Ketimine Substituted Polyphenol: Synthesis, Characterization and Investigation of Its Thermal and Electrochemical Properties

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ABSTRACT: Oxidative polycondensation of 3-(1-(2-phenylhydrazono)ethyl)phenol (3-PHEP) was studied using oxidants such as sodium hypochlorite, air (O_2) and hydrogen peroxide in an aqueous alkaline medium under various polymerization conditions. The polymerization yield, molecular weight, solubility, and thermostability of the polymer were investigated. The macromolecular structure of the resulting polymer was characterized by elemental analysis, ultraviolet–visible, Fourier transform infrared, and nuclear magnetic resonance techniques. Thermogravimetric analysis showed poly(3-PHEP) to be highly stable against thermo-oxidative decomposition. Mass loss of the polymer was found to be only 16.3% at 1000°C. In addition, the highest occupied molecular orbital–lowest unoccupied molecular orbital energy levels, electrochemical (E_g') band gaps and optical (E_g) band gaps were calculated from cyclic voltammetry and ultraviolet–visible measurements, respectively. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polyphenols have attracted much attention due to its conjugated structures, active hydroxyl (—OH) groups and thermal oxidative stabilization properties. These cause potential applications in some important fields such as the graphite materials,[1] semi conductivity,[2] antistatic and antimicrobial materials.[3,4] Polyphenols including long conjugation can easily be synthesized by oxidative polycondensation. This method occurs under mild reaction conditions without toxic reagents. Compared with other methods, oxidative polycondensation has more important advantages for polymer syntheses such as (a) having easy access, cheapness and having simple structure oxidants, (b) ease of product separation from reaction mixture, (c) enhanced thermal stability of polymers that are produced, and (d) release of environmentally friendly by-products such as NaCl and H_2O.[5]

Many researchers have been trying to improve the properties of these polymers by adding some functional groups into their structures. Kaya et al.[6] synthesized oligo-2-p-tolylazomethine-phenol (OTAP) with phenylazo pendent groups for the first time. OTAP is an imine polymer, which has long conjugation in the backbone and in subordinate groups. Imines polymers which have a lot of functionality groups can be used for cleaning poisonous heavy metals in industrial waste waters. So far, poly(phenoxy-imine)s and their derivates have been synthesized by oxidative polycondensation method, and their properties have been extensively investigated,[7–30] but surprisingly, synthesis of poly(phenoxy-ketimine)s and their thermal properties have not been reported yet.
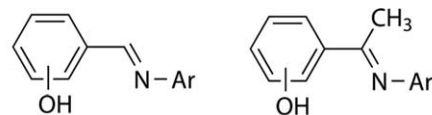
phenoxy-imines   phenoxy-ketimines

For this reason, in this study, the monomer with ketimine side group, 3-(1-(2-phenylhydrazono)ethyl)phenol, was synthesized using m-hydroxy acetophenone and phenylhydrazine. Subsequently, oxidative polycondensation using sodium hypochlorite and air oxygen as oxidants have been used, and a new kind of polyphenols containing ketimine pendent groups, poly[3-(1-(2-phenylhydrazono)ethyl)phenol], was obtained. Besides, electrochemical and thermal features of the synhesized compounds were investigated. In addition, effect of absorbed water molecules in structures of poly(phenoxy-imine)s or poly(phenoxy-ketimine)s on their thermal degredation has been put forward with this study for the first time.
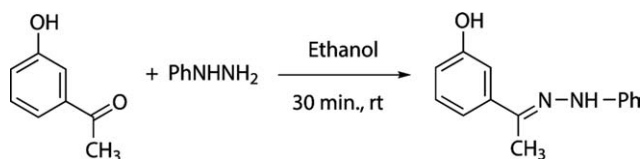
Scheme 1. Synthesis of 3-(1-(2-phenylhydrazono)ethyl)phenol.

EXPERIMENTAL

Materials

Several chemicals, including *m*-hydroxy acetophenone, phenyl hydrazine, sodium hypochlorite (NaOCl) (11%), hydrogen peroxide (H_2O_2) (30%), hydrochloric acid (HCl) (37%), sulfuric acid (H_2SO_4) (98%), potassium hydroxide (KOH), silver nitrate ($AgNO_3$), diethyl ether, dichloromethane, ethanol, ethyl acetate, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), methanol, chloroform, *n*-hexane, and acetonitrile, were purchased from Merck Schuchardt OHG (Hohenbrunn, Germany). All of these chemicals were used without further purification.

Instrumentation

Elemental analysis was carried out with a LECO CHNS-932 (LECO Corporation, St Joseph, MI). The ultraviolet–visible (UV-vis) spectra of compounds were measured by Perkin Elmer Lambda 25 (Perkin-Elmer, Shelton, CT) in methanol (210–1000 nm). The infrared spectra were measured by a Perkin-Elmer Fourier transform infrared (FTIR) Spectrum One (Perkin-Elmer, Llantrisant, UK). The FTIR spectra were recorded using universal attenuated total reflectance sampling accessories (4000-650 1/cm) whose brand is Pike GladiATR (Madison, WI). The ^{1}H-NMR spectra of 3-PHEP and poly(3-PHEP) were recorded at 25°C in $(CD_3)_2SO$ using a Bruker 300 MHz Ultrashield TM and a Varian XL-400 NMR, respectively with tetramethylsilane as an internal standard. Thermal data were obtained with a Perkin-Elmer Diamond Thermal Analyzer. The thermogravimetric analysis (TGA),

derivative thermogravimetric (DTG) and differential thermal analysis (DTA) measurements were made between 20°C and 1000°C (under N_2; flow rate, 10°C/min). The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) (Shimadzu Co., Kyoto, Japan). The following conditions were used for chromatography: SGX (100 A° and 7 nm diameter loading material) 3.3 mm i.d.x 300 mm column, eluent: DMF/methanol (v/v, 4 : 1, 0.4 mL/min), polystyrene standards. A refractive index detector was used to analyze the product at 25°C. The optical band gaps (E_g) of the synthesized compounds were calculated from their absorption edges obtained by UV-vis measurements. Cyclic voltammetry measurements were carried out using a CHI 660C Electrochemical Analyzer (CH Instruments, Austin, TX) at a potential scan rate of 20 mV/s. The electrochemical cell consists of an Ag wire as the reference electrode, a Pt wire as the counter electrode, and glassy carbon electrode as the working electrode immersed in $TBAPF_6$ (0.1 M) as the supporting electrolyte. The voltammetric measurements were carried out in acetonitrile for the monomer and acetonitrile/DMSO mixture (v/v, 2 : 1) for the polymer. An ultrasonic bath was used to dissolve the samples. The highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy levels and electrochemical band gaps (E_g') were calculated from the oxidation and reduction onset values.

Synthesis

**Preparation of 3-(1-(2-phenylhydrazono)ethyl)phenol (3-PHEP).** The monomer was prepared by a standard condensation method.[31] Solutions of phenyl hydrazine (1.08 g, 10 mmol) in ethanol (2 mL) and *m*-hydroxy acetophenone (1.36 g, 10 mmol) in ethanol (3 mL) were mixed and stirred for ~ 30 min at room temperature. The precipitated product was filtered and washed with cold ethanol. The monomer (as shown in Scheme 1) was purified by recrystallization in ethanol to provide 2.19 g compound as a pale yellow-white solid. The purity was confirmed by silica plates and melting point determination.
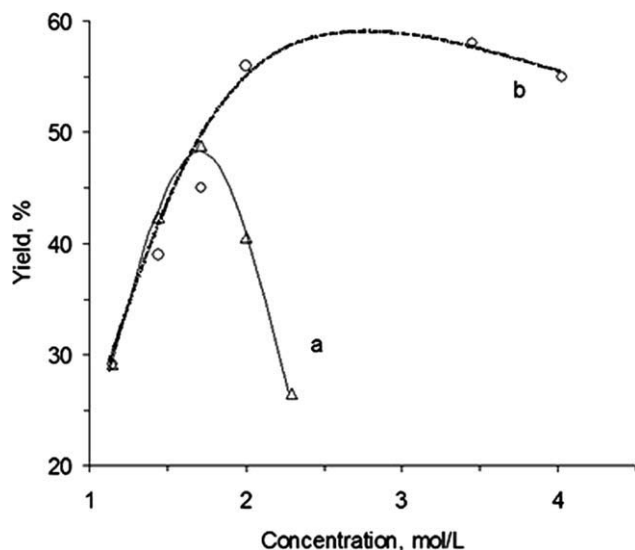
Figure 1. Effect of KOH concentrations (a) and NaOCl concentrations (b) on the yield of polymer {temperature: 80°C, time: 3 h and $[3\text{-PHEP}]_0$ = 1.15 mol/L}.
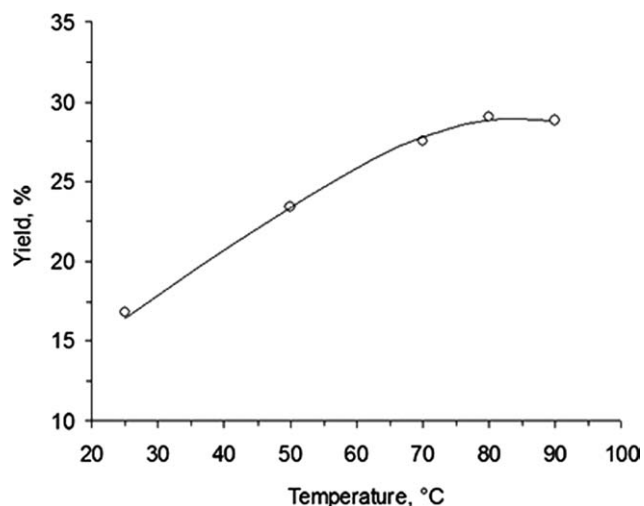
Figure 2. Effect of reaction temperatures on the yield of polymer {time: 3 h and $[3\text{-PHEP}]_0 = [\text{NaOCl}]_0$ = 1.15 mol/L and $[\text{KOH}]_0$ = 1.72 mol/L}.
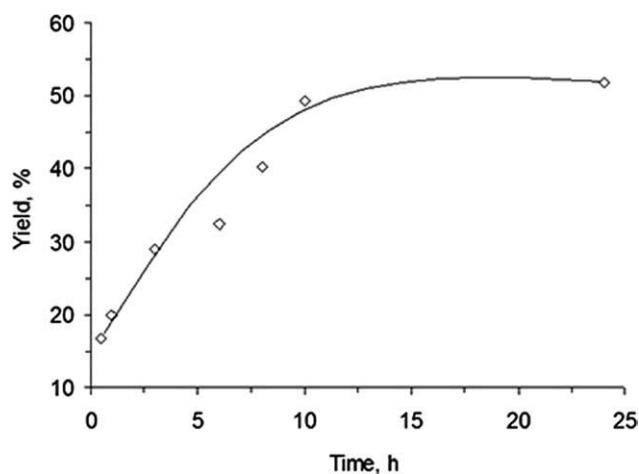
Figure 3. Effect of reaction times on the yield of polymer {temperature: 80°C and $[3\text{-PHEP}]_0 = [\text{NaOCl}]_0 = 1.15$ mol/L, $[\text{KOH}]_0 = 1.72$ mol/L}.

Analytical data for 3-PHEP: Yield: 97%. R_f : 0.42 (SiO$_2$, hexane/ethyl acetate, 3 : 1). mp: 143°C. ^{1}H-NMR (300 MHz, (CD$_3$)$_2$SO, δ, ppm): 9.39 (bs, 1H, OH or NH), 9.23 (s, 1H, NH or OH), 7.37-7.09 (m, 7H, ArH), 6.82-6.66 (m, 2H, ArH), 2.21 (s, 3H, CH_3). FTIR (1/cm): 3358 (O—H), 3199 (N—H), 3040 (C—H aryl), 3000-2800 (C—H aliphatic), 1597 (MeC=N), 1495-1366 (C=C), 1217 (C—O), 1149 (C—N), 1063 (N—N). UV-vis (Methanol) λ_{max} (nm): 240 (shoulder), 295 (shoulder) and 330. Anal. calcd. for C$_{14}$H$_{14}$N$_2$O (%): C,74.31; H, 6.24; N, 12.38. Found (%): C, 74.03; H, 6.18; N, 12.45.

The Oxidative Polycondensation of 3-PHEP Using NaOCl
The compound 3-PHEP (0.56 g, 2.5 mmol) was dissolved in an aqueous solution of KOH (0.14 g, 2.5 mmol, 10%) and placed into a 25-mL three-necked round bottomed flask that was fitted with a condenser, a thermometer and a stirrer, in addition to a funnel containing NaOCl. After heating to the appropriate temperature, NaOCl was added as dropwise for $\sim$ 30 min. The reaction mixture was stirred under different conditions (Figures 1–3). At the end of the reaction, the mixture was neutralized with HCl (1.0 M, 0.5 mL) at room temperature. The mixture was filtered and washed with hot water (25 mL, three times), and the removal of mineral salts was confirmed using an AgNO$_3$ solution. Then, unreacted 3-PHEP was separated from the reaction products by washing with diethyl ether/hexane mixture (25 mL, v/v, 3 : 2). The polymeric product was dried in an oven at 105°C (0.35 g, yield 62%) (Scheme 2).

Analytical data for poly(3-PHEP): Yield: 62%. R_f: 0 (SiO$_2$, hexane/ethyl acetate, 3 : 1) and R_f: 0.47 (SiO$_2$, methanol). ^{1}H-NMR (400 MHz, (CD$_3$)$_2$SO, δ, ppm): 10.71–8.92 (s, 1 H, OH or
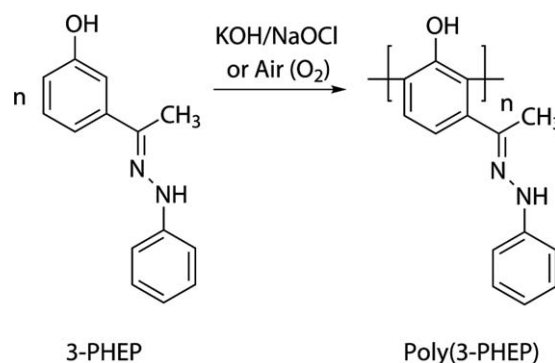
Scheme 2. Synthesis of poly[3-(1-(2-phenylhydrazono)ethyl)phenol].

NH), 8.50-5.91 (m, 8H, ArH and NH or OH), 2.48 (s, 3H, CH_3). FTIR (1/cm): 3400 (O—H), 3194 (N—H), 1596 (MeC=N), 1494–1360 (C=C), 1225 (C—O), 1065 (N—N). UV-vis (Methanol) λ_{max} (nm): 241 (shoulder), 300 (shoulder) and 332 (shoulder). Anal. calcd. for C$_{14}$H$_{12}$N$_2$O (%): C,75.56; H, 7.13; N, 11.01. Found (%): C, 74.91; H, 7.02; N, 10.87.

The Oxidative Polycondensation of 3-PHEP using air (O$_2$)
The compound 3-PHEP (0.56 g, 2.5 mmol) was dissolved in an aqueous solution of KOH (0.14 g, 2.5 mmol, 10%) and placed into a 25-mL three-necked round-bottomed flask that was fitted with a condenser, a thermometer, a stirrer, and a glass tubing condenser for sending air. To prevent water loss in the reaction mixture and to neutralize the CO$_2$ in the air to KOH, air oxygen was passed through 200 mL of an aqueous solution of KOH (30%) before passing through the reaction mixture. After heating to appropriate temperature, air oxygen was bubbled through the reaction mixture at a rate ranging from 0.25 to 1 L/h. At the end of the reaction, the mixture was cooled to room temperature and neutralized with HCl (1.0 M, 0.5 mL), and the solid product was filtered and washed with hot water (25 mL, three times), and the removal of mineral salts was confirmed using an AgNO$_3$ solution. Then, unreacted 3-PHEP was separated from the reaction products by washing with diethyl ether/hexane mixture (25 mL, v/v, 3 : 2). The polymeric product was dried in an oven at 105°C (0.07 g, yield 12%) (Scheme 2).

RESULTS AND DISCUSSION

The Investigation of Synthesis Conditions of Poly(3-PHEP)
The brown solid powder poly(3-PHEP) was synthesized from the oxidative polymerization of 3-PHEP with NaOCl and air (O$_2$) as oxidants in aqueous alkaline medium at various reaction conditions. But, hydrogen peroxide did not afford to the polymerization reaction. The effect of various parameters such as initial concentrations of KOH and NaOCl, reaction time and reaction

Table I. The Solubility of 3-PHEP and Poly(3-PHEP)

Compounds	Diethyl ether	CH$_2$Cl$_2$	Ethanol	Methanol	n-Hexane	Ethyl acetate	DMF	DMSO	CHCl$_3$	THF	KOH$_{(aq)}$	conc. H$_2$SO$_4$
3-PHEP	+	+	+	+	±	+	+	+	+	+	+	+
Poly(3-PHEP)	−	±	+	+	−	±	+	+	±	+	+	+

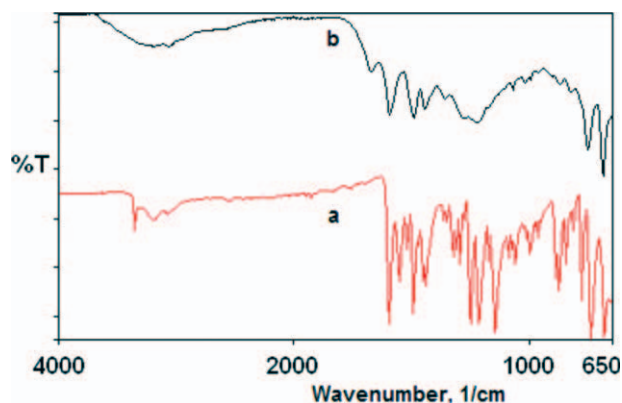Symbols: +, soluble; ± , partly soluble; and −, insoluble.
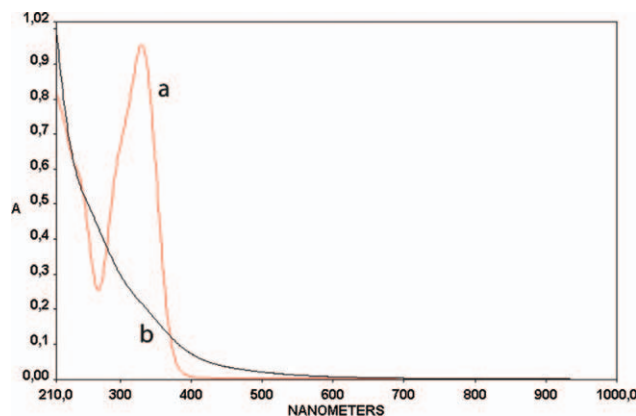
Figure 4. UV spectra of 3-PHEP (a) and poly(3-PHEP) (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature on the yield of oxidative polycondensation product were examined. The data were summarized in Figures 1–3.

According to Figure 1, the yield of the product firstly increased with an increase in reaction conditions, and then decreased. The reason of the decrease may be the conversion from polymer to monomer at higher reaction conditions. The yield of oxidative polycondensation products from 3-PHEP was 62% under the optimum reaction conditions: $[3\text{-PHEP}]_0 = 1.15$ mol/L, $[\text{KOH}]_0 = 1.72$ mol/L and $[\text{NaOCl}]_0 = 2.3$ mol/L at 80°C for 24 h. When air oxygen was used as an oxidant, the yield of oxidative polycondensation product of 3-PHEP was 12% under optimum reaction conditions; $[3\text{-PHEP}]_0 = 1.15$ mol/L, $[\text{KOH}]_0 = 1.72$ mol/L, flow rate of air oxygen = 1 L/h at 80°C for 24 h. From the comparison of the data above, NaOCl was observed to be more active than air (O_2). Consequently, the yield of the polymer was dependent upon temperature, time, the initial concentrations, and type of oxidant.

The solubility tests were performed with 1 mg sample and 1 mL solvent at 25°C. The compounds 3-PHEP and poly(3-PHEP) were stable at room temperature. Table I shows the solubility of 3-PHEP and poly(3-PHEP). Both compounds were
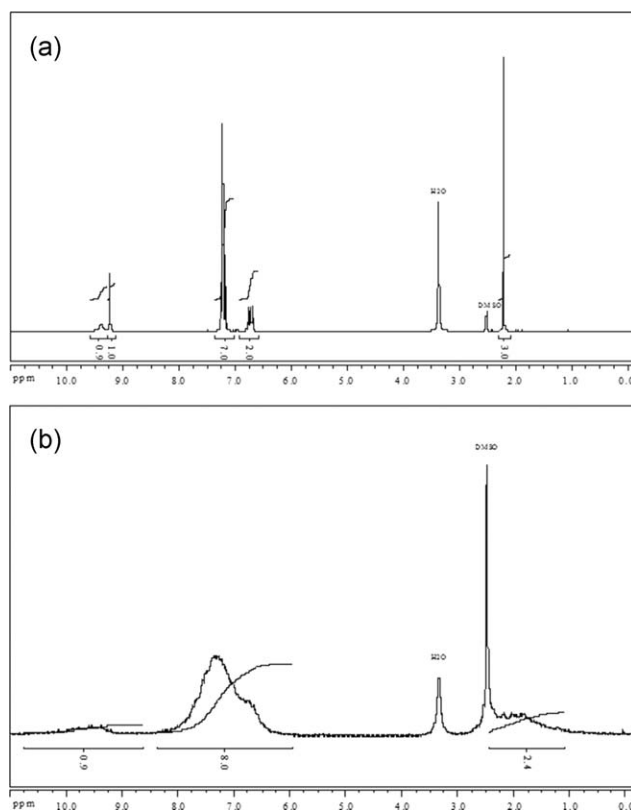
soluble in polar organic solvents, but poly(3-PHEP) was not soluble in diethyl ether and *n*-hexane.

Structures of 3-PHEP and Poly(3-PHEP)

The electronic absorption spectral data for 3-PHEP and poly(3-PHEP) were obtained in methanol at room temperature and reported in the Experimental section. Figure 4 shows the UV-visible absorption spectra of 3-PHEP and poly(3-PHEP). The UV–vis spectrum of monomer revealed three bands centered at 240 (shoulder), 295 (shoulder)and 330 nm which are attributed to $\pi \rightarrow \pi^*$ transition of benzene ─C═C─ and azomethine ─C═N─, n$\rightarrow \pi^*$ transition of phenolic ─OH and n$\rightarrow \pi^*$ transition of azomethine ─C═N─ groups, respectively. The spectra of 3-PHEP and poly(3-PHEP) were similar to each other. The UV–vis spectrum of polymer revealed three bands centered at 241 (shoulder), 300 (shoulder) and 332 (shoulder) nm which are attributed to $\pi \rightarrow \pi^*$ transition of benzene ─C═C─ and azomethine ─C═N─, n$\rightarrow \pi^*$ transition of phenolic −OH and n$\rightarrow \pi^*$ transition of azomethine ─C═N─ groups, respectively. Also, the shifting until 930 nm was observed in the poly(3-PHEP) spectrum, which was attributed to an increase in conjugation due to coupling between aromatic rings.

Comparing the FTIR spectra of 3-PHEP and poly(3-PHEP), the only difference observed was in the reduction of band strength and peak numbers from the FTIR spectrum of 3-PHEP (Figure 5). The peak at 1597 1/cm is assigned to the characteristic absorption of C═N vibration. The bands at 650-900 1/cm correspond to different substitution. In the FTIR spectrum of 3-PHEP,

Figure 6. ^{1}H-NMR spectra of 3-PHEP (a) and poly(3-PHEP) (b).

Figure 5. FTIR spectra of 3-PHEP (a) and poly(3-PHEP) (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Comparisons of M_n, M_w, and PDI Values of *m*-substituted Polyphenols

Polymers	M_n (g/mol)	M_w (g/mol)	PDI	Literature
O-B-3′-HA	2640	5130	1.942	[7]
O-3HBA	3600	8000	2.22	[16]
Poly(3-PHEP)	6500	8300	1.277	This work

the peaks at 780 and 880 1/cm show the presence of three adjacent aromatic hydrogen atoms and isolated hydrogen atom of the phenyl ring, respectively. In the case of poly(3-PHEP), the peaks at 780 and 880 1/cm disappeared after polycondensation. Also, FTIR spectrum of poly(3-PHEP) showed a new broad absorption band at 830 1/cm, this band, being most intense and characteristic of two adjacent aromatic hydrogen atoms, is located in 4- and 5- positions of the phenyl ring appears.[32,33] The small peak at 1672 1/cm is attributed to the carbonyl (C=O) stretching vibration, which may be formed by oxidation of the ketimine groups at the polymer pendent groups.[4,6] Since no additional peaks at 1100–1250 1/cm for C—O—C linkages were observed in the FTIR spectrum of polymer, it seems obvious that poly(3-PHEP) consists of phenylene units, which was in concordance with the reported value in the literatures.[7,34]

To identify the structures of the monomer and polymer, the ^{1}H-NMR spectra were recorded in (CD$_3$)$_2$SO. The ^{1}H-NMR spectra of the 3-PHEP and poly(3-PHEP) are given in Figure 6. The singlet signals of CH_3 and NH groups in ^{1}H-NMR spectrum of 3-PHEP were observed at 2.21 ppm and 9.23 or 9.39 ppm, respectively. The singlet signal of −OH group appeared at

9.39 or 9.23 ppm. The ^{1}H-NMR and FTIR spectra of poly(3-PHEP) confirmed the formation of polymer units. In the NMR spectrum of poly(3-PHEP), the signals are shown broadly. This situation is one of the proofs of polymerization. The wide singlet signal 10.71–8.92 ppm range and multiplets in the 8.50–5.91 ppm range can be attributed to the OH or NH group and, ArH—NH or ArH—OH groups, respectively. Poly(3-PHEP) exhibits wide singlet signal at 2.48 ppm which is attributed to the CH_3 group. In addition, at 3.33 ppm there is a signal which is originating from absorbed H$_2$O.[35]

According to SEC analysis, M_n, M_w, and PDI values of the polycondensation product of 3-PHEP were found to be 6500 g/mol, 8300 g/mol and 1.277, respectively. These results show that poly(3-PHEP) has the higher M_n and M_w values than the other *m*-substituted polyphenols such as O-B-3′-HA and O-3HBA (Table II).

These studies investigating polymer structure and kinetics of the process, taken together with data from the literature[36,37] suggest the following mechanism of 3-PHEP oxidative polycondensation in an alkaline medium: Scheme 3(a). The resonance forms of the intermediate radicals obtained undergo a recombination followed by enolization of dimmers: Scheme 3(b).

The recombination of radicals II and II and of II and III similarly yields the following structures: Scheme 3(c). Then, the dimers, trimers, etc., are likewise oxidized. The process-limiting step is the electron transfer from the monomer anion to the oxidant.

Analytical data of the compounds were presented in experimental section. The results from elemental analyses of the two compounds were in agreement with the theoretical calculations. The
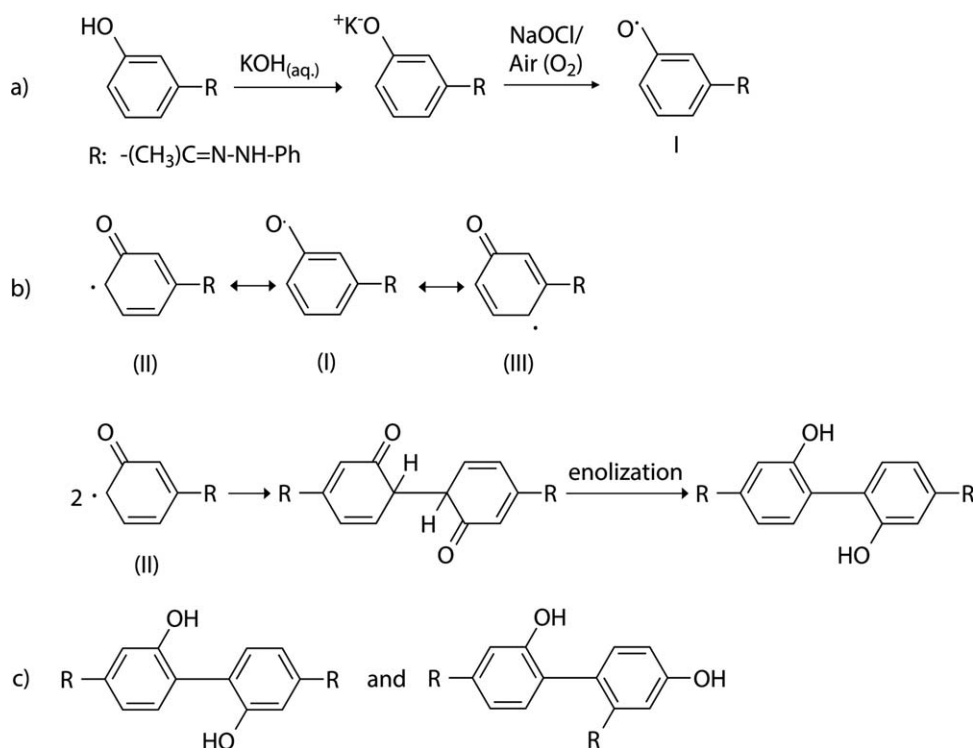
Scheme 3. Proposed mechanism for the formation of poly(3-PHEP).
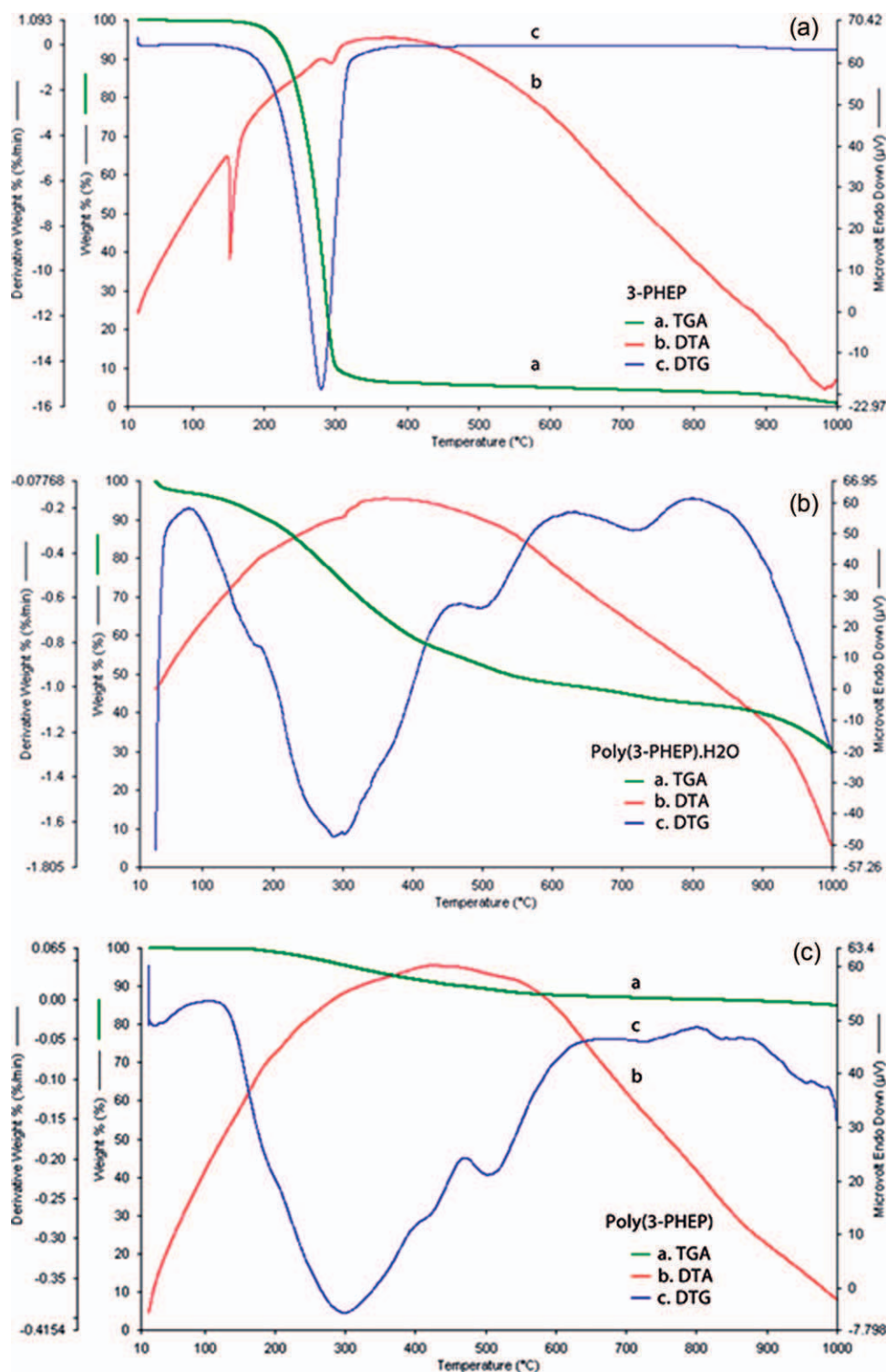
Figure 7. TGA-DTA-DTG curves of 3-PHEP (a), poly(3-PHEP).H$_2$O (b) and poly(3-PHEP) (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

analytical and spectroscopic data enabled us to predict possible structure of the compounds, as shown in Figures 4–6. On the basis of the elemental analyses and spectroscopic characterization, these compounds were presumed to have the structures shown in Scheme 2.

Thermal Properties

The thermal degradations of synthesized compounds were studied with thermal analyses in the medium N$_2$. The TGA-DTA-DTG curves of monomer and polymer were given in Figure 7. In addition, the obtained data were summarized in Table III.

Table III. Thermal Decomposition Values of the Monomer and Its Polymers

Compounds	$T_{initial}$ (°C)	5% Mass loss (°C)	50% Mass loss (°C)	Carb. Res. (%) at 1000°C
3-PHEP	156	220	276	0.7
Poly(3-PHEP). H₂O	100	146	550	31.5
Poly(3-PHEP)	176	314	>1000	83.7

Abbreviations: Carb. Res., carbon residue.

TGA-DTA-DTG curves which were obtained by drying 3-PHEP and poly(3-PHEP) in an oven are presented in Figure 7(a,b), respectively. The presence of absorbed water molecules[38,39] at the rate of 3.0% in the structure of polymer can be seen in TGA curve in Figure 7(b). With the aim of removing these water molecules in the structure of poly(3-PHEP).H₂O was dried for five days at 105°C in vacuum drying-oven and its thermal measurements were carried out again [Figure 7(c)]. As can be seen on obtained curves, along with the removal of absorbed water molecules, it was observed that thermal stability of the polymer increased surprisingly. It was observed clearly from the obtained curves that the absorbed water molecules in polymeric structure accelerated thermal degradation of the polymer and affected thermal stability of the polymer. As seen in Figure 7(c), poly(3-PHEP) lost only 16.3% of its mass at 1000°C by showing high thermal stability. This situation may be stemming from that polymer has longer conjugated bond systems in comparison with the monomer. The high thermal stability of poly(3-PHEP) demonstrated the formation of a C—C coupling system. The loss of mass at the rate of 16.3% corresponds approximately to the sum of masses of —OH ve —CH₃
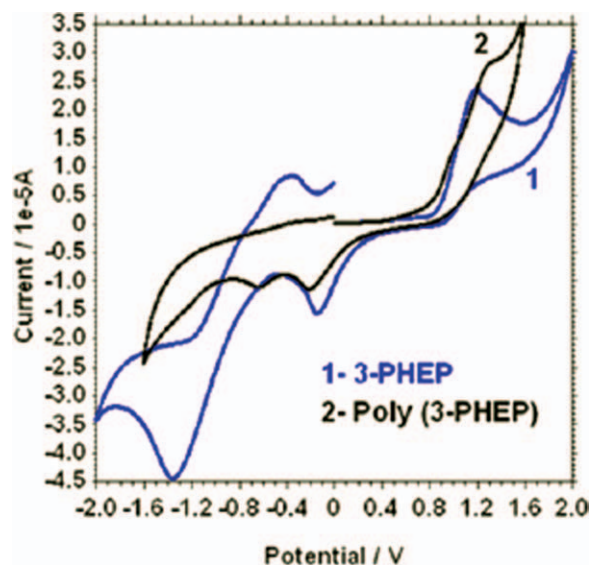
Figure 8. Cyclic voltammograms of the synthesized compounds. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

groups in the polymer structure. When the value of carbon residue at the rate of 83.7% which was obtained for poly(3-PHEP) is compared with the values obtained for *o*-substituted,[6,17–30,37] *m*-substituted[7] and *p*-substituted[8–15,40,41] poly(phenoxy-imine)s in literature, it can be seen that the highest value belongs to poly(3-PHEP). Having this feature, poly(3-PHEP) step forwards in comparison with imine-substituted polyphenols. Additionally, in the DTA curve of the monomer, two endothermic peaks were observed at 143°C, which corresponds to melting point and, the peak at 300°C corresponds to the temperature at which the monomer loses a large amount of its mass [Figure 7(a)]. And in poly(3-PHEP).H₂O, a small endothermic peak is observed at 300°C [Figure 7(b)].

Optical Properties

The absorption edges of the poly(3-PHEP) shifted to higher wavelengths than those of 3-PHEP as a result of increasing conjugation (Figure 4). As expected, polymer had lower optical band gap than the monomer. Optical band gap (E_g) values calculated from absorption edges[42] for 3-PHEP and poly(3-PHEP) were 3.35 and 2.83 eV, respectively.

Electrochemical Properties

Figure 8 shows cyclic voltammograms of 3-PHEP and poly(3-PHEP). The HOMO–LUMO energy levels and the electrochemical band gaps (E_g') were estimated by using the oxidation onset (E_{ox}) and reduction onset (E_{red}) values,[43] as shown below.

$$E_{HOMO} = -(4.39 + E_{ox})$$
$$E_{LUMO} = (4.39 + E_{red})$$
$$E_g' = E_{LUMO} - E_{HOMO}$$

3-PHEP and poly(3-PHEP) were electrochemically active in both oxidation and reduction regions. The electrochemical data of 3-PHEP and poly(3-PHEP) are listed in Table IV. As shown in Figure 8 and Table IV, poly(3-PHEP) has a lower band gap then its monomer. This is because of the polyconjugated structures of the polymers which increase HOMO and decrease LUMO energy levels resulting in lower band gaps. The E_g' value measured for poly(3-PHEP) is rather low when compared to that of other NO,[40] NNO,[41] and N2O2[44] types Schiff base polyphenols. Among these polyphenols, the lowest band gap; i.e, 1.95 eV, was found.[40] The results obtained in this study are compatible with the values in literature. It is well known that lower band gaps facilitate electronic transitions between HOMO and LUMO energy levels and make the polymers more electroconductive than their monomers.

Table IV. Electrochemical Data for the Monomer and Its Polymer

Compounds	E_{ox} (V)	E_{red} (V)	HOMO (eV)	LUMO (eV)	E_g' (eV)
3-PHEP	1.193	−1.363	−5.58	−3.03	2.55
Poly(3-PHEP)	1.309	−0.626	−5.70	−3.76	1.94

Abbreviations: HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; (3-PHEP), 3-(1-(2-phenylhydrazono) ethyl)phenol.

CONCLUSIONS

Polyphenol with ketimine pendent groups, poly(3-PHEP), has been successfully synthesized by oxidative polycondensation for the first time. Thus, a new class of functional polyaromatics, derived from ketimine sustitueted polyphenol has been developed. Reaction temperature, time and initial concentrations of alkaline and NaOCl have great effects on the yield of polymer. Poly(3-PHEP) with reactive ketimine and hydroxyl group is readily soluble in common polar organic solvents such as DMSO, DMF, ethanol, and THF, and hence will have useful applications, such as synthesis of resins, and copolymer. Thermal analysis shows that poly(3-PHEP) has highly thermal stability and graphite material properties. The observed band gaps are sufficiently low to make the polymer promising for photovoltaic applications. Those interesting properties of poly(3-PHEP) will have potentially beneficial applications in various fields such as graphite material and photovoltaic cells.

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