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The oxidative polycondensation of 2-[(4-pyridilmethylene)-imino]phenol by molecular O_2 in alkaline medium: Synthesis and characterization

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Abstract

The polymer of 2-[(4-pyridilmethylene)-imino] phenol (2-PIP) has been formed from the oxidative polycondensation (OP) reaction by using molecular O_2 as the oxidant in an aqueous alkaline medium between 60-90°C. The optimum reaction conditions and the main parameters of the process were determined. The yield of polymer was found as 50.1%. The structures of synthesized monomer and polymer were confirmed by FT-IR, UV-vis, ^{1}H-^{13}C-NMR and elemental analysis. The characterization was made by TGA-DTA, size exclusion chromatography (SEC) and solubility tests. The ^{1}H-^{13}C-NMR data shows that the polymerization proceeded with C-C and C-O-C coupling system of *ortho and para* positions and oxyphenylene according to –OH group of 2-PIP. The molecular weight distribution values of the product were determined from SEC measurement. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of poly-2-[(4-pyridilmethylene)-imino]phenol (poly-2-PIP) were found to be 11350, 12600 g.mol^{-1} and 1.110, respectively. According to thermo gravimetric analysis (TGA), the carbon residues of 2-PIP and poly-2-PIP were found to be 18.17% and 45.10%, respectively, at 1000°C.

Keywords

Molecular oxygen, oxidative polycondensation, 2-[(4-pyridilmethylene)-imino] phenol, polymer-Schiff base

Introduction

The basic properties of polyazomethines (PAM's) are due to the -CH=N linkage in the backbone. Polyazomethines are known as a class of thermally stable polymers and are usually prepared by polycondensation of diamines with dialdehydes. Because of high thermal stability, mechanical, electrical, magnetic, liquid-crystal and nonlinear optical properties, the polyazomethines have been studied widely[1-5]. They are also studied in fundamental researches [6]. Several approaches have been undertaken to improve the processability of polyazomethines by introducing different substituted benzene rings in the main chain [7-8] by using monomers containing certain heterocyclic units such as thiophene [9], pyridine [10], diphenylfluorene [11] and others. Polymers with highly conjugated chains have attracted much attention in the last years and numerous reviews have been published. The polymers which including conjugated bonding and active hydroxyl (-OH) and azomethine (-CH=N) groups have been studied [12]. These type polymers have been used in various fields because of useful properties such as paramagnetizm, semi conductivity, electrochemical cell and optic material [13, 14]. Because of these properties, they are used to prepare of composites having high resistance at high temperature, thermo-stabilizations, graphite materials, epoxy oligomer and block copolymers, photo resists, materials which are antistatic and enduring to flame [15-18]. By adding of other functional groups to these compounds, they can be profited new useful properties. Schiff base polymers had been demonstrated anti-microbial activities against various bacteria, yeast and fungus [19, 21]. Imines polymers which have a lot of functionality groups may be used for cleaning of poisonous heavy metals in the industrial waste waters. Therefore, the synthesis of oligomer-metal complexes is very important at analytic and environmental chemistry. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals and therefore there are a large range of applications. Kaya et al. studied thermal degradation of oligo-2-[(4-hydroxyphenyl) imino methyl]-1-naphtol and some of its oligomer-metal complexes [22]. In the oxidative polymerization of phenol and phenol derivatives, it is known that the two types of the linkage between the monomer units, the C-C and C-O-C bonds, can be formed during the polymerization. The reaction mechanism on the coupling selectivity has been studied by Ayyagari et al. [23] and Kaya et al. [24] and three possible reaction mechanisms for the C-C and C-O-C coupling systems had been proposed literatures. The oxidative polycondensation method is simply the reaction of compounds including –OH groups and/or active functional groups (–NH_2, –CHO, –COOH) in their structures with the oxidants like NaOCl, H_2O_2 and air oxygen in the aqueous alkaline medium.

In this paper, we have investigated the effects of different parameters such as temperature, times, flow rate of molecular O_2 and initial concentration of 2-[(4-pyridilmethylene)-imino] phenol on the preparation of poly-2-[(4-pyridilmethylene)-imino] phenol and then we determined the optimum reaction conditions for yield of poly-2-PIP. Synthesized 2-PIP and poly-2-PIP were characterized by using FT-IR, UV-vis, ^{1}H-^{13}C-NMR, elemental analysis, TG-DTG and SEC techniques.

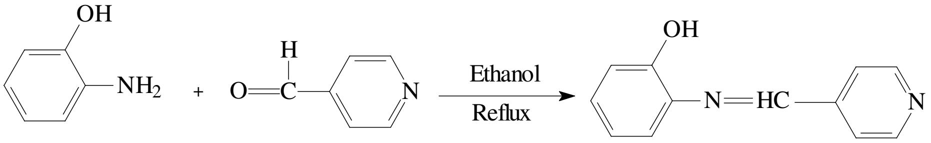
Materials and Methods

Materials

2-aminophenol, 4-pyridinecarbaldehyde, KOH, H_2SO_4 HCl (37%), ethyl acetate, ethanol, DMF, THF, DMSO, methanol, acetone, chloroform, toluene and hexane were supplied from Merck (Germany) and were used as received. Molecular oxygen was supplied from Muher (Turkey). 2-[(4-pyridilmethylene)-imino] phenol was synthesized from condensation reaction of 4-pyridinecarbaldehyde with 2-aminophenol and product recrystallized from ethanol again.

Preparation of 2-PIP

2-[(4-pyridilmethylene)-imino] phenol was prepared by the condensation of 4-pyridinecarbaldehyde (1.0711 g, 0.01 mol) with 2-aminophenol (1.0913 g, 0.01 mol) in ethanol (25 ml) achieved by boiling the mixture under reflux for 5h at 70°C (Scheme1). The precipitated product was filtered, recrystallized from ethanol and dried in vacuum desiccators (m.p.: 193°C, yield, 89%).

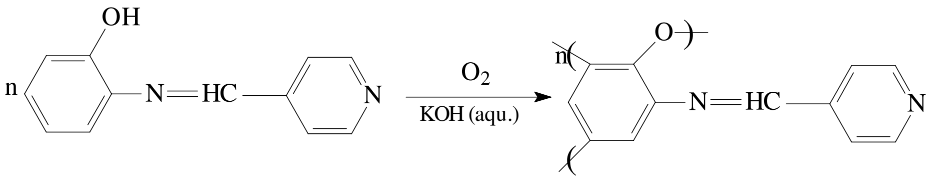


Scheme 1

Calcd. for (%) 2-PIP: C, 72.72; N, 14.14; H, 5.05. Found (%): C, 72.53; N, 14.25; H, 5.13. UV-vis (λ_{max}): 237, 255, 280 and 365 nm. FT-IR (KBr, cm^{-1}); v (O-H) 3381, v (C-H aryl) 3053, v (CH=N) 1600, v (C-O) 1217, v (aromatic C=C) 1504, 1417, v (aromatic -C=N) 1159. ^{1}H-NMR (DMSO): δ ppm, 9.24 (s, 1H, OH); 8.79(s, 1H, CH=N); 6.85 (d, 1H, Ar-Ha); 7.15 (t, 1H, Ar-Hb); 6.95 (t, 1H, Ar-Hc); 7.29 (d, 1H, Ar-Hd); 7.96 (d, 2H, Ar-Hee'); 8.74 (d, 2H, Ar-Hff'). ^{13}C-NMR (DMSO):δ ppm, 152.14 (C1-ipso-OH); 116.87 (C2-H); 129.03 (C3-H); 122.84 (C4-H); 119.91(C5-H); 137.32 (C6-ipso-N=); 157.82 (C7-N=); 143.36 (C8-ipso); 119.99 (C9, 12-H); 150.74 (C10, 11-H).

The OP of 2-[(4-pyridilmethylene)-imino]phenol using molecular oxygen

2-PIP (0.9912 g, 0.005 mol) was dissolved in an aqueous solution of KOH (10%, 0.005 mol) and placed into a 50 ml three-necked round-bottom flask, fitted with a condenser and a thermometer in addition to a glass tubing over the condenser for sending molecular O_2. The molecular O_2 was bubbled through the reaction medium at the rates of between 0.6 and 3.6 L h^{-1} after the reaction mixture was heated at the various temperatures (Figs.1-3). The mixture was neutralized using 0.410 ml HCl (37%) at the end of the reaction at room temperature. It was filtered, washed with hot distilled water (3 x 25 ml) for separating from mineral salts. The unreacted 2-PIP was removed by extraction with methanol than polymer products (Scheme 2). The polymer was dried in the oven at 105°C.



Scheme 2

Calcd. for (%) poly-2-PIP: C, 73.47; N, 14.28; H, 4.08. Found (%): C, 71.70; N, 13.45; H, 4.84. UV-vis (λ_{max}): 254, 295, 346 and 415 nm. FT-IR (KBr, cm^{-1}): ν (O-H) 3400, ν (C-H aryl) 3070, ν (C-H aliphatic) 2999, 2881, ν (CH=N) 1615, ν (C-O) 1268, ν (aromatic C=C) 1523-1421, ν (aromatic C=N) 1165. ^{1}H-NMR (DMSO): δ ppm, 10.03 (s, 1H, OH); 9.64 (s, 1H, CH=N); 6.86-7.75 (m, 1H, Ar-Hb and 2H, Ar-Hee'); 8.68 (s, 1H, Ar-Hd); 8.38 (d, 2H, Ar-Hff'). ^{13}C-NMR (DMSO):δ ppm, 155.10(C1-ipso-OH); 131.03 (C2-ipso); 124.84 (C3-H); 133.15 (C4-ipso); 127.32(C5-H); 138.23 (C6-ipso-N=); 160.01 (C7-N=); 144.63 (C8-ipso); 122.57 (C9, 12-H); 149.27 (C10, 11-H).

Solubility and Characterization Techniques

2-PIP was soluble in DMF, THF, DMSO, ethanol, methanol, acetone, ethyl acetate, hexane, chloroform and KOH (aqu.). It was partly soluble in toluene. Poly-2-PIP was soluble in DMF, THF, DMSO and KOH (aqu.). However, poly-2-PIP was insoluble ethanol, methanol, acetone, ethyl acetate, hexane, chloroform and toluene. FT-IR spectra of 2-PIP and poly-2-PIP were taken by MATTSON 1000 FT-IR using KBr disc (4000-400 cm^{-1}) and UV-visible spectra were recorded by SHIMADZU UV-1700 in methanol and THF solvent, respectively. Elemental analysis was carried out with a LECO CHNS 932. ^{1}H-NMR and ^{13}C-NMR spectra (Bruker DPX FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) were recorded at 25°C using DMSO-d_6 as a solvent. Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. TG-DTG measurements were made between 20-1000°C (in N_2, heating 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) of SHIMADZU. For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 7.7 mm i.d.x 300 mm columns was used; eluent: DMF/Methanol (4/1 v/v; 0.4 ml min^{-1}), polystyrene standards. A refractive index detector (at 25°C) was used to analyze the product.

Results and Discussion

The investigation of synthesis conditions of Poly-2-PIP

The effects of parameters such as temperature, reaction duration, flow rate of molecular O_2 and initial concentration of alkaline were investigated for 2-PIP polymerization. The 2-PIP was not oxidized in organic solvent medium by molecular O_2, but it was oxidized with sending of molecular O_2 to reaction mixture in alkaline medium. The OP reaction of 2-PIP was examined in an aqueous alkaline solution. The color of solution turned into brown by sending molecular O_2. The yield of poly-2-PIP was 20.6% at the polymerization conditions of $[\text{2-PIP}]_0=[\text{KOH}]_0=0.34$ mol/L and $[O_2]_0=0.1$ L/h at 80°C for 2h. The yield of poly-2-PIP was affected by increasing of the flow rate of O_2. The yield of poly-2-PIP increased from 20.6% to 46.6%, when flow rate of molecular O_2 increased from 0.1 L/h to 3.6 L/h and than level off. Also, the yield of poly-2-PIP was affected by increasing of initial concentration of 2-PIP. The conditions of OP reaction of 2-PIP with molecular O_2 in aqueous alkaline medium are given in Figs.1, 2 and 3. The yield of poly-2-PIP was 50.1% at the reaction conditions such as $[2\text{-PIP}]_0=[KOH]_0=0.34$ mol/L and $O_2=1.2$ L/h, at 90°C for 4 h. The polymerization of 2-PIP under the mentioned conditions is influenced, as expected, by the effected temperatures, initial concentration of 2-PIP and times and flow rates of O_2 (see Figs. 1-3). As seen in the Figures.1-3, the effects of the reaction times and temperatures on the yield of poly-2-PIP were investigated.

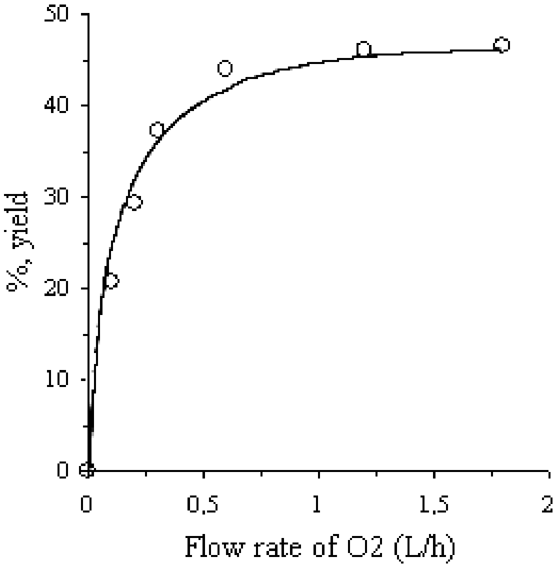


Figure 1. According to flow rate of molecular O_2, change of % yield of poly-2-PIP {Temp.: 80°C, Time: 2 h and [2-PIP]: 0.34 mol/L}

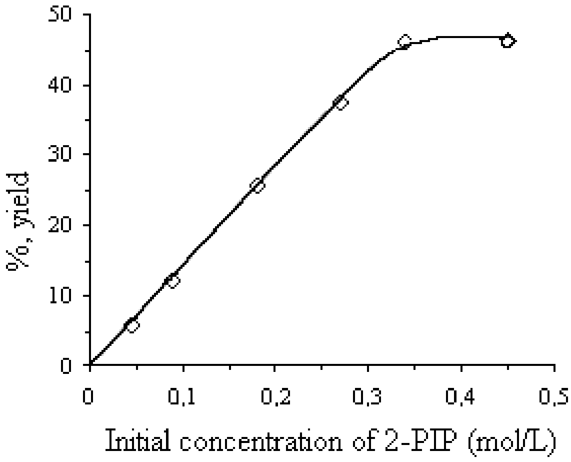


Figure 2. According to initial concentration of 2-PIP, change of % yield of poly-2-PIP [Temp.: 80°C, Time: 2 h and O_2: 1.2 L/h]

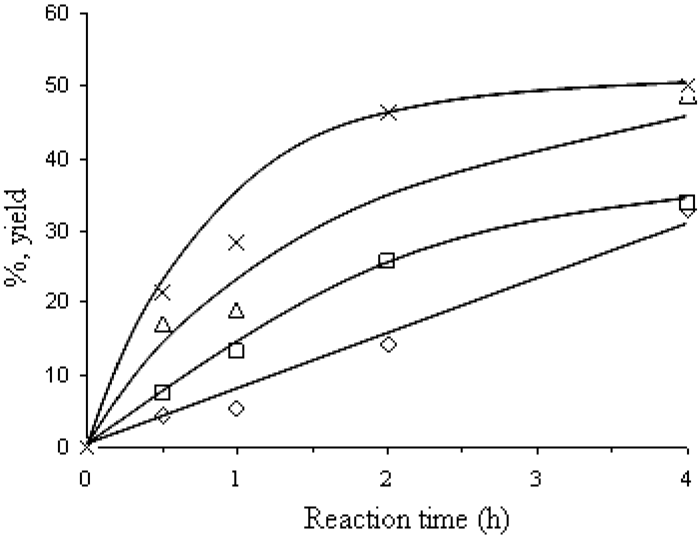


Figure 3. Change of % yield of poly-2-PIP, according to temperature and times {[2-PIP]: 0.34 mol/L and O_2: 1.2 L/h and [x: 90 °C, Δ: 80 °C, □:70 °C, ◊: 60 °C]}

Molecular weight distribution of poly-2-PIP

A sample size exclusion chromatogram of poly-2-PIP obtained at the polymerization conditions of 1.2 $L.h^{-1}$ O_2 {Temp. (°C): 90, Time: 4 h, $[2\text{-PIP}]_0=[KOH]_0$= 0.34 mol/L} is given in Fig.4. The M_n, M_w and PDI values of poly-2-PIP were found to be 11350,

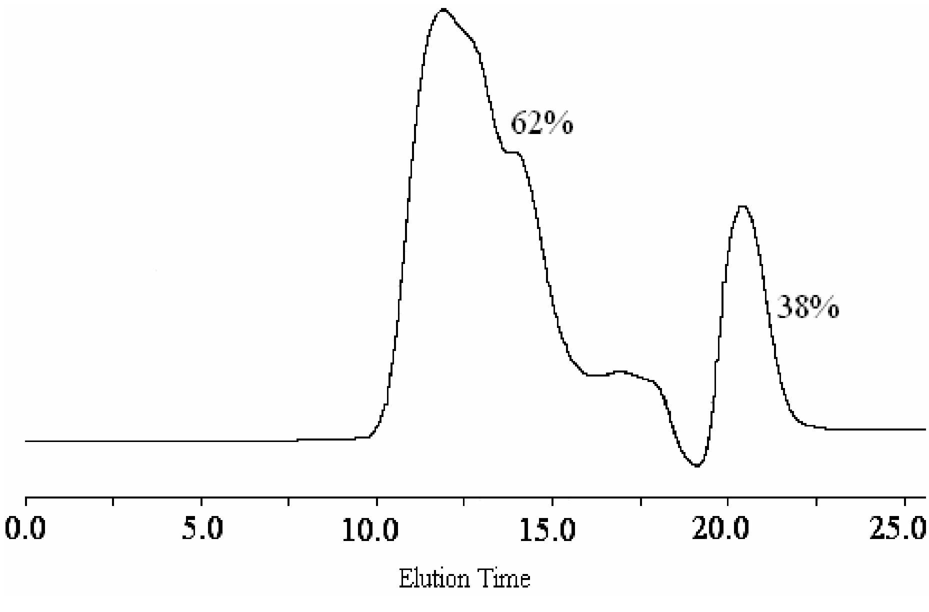


Figure 4. The chromatographic curve of the OP product of 2-PIP. {Temp. (°C): 80, Time: 1 h, $[2\text{-PIP}]_0=[KOH]_0$= 0.34 mol/L and O_2: 1.2 L/h}

12600 g mol^{-1} and 1.110, respectively. Two peaks were observed in the chromatogram of poly-2-PIP. 38 % of the mass of poly-2-PIP was low molecular weight (M_n =2000, M_w =2300 g mol^{-1}, PDI=1.150) but 62% of its weight was high molecular weight (M_n =35400, M_w =39300 g mol^{-1}, PDI=1.110).

The effects of some parameters such as temperature, time and NaOCl, H_2O_2 and air O_2 oxidants on the molecular weight distribution had been examined for oligo-4-[(phenylimino) methyl] phenol and change of these values had been observed connecting with these parameters [25].

UV-vis, FT-IR and ^{1}H- ^{13}C-NMR spectra of 2-PIP and poly-2-PIP

The electronic spectra of 2-PIP and poly-2-PIP were recorded in methanol and THF, respectively. On the UV-vis spectra of 2-PIP, the bands were observed in 237, 255, 280 and 365 nm. K band belongs to –OH and azomethine groups of 2-PIP were observed in 255 and 280 nm, respectively. B and R bands of 2-PIP were observed in 237 and 365 nm. R band of CH=N group of 2-PIP was observed in 365 nm. On the UV-vis spectra of poly-2-PIP, the same bands were observed in 254, 295, 346 and 415 nm. K bands belong to –OH and azomethine groups of poly-2-PIP were observed in 254 and 295 nm, respectively. R band of CH=N group of poly-2-PIP was observed in 415 nm. The UV-vis spectra shows specific bands for λ_{max} assigned to aromatic and azomethinic π-π^* transitions at about 280 and 350 nm, respectively, [26]. The shifting of the –CH=N– group band from 365 nm to 415 nm has been demonstrated to the formation of the oligomeric conjuge π system.

At the FT-IR spectrum of 2-PIP, the characteristic peaks of the functional groups were observed: Phenyl-OH group at 3381 cm^{-1}, aromatic –CH groups at 3053 cm^{-1}, azomethine (-CH=N) group at 1600 cm^{-1} and –C=C double bonds at 1504, 1417 cm^{-1}. At the FT-IR spectrum of poly-2-PIP, the characteristic peaks of the functional groups were observed: Phenyl-OH group at 3400 cm^{-1}, aromatic –CH groups at 3070 cm^{-1}, azomethine (-CH=N) group at 1615 cm^{-1} and –C=C double bonds at 1523, 1421 cm^{-1}. In order to identify the structures of 2-PIP and poly-2-PIP, the ^{1}H-^{13}C-NMR spectra were recorded by DMSO-d_6 as a solvent. The ^{13}C-NMR spectra of the 2-PIP and poly-2-PIP are given in Fig. 5. At the ^{1}H-NMR spectra (Fig.6 and 7) of 2-PIP and

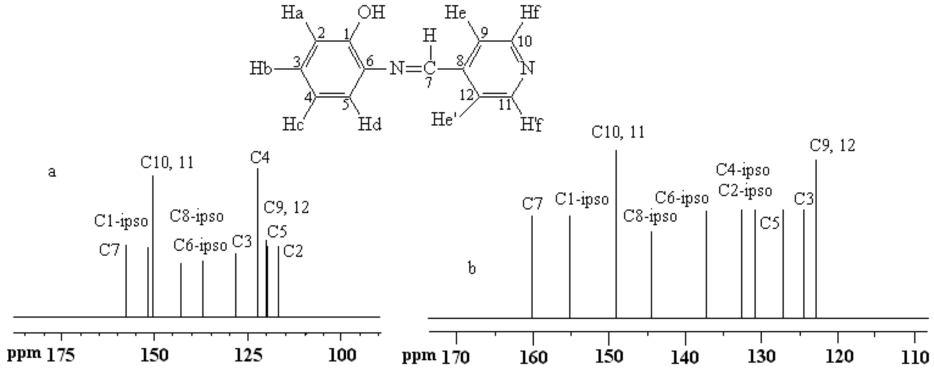


Figure 5. ^{13}C-NMR spectra of 2-PIP (a) and poly-2-PIP (b) {Temp. (°C): 80, Time: 1 h, $[2\text{-PIP}]_0=[KOH]_0$= 0.34 mol/L and O_2: 1.2 L/h}

poly-2-PIP, the characteristic peaks of -OH and -CH=N functional groups were observed in 9.24 and 8.79 ppm and 10.03 and 9.64 ppm, respectively. According to ^{13}C-NMR, the peak values for C2 and C4 observed in 116.87 and 122.84 ppm in the monomer and 131.03 and 133.15 ppm in the polymer, respectively. These values are in agreement with the theoretically calculated peak position for *ortho* and *para* linkages on the ring. The oxyphenylene are involved in the formation of free radicals leading to polymer formation and they appeared to be involved in bond formation. Thus the phenyl rings in the polymer appears to be linked primarily at *ortho* and *para* positions and oxyphenylene. The ^{1}H-^{13}C-NMR results showed that the polymerization of 2-PIP proceeded by C-C and C-O-C coupling from *ortho* and *para* positions according to –OH group and oxyphenylene, respectively [23]. According to spectral analyses, a segment of poly-2-PIP chain can be formulated as follows (Scheme 3): Ar–O*H* and Ar–C*H*=N protons of oligo-4-[(2-hydroxybenzylidene)amino]benzoic acid has resonated at δ = 10.74 (singlet) and δ = 10.27 (singlet), respectively, [24].

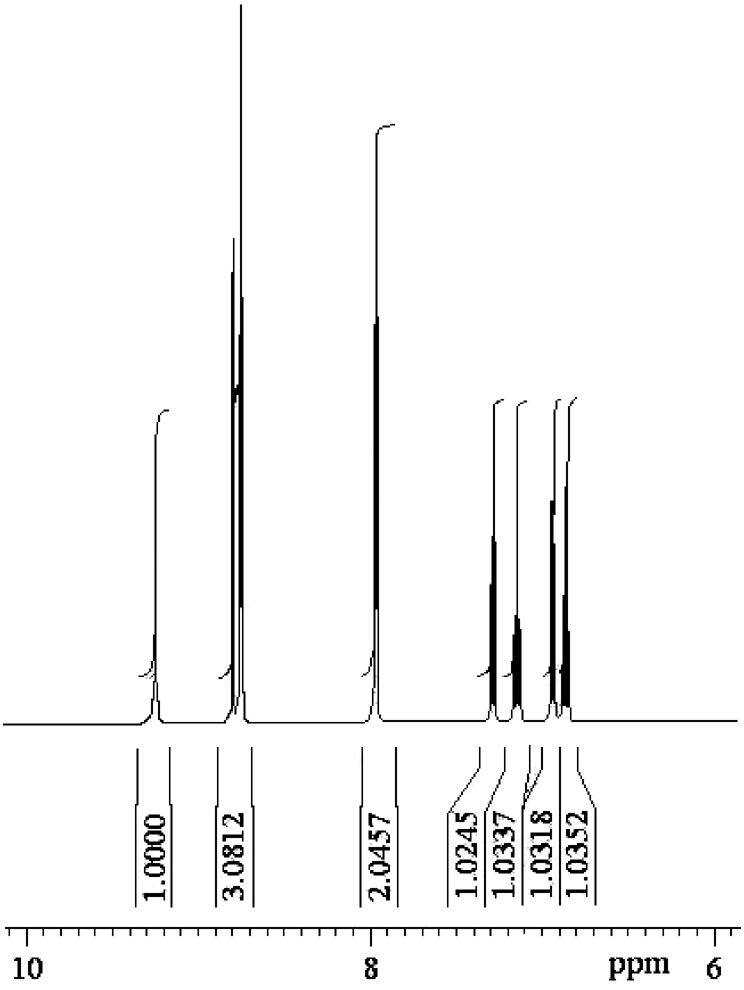


Figure 6. ^{1}H-NMR spectra of 2-PIP

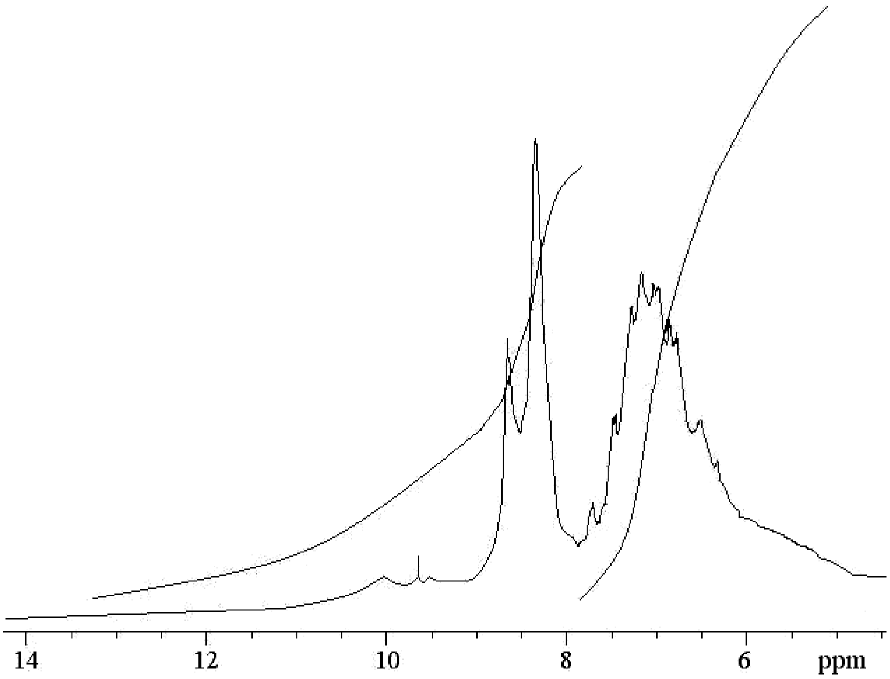
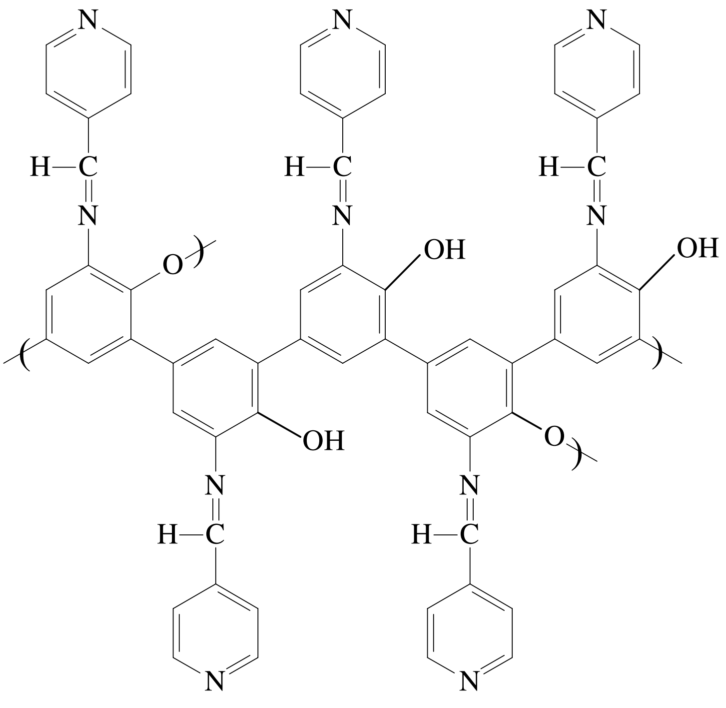


Figure 7. ^{1}H-NMR spectra of poly-2-PIP {Temp. (°C): 80, Time: 1 h, $[2\text{-PIP}]_0=[\text{KOH}]_0=0.34$ mol/L and O_2: 1.2 L/h}



Scheme 3. The structure of poly-2-PIP

Thermal analyses of 2-PIP and poly-2-PIP

TG-DTG curves of 2-PIP and poly-2-PIP were measured under an N_2 atmosphere in the temperature ranges of 20-1000°C, to investigate thermal stability. Figure 8 and 9 shows the TG-DTG tracing for the 2-PIP and poly-2-PIP. The 2-PIP was broken up to the high rate between 270-600°C. The respective weight loss of 2-PIP was found 81.83% at 1000°C. 50% weight losses of 2-PIP and poly-2-PIP were observed in 364°C and 571°C, respectively. The initial degradation temperature of 2-PIP and poly-2-PIP was found to be 152 and 231°C, respectively. The TG data indicate that the 2-PIP decomposed at lower temperature than poly-2-PIP. According to DTG curve, T_{max} values of 2-PIP were observed in 158, 271, 330 and 422°C. The poly-2-PIP was broken up to the high rate between 150-650°C. The respective weight loss of poly-2-PIP was found 54.90% at 1000°C. According to DTG curve, T_{max} values of

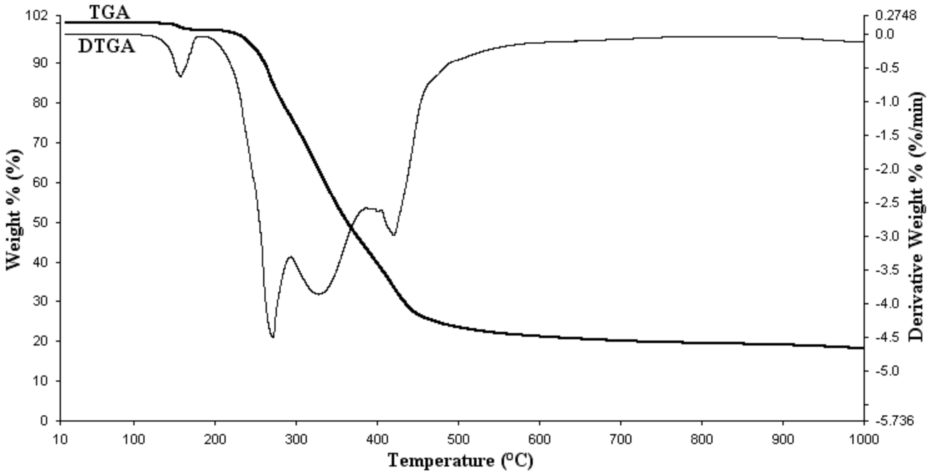


Figure 8. TG-DTG curves of 2-PIP

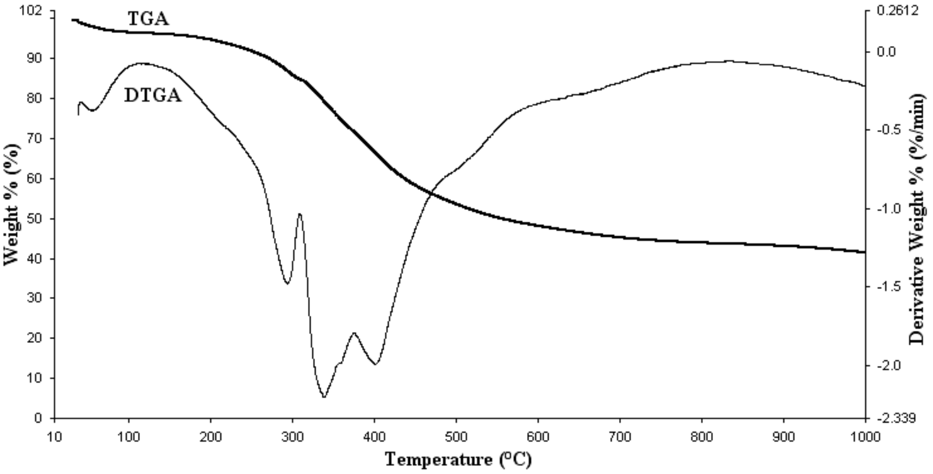


Figure 9. TG-DTG curves of poly-2-PIP{Temp. (°C): 80, Time: 1 h, $[2\text{-PIP}]_0=[KOH]_0=0.34$ mol/L and O_2: 1.2 L/h}

poly-2-PIP were observed in 294, 339 and 402°C. The water presence is also seen in TG curves of polymer compound (Figure 9) which appeared until 3.61% wt losses in the 50-125°C range and required water removal [22, 26].

Conclusion

The spectral analyses (^{1}H- and ^{13}C-NMR) data showed that the polymerization proceeded by the C-C and C-O-C coupling of *ortho* and *para* positions and oxyphenylene according to –OH group of 2-PIP. According to molecular weight distribution, the M_n, M_w and PDI values of poly-2-PIP were found to be 11358, 12624 g mol^{-1} and 1.112, respectively. The highest yield of poly-2-[(4-pyridilmethylene)-imino]phenol was found to be 50.1 % by using molecular O_2 in an aqueous alkaline medium. The yield of 2-[(4-pyridilmethylene)-imino]phenol effected from the rate times and flow rate of molecular O_2. According to TG-DTG analyses, poly-2-PIP was shown to be stable through to temperature and thermal decomposition. Poly-2-PIP and 2-PIP lost 54.90 and 81.83% of weights at 1000°C, respectively.

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