catalyzed polymerization of an aromatic compound, 1-hydroxypyrene, was reported by Liu et al. [25]. They reported that these types of polynuclear aromatic hydrocarbons offer exciting new possibilities for electronic and photonic materials.

Carbazole is another compound that has interesting optoelectronic properties such as photoconductivity and photorefractivity. Carbazole derivatives are used as hole-transporting layers of electroluminescent devices because of their high charge mobility [26].

2-Hydroxy-carbazole combines the advantages of phenol and carbazole moieties. From this point of view, the type of linkage

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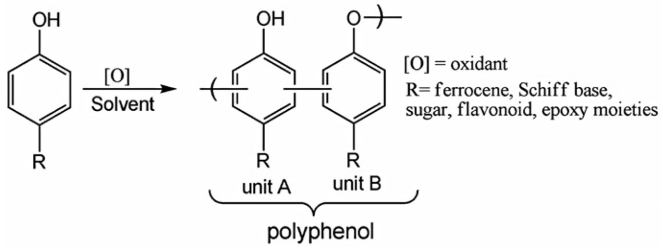


Scheme 1. Enzymatic polymerization of phenol derivates.

between the monomer units is of crucial important. Although various methods have been reported for preparation of carbazole polymers, enzymatic preparation of carbazole polymers has no precedent to our knowledge.

Therefore, the main objective of this work is to synthesize enzymatically a novel kind of semi-conductive polyphenol derived from 2-hydroxycarbazole and investigate its thermal, optical, electrochemical, and morphological properties in addition to conductivity properties.

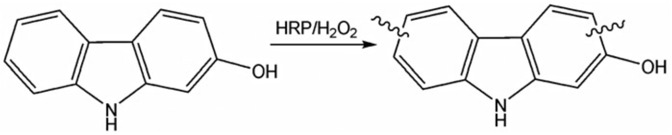
2. Experimental

2.1. Materials

HRP was purchased from Sigma Chemical Company and had a specific activity of 259 purpurogallin units/mg and RZ = 3.0 and used directly as supplied. All other commercially supplied chemicals are chemically or analytically pure and used as received.

2.2. Characterization techniques

The infrared and ultraviolet–visible (UV–vis) spectra were measured by PerkinElmer FT-IR Spectrum One and PerkinElmer Lambda 25, respectively. ^{1}H NMR spectrum of PHC (Bruker Avance DPX-400 MHz) was recorded at 25 °C using deuterated DMSO as solvent. Tetramethylsilane (TMS) was used as internal standard. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) techniques of Shimadzu Co. For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. × 300 mm column was used; eluent: DMF (0.4 mL/min), polystyrene standards. A refractive index detector (RID) and UV detector were used to analyze the products at 25 °C. Thermal data were obtained using a PerkinElmer Diamond Thermal Analysis. The TG–DTA measurements were made between 15 and 1000 °C (in N_2, rate 10 °C min^{-1}). DSC analysis was carried out using PerkinElmer Pyris Sapphire DSC. DSC measurement was made between 25 and 420 °C (in N_2, rate 20 °C min^{-1}). Cyclic voltammetry (CV) measurements were performed using a CH instruments 660C electrochemical workstation. The electrochemical cell consists of an Ag wire pseudo-reference electrode (RE), Pt wire as counter electrode (CE), and platinum working electrode (WE) immersed in 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte. The experiments were carried out in acetonitrile/DMSO (4/1, v/v) solvent mixture under argon atmosphere. The scan rate and the temperature were 100 mV/s and 25 °C, respectively. The potentials were calibrated to the ferrocene redox couple ($E^{1/2}$) (Fc/Fc$^+$) 0.39 V versus Ag/Ag$^+$. All reported potentials were given versus Ag/Ag$^+$. The fluorescence spectra were recorded by using a Shimadzu RF-5301PC spectrofluorophotometer. Polymer film was prepared on indium–tin-oxide (ITO) glass plate by dip-coating technique using a KSV Dip Coater instrument. The process has been carried out by successive dipping and withdrawal of ITO-glass plate in 50 mg/mL concentrated homogenous solution of PHC in MeOH/THF (1/1, v/v) for 250 times. After each dipping the film was kept for 1 min for drying [27]. Conductivities of PHC were measured on a Keithley 2400 electrometer, using four point probe technique. Instrument was calibrated with ITO-glass plate. Iodine doping was carried out by exposure of the polymer film to iodine vapour at atmospheric pressure in a desiccator at 25 °C [28,29]. Absorption spectra of the polymer film were measured before and after iodine doping by Analytikjena Specord S 600 single beam spectrophotometer. The surface morphology of PHC was evaluated by scanning electron microscopy (SEM), using a Philips XL 30S FEG apparatus.



Scheme 2. Enzymatic polymerization of HC monomer.

2.3. Polymerization

Typical procedure is as follows [14]: to 35 mL dioxan and 15 mL sodium phosphate buffer mixture, 5 mmol monomer and 7.5 mg HRP were added. The reaction was initiated by the addition of H_2O_2. The reaction mixture was vigorously stirred. After the addition of H_2O_2, the brown precipitate formed during the reaction which was collected by filtration, washed thoroughly with water to remove any residual enzyme, phosphate salt, and finally washed with ether to remove unreacted monomer and then dried in a vacuum oven for 24 h. The polymerization process is outlined in Scheme 2.

3. Results and discussion

3.1. The structure of PHC

HRP-catalyzed polymerization of HC was carried out using hydrogen peroxide as the oxidant at room temperature for 24 h under air. The reaction solution converted to dark-red color as soon as hydrogen peroxide was added. The precipitates formed during the polymerization, which were isolated by filtration.

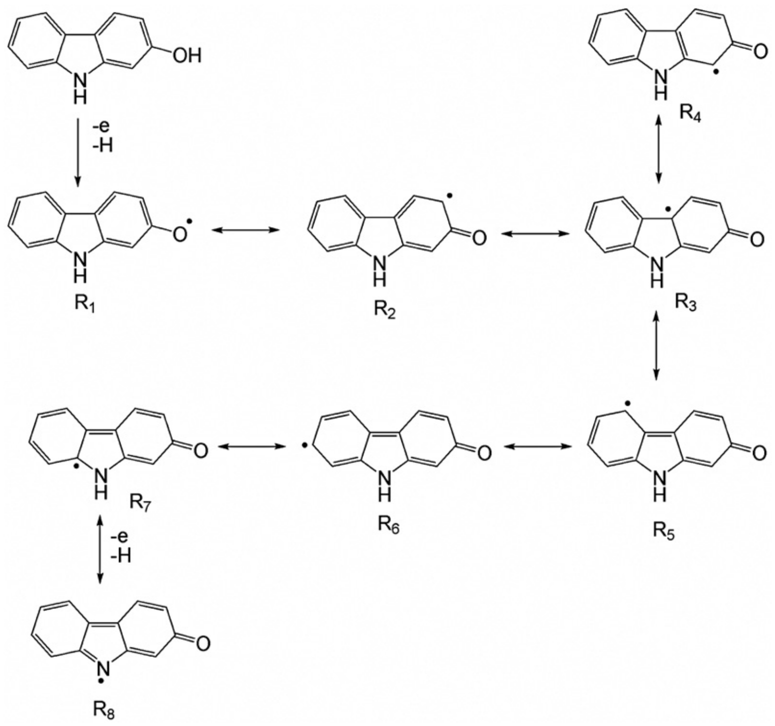
The product was insoluble in toluene, chloroform, ethyl acetate, and ethanol, while it was completely soluble in DMF. However, the resulting product could be separated into two components; as THF soluble part and THF insoluble part. The molecular weight of THF soluble part of the product was analyzed by a HPLC equipped with a GPC column. According to the GPC chromatograms obtained from both detectors, PHC has single fraction with M_n, M_w, and PDI values of 1850, 2800 g mol^{-1}, and 1.51; and 2300, 2950 g mol^{-1}, and 1.28 with using RID and UV detectors, respectively.

It is well known that in the presence of H_2O_2, HRP can polymerize hydroxy-functionalized aromatic compounds to produce corresponding radicals. These radicals may couple together through radical coupling to form dimers, oligomers, and finally polymers [20]. As one can see from the molecular structure of 2-hydroxycarbazole, several radical resonance structures may be proposed. Thus, more sites on the carbazole ring are available for coupling compared to that of the phenol. Possible coupling sites for 2-hydroxycarbazole are given in Scheme 3. These coupling sites may help predict possible resulting products.

C–O coupling; R1–R2, R1–R3, R1–R4, R1–R5, R1–R6, R1–R7

C–C coupling; R2–R3, R2–R4, R2–R5, R2–R6, R2–R7, R2–R2, R4–R5, R5–R6, R4–R4, R5–R5,

C–N coupling; R8–R2, R8–R3, R8–R4, R8–R5, R8–R6, R8–R7.



Scheme 3. The resonance forms of 2-hydroxy carbazole monomer.

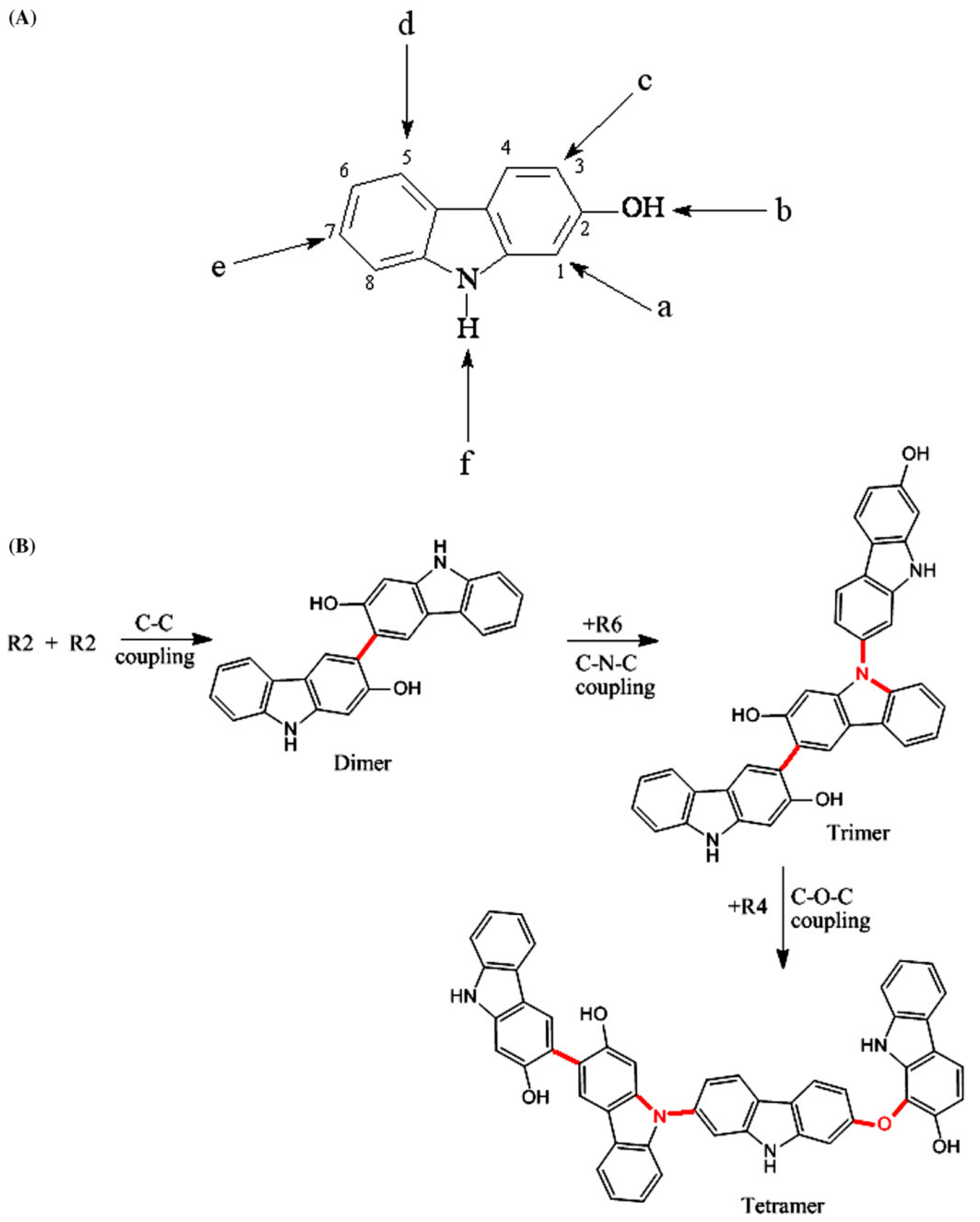
As shown in Scheme 3, there are multi-possibilities for carbazole radical coupling. However, the possible existence of a multitude of coupling modes within one single polymer chain makes it difficult to predict a model repeat unit. For this reason, the determination of precise structure for final product is extremely hard. Similar spectral complications were also seemed for the other phenol polymers [30].

It is well known that phenol polymers are composed of phenylene units [6,8,9] and/or oxyphenylene units. The comparison of the UV–vis, FT-IR, and NMR spectra of the monomers and polymers provides valuable information. UV–vis spectrum of the polymer shows an absorption tail in the region of 325–530 nm. This is attributed to conjugation length in the polymeric structure. The other phenol derivates were enzymatically polymerized and similar absorption spectra were obtained [20]. Optical band gap values of the synthesized compounds are also calculated as in the literature using the following equation: $E_g = 1242/\lambda_{\text{on}}$, where λ_{on} is the onset wavelength which can be determined using the absorption edges by intersection of two tangents [31]. Obtained optical band gaps are found to be 3.69 and 3.22 eV for HC and PHC, respectively. These results indicate that due to the polyconjugated structure the synthesized polymer has lower band gap than its monomer compound.

As examined of the FT-IR spectra a significant shift to lower frequency was observed for the polymer in the –OH stretch region (3000–3500 cm^{-1}) with comparison to the monomer. This shift is believed to be due to stronger hydrogen bonding in the polymeric structure that is formed during the polymerization reaction. Also, the peak observed at 3400 cm^{-1} at the spectrum of HC indicates N–H stretch of carbazole unit. This peak clearly disappears at the spectrum of PHC showing that the polymerization reaction also proceeds by forming intermolecular C–N–C coupling which terminates N–H stretch peak. This is the result of the combination of R8 radical with another radical form as shown above. However, some possible couplings such as C–N–N, C–N–O, and C–O–O couplings between R8–R8, R8–R1, and R1–R1 are not expected to form due to their unstable structures. Another important feature noted in the spectra is the emergence of a broad peak centered 1690 cm^{-1}, which is attributed to the presence of conjugation of double bonds in main chain [11]. Obtained results agree with the previously reported systems with similar structures. The peaks at 1213 and 1183 cm^{-1} are ascribed to C–O and C–OH vibrations, and the peak at 1115 cm^{-1} is due to the symmetric vibration of the ether [20]. These data clearly show that the polymer is composed of a mixture of phenylene and oxyphenylene units.

The typical band at 870 cm^{-1} indicates that the synthesized polymer is mainly composed via linked phenylene units. In addition, the retention of a strong OH stretch region in the polymer suggests that the resulting polymer has significant phenol functionality [30].

^{1}H NMR spectrum of PHC shows a singlet peak at 8.53 ppm indicating –O$\underline{\text{H}}$ proton. As mentioned above, the polymerization mainly proceeds by C–C and C–N couplings, with lower C–O coupling. After the polymerization, sharp aromatic proton signals of HC disappear with appearing of broadened signals of the product at 6.6–8.4 ppm. This is due to various intermolecular combinations of possible HC radical forms. The peak at 7.92 ppm is attributed to C4–$\underline{\text{H}}$, whose singlet form supports the polymer formation by C–C coupling at o-position of –OH group (at C3). Also, the peaks owing to C5–$\underline{\text{H}}$, C6–$\underline{\text{H}}$, C7–$\underline{\text{H}}$, and C8–$\underline{\text{H}}$ are clearly observed at 8.32 (d), 7.04 (d), 7.11 (d), and 7.48 (d) ppm, respectively. The presence of these peaks indicates that R5 and R6 radical forms do not contribute to the polymer formation considerably. The broad features in the ^{1}H NMR spectrum may be due to a number of closely spaced and overlapping individual proton resonances as proposed by Premachandran et al. [30]. Additionally, Ar–N$\underline{\text{H}}$ peak owing to carbazole unit which is expected to be observed above 11.50 ppm disappears at the ^{1}H NMR spectrum of PHC. This is probably due to C–N couplings of the monomer units, as mentioned above. This result also agrees with the FT-IR results. Possible polymerization sites for HC monomer are given in Scheme 4A. As a result of the spectral data HC mainly polymerizes at a, b, c, and f positions. On the other hand, according to the ^{1}H NMR spectrum C–C coupling of phenylene units at the o-positions of –OH group is generally favored. Model presen-



Scheme 4. (A) Possible polymerization sites of HC [a and c = o-carbon atoms of phenol units (C1 and C3 carbons), b = O–H group, d and e = C5 and C7 positions of carbazole ring; f = N–H unit] and (B) possible proceeding of the polymerization by different coupling mechanisms.

tation of the polymerization reaction of HC by different coupling mechanisms is given in Scheme 4B.

3.2. Thermal analysis

Thermal properties of enzymatically synthesized PHC were studied by thermogravimetric/differential thermal analysis (TG–DTA) and differential scanning calorimetry (DSC) under nitrogen atmosphere. DSC measurements were run at a scan rate of 10 °C/min.

Fig. 1 shows TG–DTG–DTA curves of PHC. According to the TG–DTG measurements when heated up to 1000 °C PHC thermally degrades in four steps whose maximum weight loss temperatures are 248, 431, 762, and 986 °C. The first degradation step starts upon 110 °C with an onset temperature of 173 °C. PHC showed a 49% weight decrease at 1000 °C. Also, DTA measurement showed an

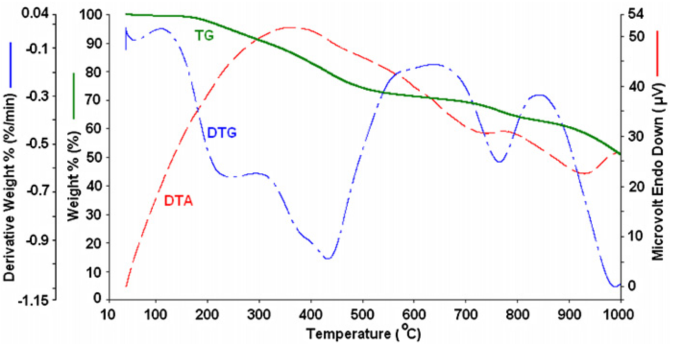


Fig. 1. TG (bold line), DTG (dotted line), and DTA (dashed line) curves of PHC.

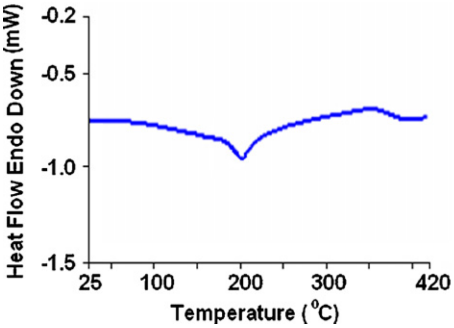


Fig. 2. DSC curve of PHC.

exothermic peak at 362 °C and two endothermic peaks at 730 and 926 °C. Fig. 2 shows DSC thermogram of PHC. As calculated from Fig. 2, glassy transition temperature (T_g) of PHC is approximately 196 °C. During the glassy transition, change of the specific heat was also determined and found to be 0.121 J/g K. T_g value of PHC is relatively higher than those of the other enzymatically obtained phenol polymers [32]. Different bisphenolic monomers were enzymatically polymerized by Uyama et al. and T_g values of these polymers were in the range of 108–171 °C [33]. Several Schiff base substituted polyphenol species were also synthesized by oxidative polymerization process with T_g values in the range of 160–255 °C [29].

3.3. Electrochemical properties

Cyclic voltammograms of the synthesized compounds are shown in Fig. 3. According to CV measurements HC and PHC were oxidized at 1120 and 997 mV, respectively. Also, the reduction peaks were obtained at −1746 and −917 mV, respectively. HOMO–LUMO energy levels and electrochemical band gaps (E'_g) of HC and PHC were calculated by using the following equations [21] and found to be −5.51, −2.64, and 2.87 eV for HC; and −5.39, −3.47, and 1.92 eV for PHC.

$$E_{\text{HOMO}} = -(4.39 + E_{ox}) \tag{1}$$

$$E_{\text{LUMO}} = -(4.39 + E_{red}) \tag{2}$$

$$E'_g = E_{\text{LUMO}} - E_{\text{HOMO}} \tag{3}$$

where E_{ox} is the oxidation peak potential and E_{red} is the reduction peak potential.

The obtained electrochemical band gaps clearly indicate that the enzymatically synthesized PHC has quite lower band gap than its monomer compound (HC) due to its polyconjugated structure.

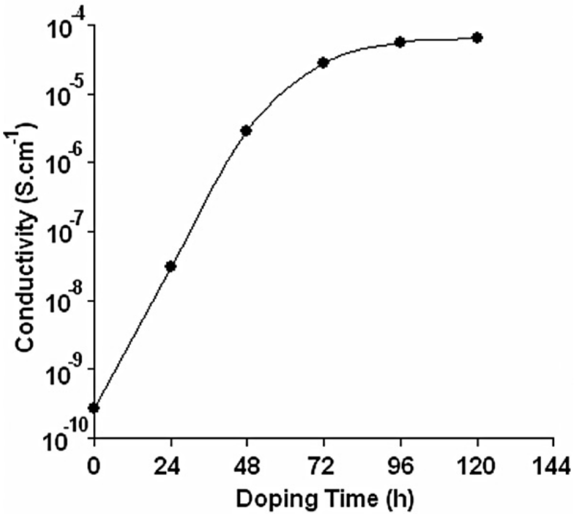


Fig. 4. Conductivity measurement of PHC versus doping time with iodine at 25 °C.

3.4. Electrical conductivity and doping procedure of PHC

Electrical conductivities of PHC related to doping time with iodine were also determined and shown schematically in Fig. 4. According to Fig. 4 the initial conductivity of the synthesized polymer was 2.66×10^{-10} S cm^{-1}. With exposure to iodine vapour it was drastically doped and after 120 h the conductivity increased up to 6.52×10^{-5} S cm^{-1} which was nearly five orders of magnitude. However, it is clearly observed in Fig. 4 that the conductivity of PHC firstly increases greatly with doping time, but then tend to level-off. PHC nearly reaches to the saturated conductivity in 96 h, as seen in Fig. 4. The increasing conductivity could indicate that a charge-transfer complex between the PHC and dopant iodine is continuously formed. Consequently, Fig. 4 not only shows the conductivity and doping time relationship but also indicates how quickly the doping reaction takes place. The experimental results showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curves vary with doping conditions. Conducting and semi-conducting polymers have been widely studied with their doping processes and several doping mechanisms have been suggested to clarify the doping/dedoping reactions [34].

According to these results, the synthesized polymer has higher initial and maximal conductivities than the previously synthesized phenol polymers [35–37].

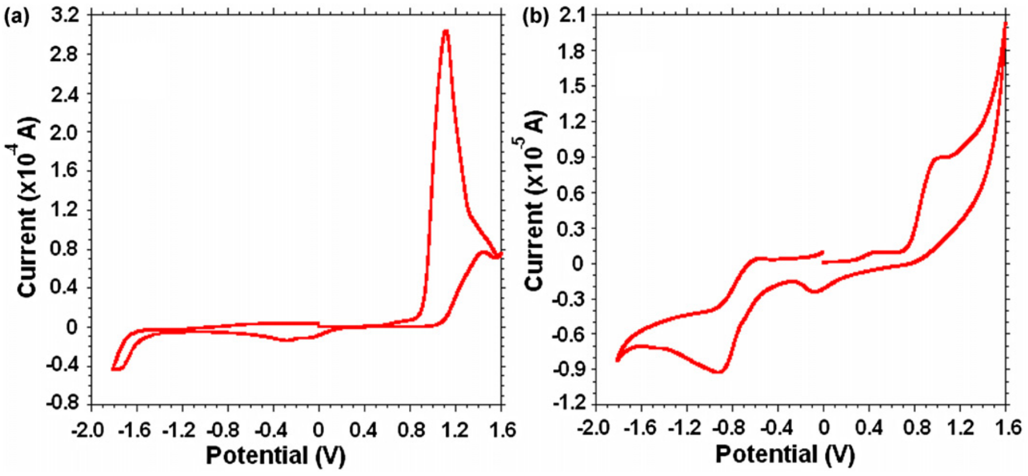
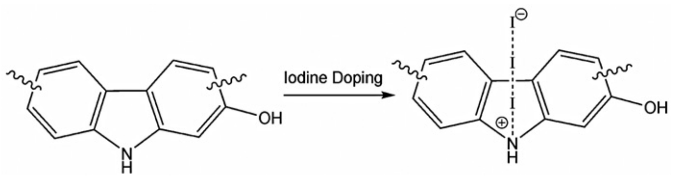


Fig. 3. Cyclic voltammograms of HC (a) and PHC (b) in acetonitrile/DMSO (4/1, v/v) solution of 0.1 M Bu_4NPF_6 at a scanning rate of 100 mV s^{-1}.



Scheme 5. Possible doping reaction of PHC with iodine vapour.

Doping procedure of conducting polymers has been used in various applications [38–40]. Also, Diaz et al. had suggested the conductivity mechanisms of Schiff base polymers for doping with iodine [41]. According to the proposed mechanism nitrogen is a very electronegative element and it is capable of coordinating an iodine molecule. Polycarbazole derivatives could also be doped by electroacceptor chemical vapours resulting in to form radical cation (polaron) on the carbazole nitrogen [42]. According to the proposed mechanism iodine being an electroacceptor vapour could accept the non-shared electron pair of nitrogen that results in forming of polaron structure. Possible iodine doping reaction of PHC was shown in Scheme 5.

The effect of the doping reaction on the absorbance spectrum of PHC was also determined on ITO-glass surface and given in Fig. 5. As seen in Fig. 5, a new peak was grown at 359 nm during the doping reaction. Resultantly, red shift in the absorption edge was obtained. This confirms the conductivity measurements. As a result of the red shift in absorption edge the optical band gap of PHC decreased and so on the conductivity increased, after doping reaction. As known, the lower band gap causes the higher electrical conductivity due to easy electron transition from bulk to vacuum molecular orbital. The changes in absorption spectra of some other semi-conductive polymers after iodine doping have been previously studied and similar results have been reported [43].

3.5. Fluorescence characteristics

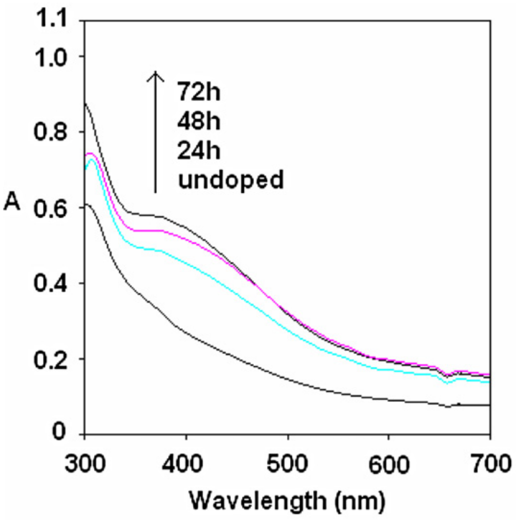


Fig. 5. The effect of doping procedure on the absorption spectra of PHC (from bottom to top: undoped, 24, 48, and 72 h doped).

Table 1
Fluorescence spectral data of PHC.

Compound	Conc. (mg/L)	λ_{Ex}[a]	λ_{Em}[b]	$\lambda_{max\,(Ex)}$[c]	$\lambda_{max\,(Em)}$[d]	I_{Ex}[e]	I_{Em}[f]
THF	100	378	415	376	410	36	36
DMF	100	377	435	376	428	106	105
DMF	33	377	435	369	425	166	145
DMF	11	377	435	366	425	105	94

Slit width: 5 nm.

[a] Excitation wavelength for emission.
[b] Emission wavelength for excitation.
[c] Maximum emission wavelength.
[d] Maximum excitation wavelength.
[e] Maximum excitation intensity.
[f] Maximum emission intensity.

Fluorescence measurements of PHC were carried out in DMF and THF solutions. The observed results were summarized in Table 1. Emission and excitation spectra of PHC in 100 mg/L concentrated DMF and THF solutions were also given in Fig. 6a. As seen in Fig. 6a PHC has higher fluorescence intensity in DMF solution at the same concentration. As seen in Fig. 6b, with increasing the concentration of DMF solution fluorescence intensity firstly increases drastically, reaches to optimal value at 33 mg/L and then tend to level-off. This result clearly indicates that the optimum concentration to take maximum fluorescence quantum yield for PHC is 33 mg/L.

It is well known that the morphological characteristics of the phenol polymers are significantly affected on the reaction conditions including solvent composition, oxidant, and buffer pH. By changing of these parameters, polymer morphologies can be controlled [12]. For example, HRP-catalyzed polymerization of 2-naphtol in reversed micelles produced polyphenols with microspherical morphology [30]. Fig. 7 shows SEM images of PHC obtained by dioxan–buffer mixture (35/15; v/v). This image is different than that of characteristic polyphenol microsphere structure

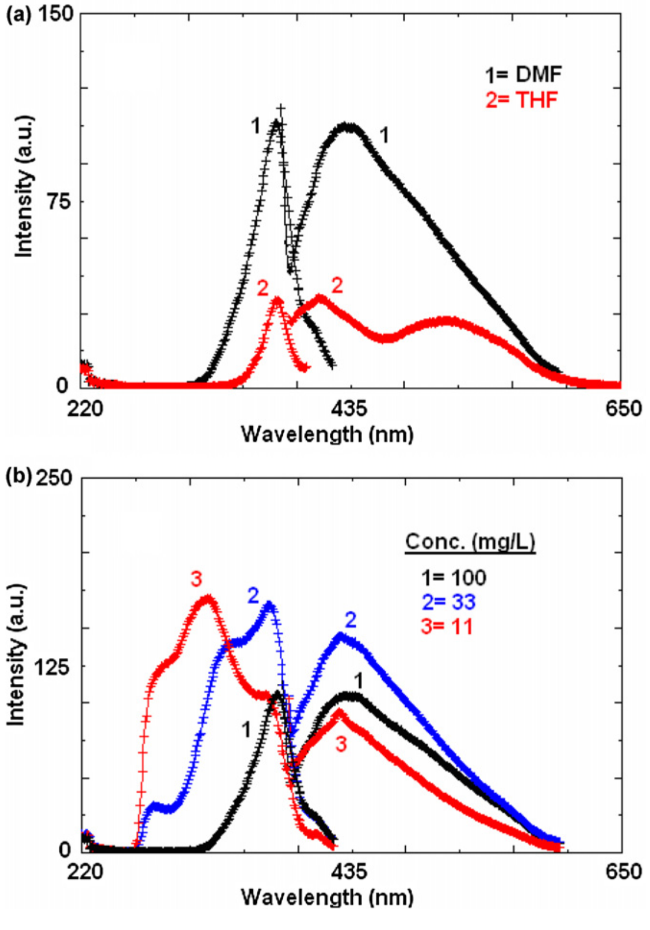


Fig. 6. (a) Fluorescence spectra of 100 mg/L concentrated PHC solutions in different solvents; 1 = DMF and 2 = THF and (b) fluorescence spectra of PHC in DMF at various concentrations; 1 = 100 mg L^{-1}, 2 = 33 mg L^{-1}, and 3 = 11 mg L^{-1} (λ_{Ex} 377 nm, λ_{Em} 435 nm for DMF, λ_{Ex} 378 nm, λ_{Em} 415 nm for THF; slit width: 5 nm).

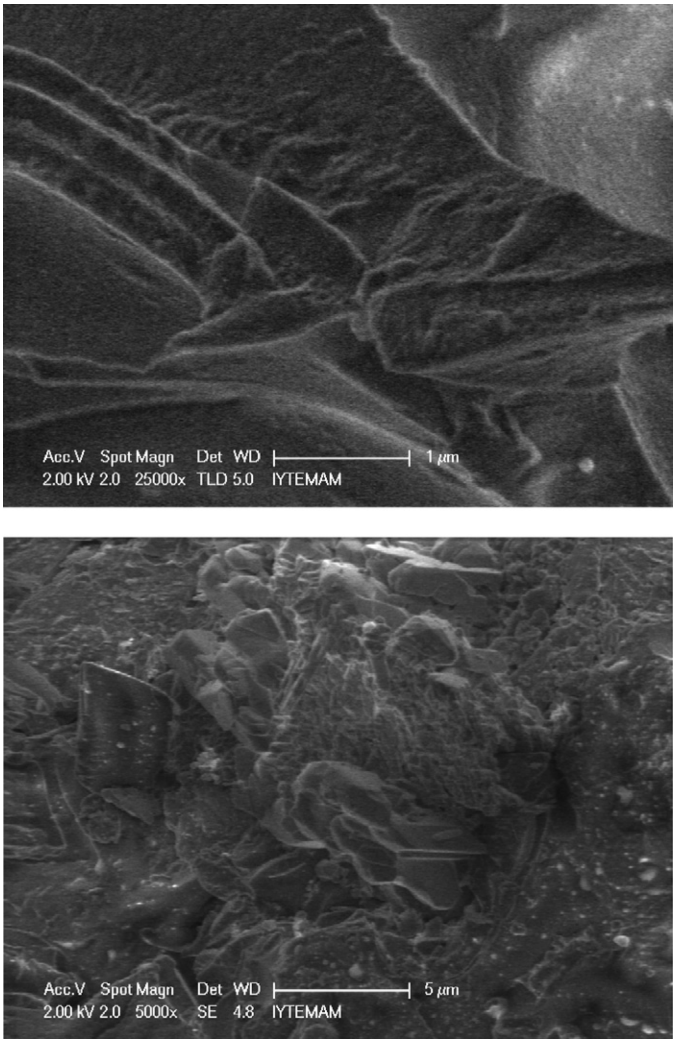


Fig. 7. Scanning electron microscopy photographs of PHC.

[30]. As seen in Fig. 7, a wide range of particle size distribution was observed. The particles were condensed, unhomogeneous and not so well-ordered structure and shape.

4. Conclusions

HC was oxidative polymerized by a peroxidase catalyst to give PHC. The polymerization using HRP in a mixed solvent of dioxane and phosphate buffer (pH = 7) afforded PHC. T_g value of obtained polymer relatively higher than that of the other polyphenols synthesized by enzymatic process. According to solid state conductivity measurement, the synthesized polymer has relatively higher initial and maximal conductivities in comparison to the previously synthesized phenol polymers. Applying this method for the other hydroxy-functionalized carbazole derivates, polymeric products with novel electronic and optical properties can be synthesized for a wide variety of industrial applications.

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