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Synthesis, characterization, conductivity and antimicrobial study of a novel thermally stable polyphenol containing azomethine group

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ABSTRACT

Poly(4-[[(4-methylphenyl)methylene]amino]phenol) (P(4-MMAP)), which is a Schiff base polymer, was synthesized by an oxidative polycondensation reaction of 4-[[(4-methylphenyl)methylene]amino]phenol (4-MMAP) with the oxidants NaOCl, H_2O_2 and O_2 in an aqueous alkaline medium. The polymerizations were carried out at various temperatures and times, and the highest polymer yield could be obtained when using 37% with NaOCl oxidant. The structures of the monomer and polymer were characterized by UV–Vis, FTIR ^1H NMR and X-ray diffraction techniques. The thermal behaviors of the monomer and polymer were identified by the TG and DTG techniques. The thermal degradation of the polymer which was observed thermally stable up to 1000 °C, was also supported by the Thermo-IR spectra recorded in the temperature range of 25–800 °C. The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) of the polymer were found to be 16682, 57796 g/mol and 3.4, respectively. The highest electrical conductivity value of P(4-MMAP) doped with iodine vapor at different temperatures and times was measured to be 7.8×10^{-5} Scm^{-1} after doping for 48 h at 60 °C. The antibacterial and antifungal activities of 4-MMAP and P(4-MMAP) were also assayed against the bacteria *Sarcina lutea, Enterobacter aerogenes, Escherichia coli, Enterococcus faecalis, Klebsiella pneumoniae, Bacillus subtilis* and the fungi *Candida albicans, Saccharomyces cerevisiae,* respectively.

1. Introduction

Schiff base polymers are one class of conjugated polymers, which are also called as poly(azomethines). They have drawn the attention of researchers in recent years due to their some properties such as, optoelectronic [1–3], semiconductive [4,5], and photovoltaic [6,7], antimicrobial activities [8] and high thermal stability [8,9].

Schiff base polymers have been synthesized using electrochemical [10] and chemical [11,12] methods. Oxidative polycondensation reactions carried out using NaOCl, H_2O_2 and O_2 oxidants are one of the most widely used method for the chemical polymerization. The advantages of this approach are the cheapness of the oxidants, high solubility of the synthesized polymer, mild reaction conditions and occurrence of environmentally friendly byproducts, such as NaCl and H_2O [13,14]. A number of studies have been reported on the synthesis of this class of polymers using these oxidants up to the present by Kaya and co-workers [15–18].

It has been reported that Schiff base polymers can be synthesized by oxidative polycondensation with good thermal stability and conductivity that could be increased with doping up to a certain level [13,18]. The conductivities of undoped Schiff base polymers are generally about 10^{-10}–10^{-15} Scm^{-1} [19,20]. However, the conductivities of these polymers could be increased by doping with various dopants. It was reported that iodine was the most suitable dopant for Schiff base polymers [21]. Moreover, this easy process also improved the thermal and optical properties of the polymer [22]. Therefore, researchers have widely investigated the application of iodine-doped Schiff base polymers for lithium batteries [23]. Kaya et al. reported that the conductivity of the Schiff base polymer, poly(4-{[(4-hydroxyphenyl)imino]methyl}benzene-1,2,3-triol) [PHPIMB], increased from 10^{-10} Scm^{-1} to 10^{-8} Scm^{-1} after doping with iodine vapor for 48 h at 25 °C and that the polymer showed thermal stability to 1000 °C without remaining any carbon residue [15]. In another study, it was reported that the conductivities of poly(2-(4-bromobenzylideneamino)phenol) and

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poly(2-(4-bromobenzylideneamino)-5-methylphenol]) increased from 11.33 × 10^{-10} and 6.40 × 10^{-10} Scm^{-1} to 25.10 × 10^{-10} and 219 × 10^{-10} Scm^{-1}, respectively, after doping with iodine for 48 h at 25 °C and concluded that the products were thermally resistant because carbon residues of the polymers were 23.63% and 28.21%, respectively at 1000 °C [16]. In the present study, it was determined that the conductivity of P(4-MMAP) increased from 5 × 10^{-11} Scm^{-1} to 7.30 × 10^{-6} and 7.75 × 10^{-5} Scm^{-1} after doping for 48 h at 20 °C and 60 °C, respectively, and it was thermally resistant to 1200 °C (30% carbon residue at 1000 °C).

In the present study, it was aimed at preparing a Schiff base polymer which had good solubility, thermal resistivity and semiconductivity. For this purpose, P(4-MMAP) with an active hydroxyl group was synthesized by the oxidative polycondensation of 4-MMAP using NaOCl, H_2O_2 and O_2 mild oxidants in an aqueous alkaline medium. The structures of 4-MMAP and P(4-MMAP) were then characterized by various techniques. Finally, the antimicrobial and thermal degradation properties of the polymer were compared to the monomer and electrical conductivity of P(4-MMAP) was measured depending on the doping temperature and time.

2. Experimental

2.1. Materials

4-aminophenol, *p*-tolualdehyde, KOH, hydrochloric acid (HCl, 37%), methanol, ethanol, ethyl acetate, acetone, n-heptane, 1,4-dioxane, *N*-methylpyrrolidone, tetrahydrofuran (THF), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), iodine, sodium hypochlorite (NaOCl) (15% aqueous solution) and H_2O_2 were used as supplied by Merck Chem. Co. (Germany). *Sarcina lutea* (ATCC 9341NA), *Enterobacter aerogenes* (ATCC 13048), *Escherichia coli* (ATCC 39628), *Enterococcus feacalis* (ATCC 29212), *Klebsiella pneumonia*, *Bacillus subtilis* (ATCC 6633) bacteria, and *Saccharomyces cerevisiae*, *Candida albicans* yeasts obtained from Biology Department of University of Celal Bayar and Medical Faculty-Microbiology laboratory of University of Kahramanmaraş Sütçü İmam were used to investigate the antimicrobial activities of the monomer and polymer.

2.2. Method

2.2.1. Synthesis of 4-MMAP

As can be seen from Scheme 1, 4-MMAP Schiff base was synthesized with the mechanism of a general condensation reaction [24]. Solution of *p*-tolualdehyde (10 mmol) in 5 mL of methanol was added drop by drop into the solution of 4-aminophenol (10 mmol) prepared in 15 mL of methanol. The reaction was performed at 60 °C with continuous stirring. A yellow product formed approximately 6 h later in the solution, and it was separated by filtering and washed with cold methanol. After the monomer was recrystallized from methanol for purifying, it was dried in a vacuum desiccator and 88% yield was obtained with melting point of 135 °C.

2.2.2. Synthesis of P(4-MMAP)

P(4-MMAP) was synthesized by oxidative polycondensation of 4-MMAP in an aqueous alkaline medium using NaOCl (15%), H_2O_2 (30%) and O_2 (flow rate: 0.56 Lh^{-1}) oxidants (Scheme 1). 4-MMAP (1 mmol) was dissolved in an aqueous KOH solution (10%, 1 mmol) in a 50 mL flask with three necks. The reaction was carried out under a nitrogen atmosphere. After reaching the reaction temperature, 1 mmol NaOCl (15%) or H_2O_2 (30%) was added drop by drop into the monomer solution. The color of the solution immediately turned from yellow to brown with the addition of the oxidant. When O_2 was used, it passed through the reaction solution during the polymerization. After the reaction was completed, the polymer was precipitated by neutralizing the reaction medium with the addition of solution of HCl into the mixture that had been cooled to room temperature. After the precipitated polymer was filtered and washed with hot water (3 × 25 mL) and methanol to remove the mineral salts and unreacted monomer, respectively. It was dried at 60 °C in a vacuum oven.

The polymer yield was determined using Eq. (1):

$$\text{Polymer Yield}(\%) = \frac{w_p}{w_m} \times 100 \tag{1}$$

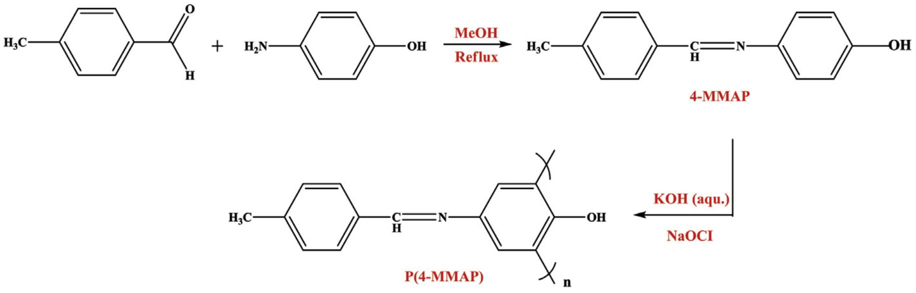
Where w_p and w_m correspond to the polymer and initial monomer mass, respectively.

2.3. Characterization

The UV–Vis spectra measurements of 4-MMAP and P(4-MMAP) were carry out with Shimadzu UV-1700 PharmaSpec UV–Visible Spectrophotometer by dissolving them in DMSO. The FTIR spectra of the samples were taken using Perkin Elmer FTIR Spectrometer. The ^1H NMR spectra were recorded using Bruker Avance 500 MHz NMR in solutions of DMSO. The X-ray diffraction (XRD) patterns were performed using Rigaku D max 2000 Diffractometer with monochromic CuKα radiation (1.5405 Å) operated at 40 kV, 30 mA and 2θ with a scan angle from 5° to 60°.

TG and DTG measurements were recorded with EXSTAR S11 7300 model thermal analyzer under nitrogen atmosphere with a heating rate of 10 °C/min. For the determination of M_n, M_w and PDI values of the synthesized polymer, Shimadzu Prominence Gel Permeation Chromatography equipped with a preparative Nucleogel GPC 103-5 VA300/7.7 column was used (eluent: dimethylformamide, flow rate: 0.5 mL min^{-1}, calibrated with polystyrene standards).

To measure the surface resistivity of P(4-MMAP), pellet samples with 2 mm thick and diameter of 1.3 cm were prepared under a hydraulic pressure of 1.7 ton/cm^2. The measurements of the surface



Scheme 1. Synthesis of 4-MMAP and P(4-MMAP).

resistivity were performed by two probe method using either Thurlby 1503 or Keithley 6517A digital multimeter, depending on the surface resistivity of the samples.

2.4. Antimicrobial test

The antimicrobial activities of the monomer and polymer were monitored using Mueller-Hinton agar and Sabouraud dextrose agar with the agar-well diffusion method [25] against the bacteria *Sarcina lutea* (ATCC 9341NA), *Enterobacter aerogenes* (ATCC 13048), *Escherichia coli* (ATCC 39628), *Enterococcus feacalis* (ATCC 29212), *Klebsiella pneumonia* and *Bacillus subtilis (*ATCC 6633) as well as the yeasts *Saccharomyces cerevisiae* and *Candida albicans.* Culture suspensions were prepared from standardized inoculums of the bacteria and yeasts containing 10^8 cfu mL^{-1} and 10^6 cfu mL^{-1}, respectively [26]. After inoculation, the suspensions were gently shaken and then poured into sterile petri dishes. Solutions of 4-MMAP and P(4-MMAP) in DMSO with different concentrations (100 and 200 μg/100 μL) were loaded into wells 6 mm in diameter. Nystatin (100U) and Chloramphenicol (30 μg) were used as the standards and DMSO was used as the solvent control. The plates were incubated at 36 °C for bacteria and at 30 °C for yeasts for 24 h. At the end of the incubation, the evaluation was performed by measuring the diameters of the inhibition zones.

3. Results and discussion

3.1. Effect of synthesis conditions on polymerization of 4-MMAP

3.1.1. Oxidant type

The changes in the yield, conductivity, molecular weights (M_w, M_n) and PDI values of P(4-MMAP) obtained by an oxidative polycondensation reaction of 4-MMAP using various oxidants such as NaOCl, H_2O_2 and O_2 are given Table 1. In the experiments carried out to detect the effects of the oxidant types, oxidant were used oxidants at concentrations of $[NaOCl]_0 = [H_2O_2]_0 = 0.1$ mol L^{-1} or O_2 at a flow rate of 0.56 L h^{-1}. After the conductivity values for all the polymer samples synthesized with each oxidants and doped with I_2 for 24 h at 20 °C were obtained, they were compared to the other oxidant types and it was observed that, while the conductivities of products after doping increase about 10^9 fold, the changes were all related to the initial conductivity values. As seen from Table 1, the conductivity values of P(4-MMAP) were in the descending order of NaOCl>H_2O_2> O_2. The highest yield was also obtained as 36.4% with the NaOCl oxidant. In addition, the polymer synthesized with the NaOCl oxidant had the highest molecular weight values (M_w: 57796, M_n: 16682 g/mol and PDI: 3.4). According to the evaluations of the molecular weight, yield and conductivity values of P(4-MBAP), it can be concluded that NaOCl was found to be the most suitable oxidant. Therefore, the following experiments were performed with this oxidant. According to the evaluations of the molecular weight, yield and conductivity values of P(4-MMAP), it can be concluded that NaOCl was found to be the ideal oxidant.

Table 1
Effect of oxidants types on yield (%), M_w, M_n, PDI and conductivity of P(4-MMAP).

Oxidant	Yield (%)	M_w	M_n	PDI	Conductivity (Scm^{-1})	
					Initial	Doped
NaOCl	36.4	57796	16682	3.4	5×10^{-11}	7.3×10^{-6}
H_2O_2	14.2	9305	6633	1.4	2.2×10^{-15}	1.9×10^{-6}
O_2	23.4	9184	8800	1.04	6.2×10^{-15}	3.7×10^{-7}

($[4\text{-MMAP}]_0 = [KOH]_0 = [NaOCl]_0 = [\ H_2O_2]_0 = 0.1$ mol L$^-$ and flow rate of $O_2 = 0.56$ L h$^-$, doping time: 24 h).

3.1.2. Polymerization temperature and time

To monitor the effect of the polymerization temperature and time on the yield of P(4-MMAP) the polymerizations were performed at 70, 80 and 90 °C for different periods, and the polymerization conditions that gave the highest yield were determined (Fig. 1). As can be seen from the figure, the yield increased with an increase in the polymerization time at 70 °C. At the temperatures of 80 and 90 °C, for the polymerizations went on for further 2 h, it was observed that the yields did not increase. This shows that the effects of polymerization temperature and time on the yield are in agreement with data reported in the literature [20].

3.2. Solubility behavior

The solubility behavior of 4-MMAP and P(4-MMAP) were studied qualitatively by dissolving 1 mg samples in 1 mL of solvent at 25 °C, and the observations are given in Table 2. The monomer dissolved exactly in all the solvents tested except heptane. While the polymer was soluble in *N*-methylpyrrolidone (NMP), dimethylformamide (DMF), dimethylsulphoxide (DMSO) and ethylacetate; it was insoluble in ethanol, heptane, and tetrahydrofuran (THF). In addition, it was observed that the polymer was poorly soluble in methanol, acetone and 1,4-dioxane. In addition to the solubility of the synthesized polymer in common organic solvents, the dissolution of the polymer in mild solvents such as ethylacetate, derivative of ester, also plays a facilitator role in the processability of the polymer.

3.3. UV–vis spectra

The UV–Vis spectra of 4-MMAP and P(4-MMAP) taken in DMSO in the wavelength range of 260–700 nm (Supplementary data). Two bands at the wavelengths of 278 and 348 nm as well as 293 and 409 nm can be observed in the UV–Vis spectra of 4-MMAP and P(4-MMAP), respectively. The bands observed at 278 and 293 nm in the spectra of the monomer and polymer, respectively, can be attributed to the π–π* transitions of benzene (–C=C-) while the other peaks at 348 and 409 nm are due to the π–π* transitions of the –CH=N– functional group [8,20]. It was observed that the bands in the P(4-MMAP) spectrum were broadened and the band of the –CH=N– functional group shifted when compared to the 4-MMAP spectrum. Moreover, while the spectrum of 4-MMAP

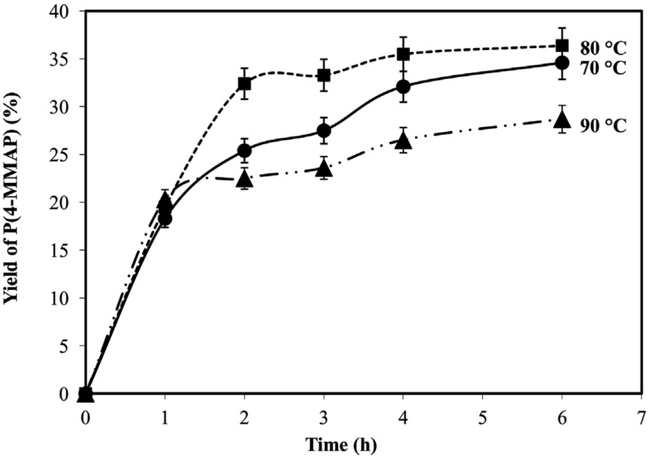


Fig. 1. The change on yield of P(4-MMAP) (%) with the polymerization temperature and time ($[4\text{-MMAP}]_0 = [KOH]_0 = [NaOCl]_0 = 0.1$ mol L$^-$).

Table 2
The results of solubility test of 4-MMAP and P(4-MMAP) in various solvents.

	Ethanol	Methanol	Acetone	Dioxane	DMF	DMSO	NMP	Ethyl acetate	Heptane	THF
4-MMAP	+	+	+	+	+	+	+	+	±	+
P-4-MMAP	−	±	±	±	+	+	+	+	−	−

(+): soluble, (±): partially soluble, (−): insoluble.

ended at 420 nm, the spectrum of P(4-MMAP) was extended up to 700 nm. This case can be explained by the extension of the conjugation in the polymeric structure [8,20], which is evidence that polymer structure is formed.

3.4. *FTIR spectra*

Fig. 2 shows the FTIR spectra of 4-MMAP and P(4-MMAP). The peaks observed at 3150 and 3272 cm^{-1} are due to the phenolic −OH groups of 4-MMAP and P(4-MMAP), respectively. While the sharp peak observed at 1621 cm^{-1} in the spectrum of the monomer belongs to the characteristic −CH=N− vibration, and the same peak is seen as a shoulder at 1624 cm^{-1} in the spectrum of the polymer [8,14,20]. The presence of the characteristic −CH=N− peak of the Schiff base in the FTIR spectrum of P(4-MMAP) indicates that the azomethine groups are preserved in the polymeric structure [20]. Additionally, the bands observed at 1586, 1568, 1512, 1506 and 1445 cm^{-1} correspond to −C=C− vibrations in the spectrum of the monomer [20]. These peaks are seen at 1542, 1509 and 1448 cm^{-1} in the spectrum of the polymer [20]. While the peaks recorded at 1377 and 1365 cm^{-1} originate from the aliphatic C−H bending vibrations, and the peaks at 1280 and 1217 cm^{-1} are due to −C−O− stretching vibrations in the spectra of 4-MMAP and P(4-MMAP), respectively [20]. Moreover, (I) the shift of the peaks in the polymer spectrum, (II) the decrease in the number of the peaks and (III) the broadening of the peaks in the spectrum of the polymer compared to that of the monomer can all be ascribed to the polymer structure [20,27].

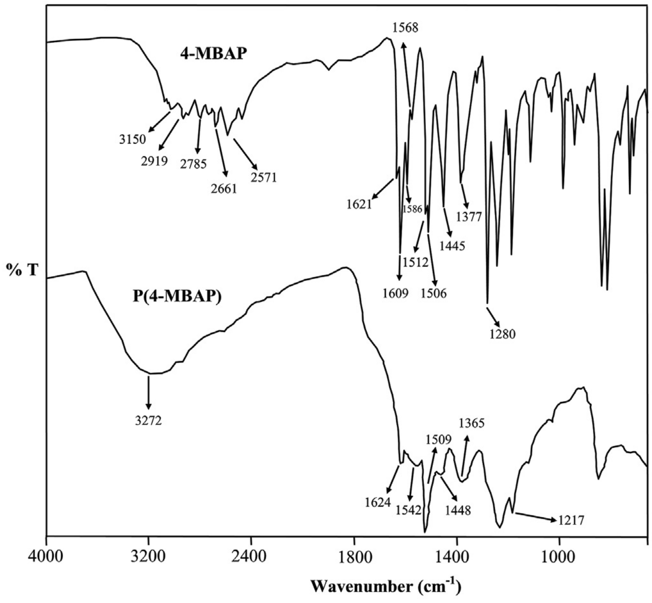


Fig. 2. FTIR spectra of 4-MMAP and P(4-MMAP).

3.5. ^{1}*H NMR spectra*

The ^{1}H NMR spectra of 4-MMAP and P(4-MMAP) recorded in DMSO-d_6 are given in Fig. 3. In the ^{1}H NMR spectrum of 4-MMAP, while the protons belonging to the characteristic −OH and −CH=N− functional groups are observed at $\delta = 9.52$ (s, 1H) ppm and $\delta = 8.54$ (s, 1H) ppm, respectively, the peak of the protons from the $-CH_3$ group is at $\delta = 2.33$ (s, 3H) ppm. These peaks are at $\delta = 9.90$, 9.12 (s, 1H) and $\delta = 2.51$ (s, 3H) ppm in the spectrum of P(4-MMAP), respectively. The other peaks that verify the aromatic structure of 4-MMAP and P(4-MMAP) were detected in the spectra at $\delta = 7.78$ (d, 2H, Ar-H_a), 7.27 (d, 2H, Ar-H_b), 7.18 (d, 2H, Ar-H_c) and 6.82 (d, 1H, Ar-H_d) ppm as well as $\delta = 7.17$ (d, 1H, Ar-H_a), 7.08 (d, 1H, Ar-H_b) and 6.84 (s, 2H, Ar-H_d) ppm, respectively [20]. The observed broadening of the peaks belonging to the aromatic region in the spectrum of the polymer indicates the polyconjugated structure [20]. Additionally, (I) the absence of the doublet peaks originating from the H_c protons belonging to the monomer in the polymer spectrum and (II) the observation of the doublet H_d protons of the monomer as singlet in the spectrum of the polymer indicate that the polymerization proceeds from the ortho positions according to the OH groups due to the C−C bonds formed during polymerization [20,17]. Possible resonance structures forming during the polymerization of the Schiff base polymers, which are derivatives of polyphenol have been reported in the literature [14,17]. In accordance with these reports, it was determined that the Schiff base monomer can have three different possible resonance structures for the polymerization in an aqueous alkaline medium by the oxidative polycondensation method (Scheme 2(a)). The ^{1}H NMR data of P(4-MMAP) showed the polymerization proceeds from II and III resonance structure given Scheme 2(a) [14,17]. Dimers which form with the combining of the resonances undergo enolization [14,17]. In this way, the suggested polymerization mechanism of P(4-MMAP), which consists of a recombination of dimers, trimers, etc. is introduced in Scheme 2(b).

3.6. *XRD patterns*

The XRD patterns of 4-MMAP and P(4-MMAP), which were recorded in the region $2\theta = 5-60°$ to investigate the crystalline structure differences of the monomer and polymer, are displayed in Fig. 4. There are various sharp diffraction peaks in the monomer diffractogram, which indicate a high degree of crystalline structure in the Schiff base. However, only two sharp diffraction peaks can be observed at about $2\theta = 28°$ and 40° in the polymer diffractogram and the peaks indicate that the polymer has semicrystalline structure [28]. It was reported in the literature that the presence of −CH=N− polar group and C=C bonds in the aromatic ring of structure leads to some crystallinity [29]. Moreover, the broadening of the polymer diffractogram according to that of the monomer point out that the polymer has also amorphous nature in addition to semicrystalline behavior [29].

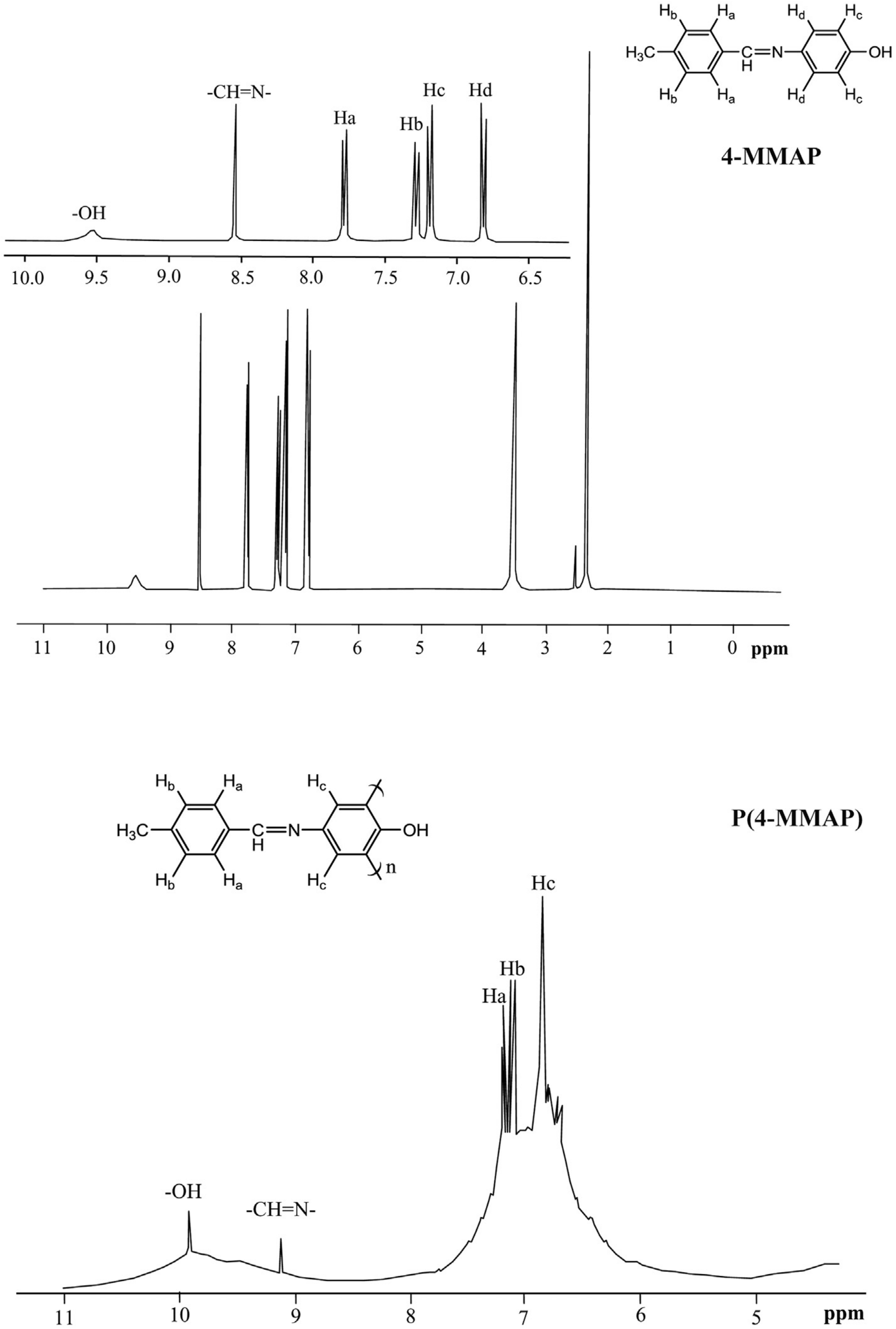
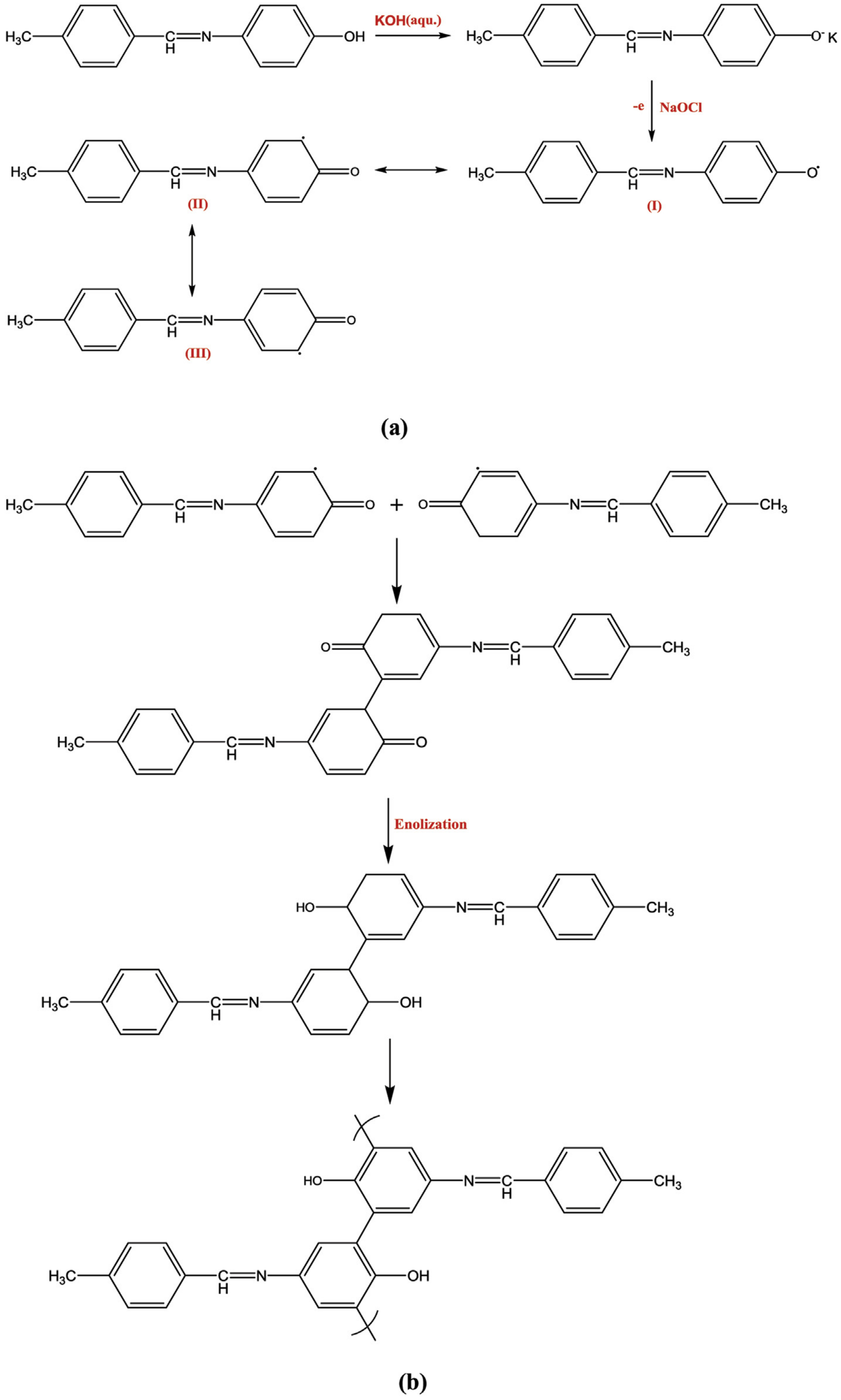


Fig. 3. ^{1}H NMR spectra of 4-MMAP and P(4-MMAP).

3.7. Thermal analysis and thermal degradation process of P(4-MMAP)

The TG and DTG curves belong to 4-MMAP and P(4-MMAP) are shown in Fig. 5. Additionally, to support the thermal analysis measurements of the polymer, the thermo-IR spectra recorded in the temperature range of 25–800 °C (Supplementary data). 8. It was determined from the TG curve of 4-MMAP that the degradation occurred in three steps (Fig. 5). In the first step (180–350 °C) 58.4%, in the second step (350–470 °C) 11.9% and in the third step (470–650 °C) 7.6% weight losses were determined. The maximum degradation temperatures (T_{max}) obtained from the DTG curves were observed at 285 °C, 404 °C and 547 °C for each degradation step, respectively. It was determined that 77.9% of the monomer degraded between 180 and 650 °C, with 22.1% left as a carbon residue.

It was observed from the TG-DTG curves of P(4-MMAP) that the weight losses occurred in three steps within the temperature range of 30–1000 °C. In the first step with a minimum of DTG at 190 °C, 7.9% (theoretically calculated: 7.9%) weight loss was observed in the temperature range of 30–200 °C, which indicates the removal of crystallization water [30,31]. In addition, in the thermo-IR spectra of P(4-MMAP), there was a decrease in the intensity of the –OH peak around 3200 cm^{-1} with the increase in the temperature in the



Scheme 2. (a) Possible resonance structures for the polymerization of 4-MMAP, (b) the polymerization mechanism of P(4-MMAP).

range of 30–200 °C, which was further evidence for the water loss. In the second step, 52% (theoretically calculated: 51.5%) weight loss was recorded in the temperature range of 200–767 °C in the TG curve of P(4-MMAP), which shows the degradation of the –N=CH–Ar–CH_3 group. The peak with a maximum at 410 °C in the DTG curve corresponds to this degradation step. It was determined from the thermo-IR spectra that the absence of the –CH=N– functional group around 1600–1610 cm^{-1} at 500 °C and higher temperatures, indicated that the degradation of this functional group was completed at 500 °C. Moreover, in the range of 200–600 °C, with the increase in the temperature, the decrease observed in the number and intensities of the –C=C– (1500 cm^{-1}) stretching and

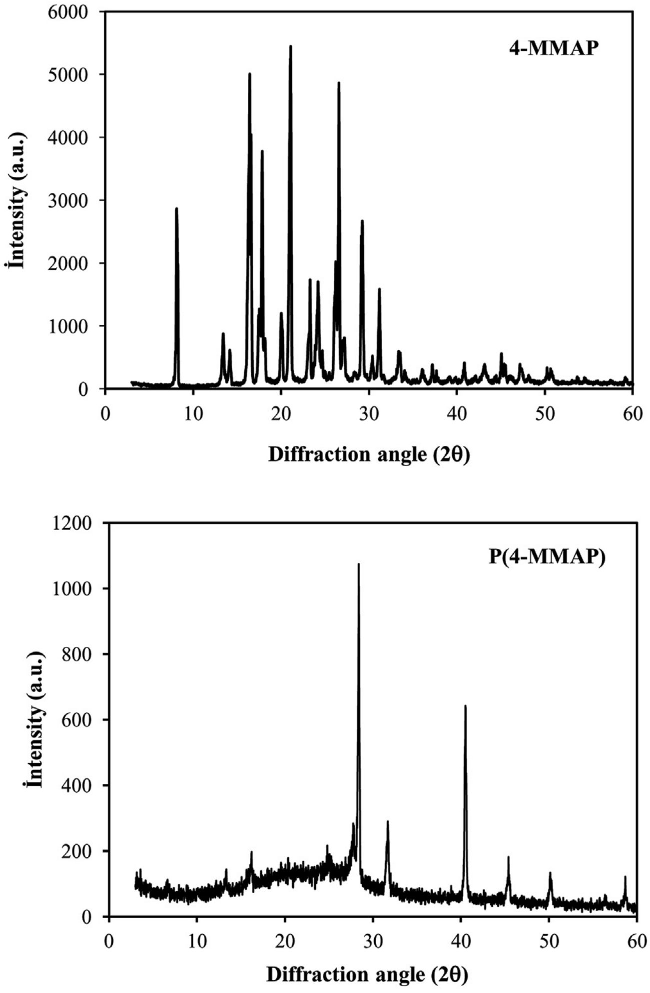


Fig. 4. XRD patterns of 4-MMAP and P(4-MMAP).

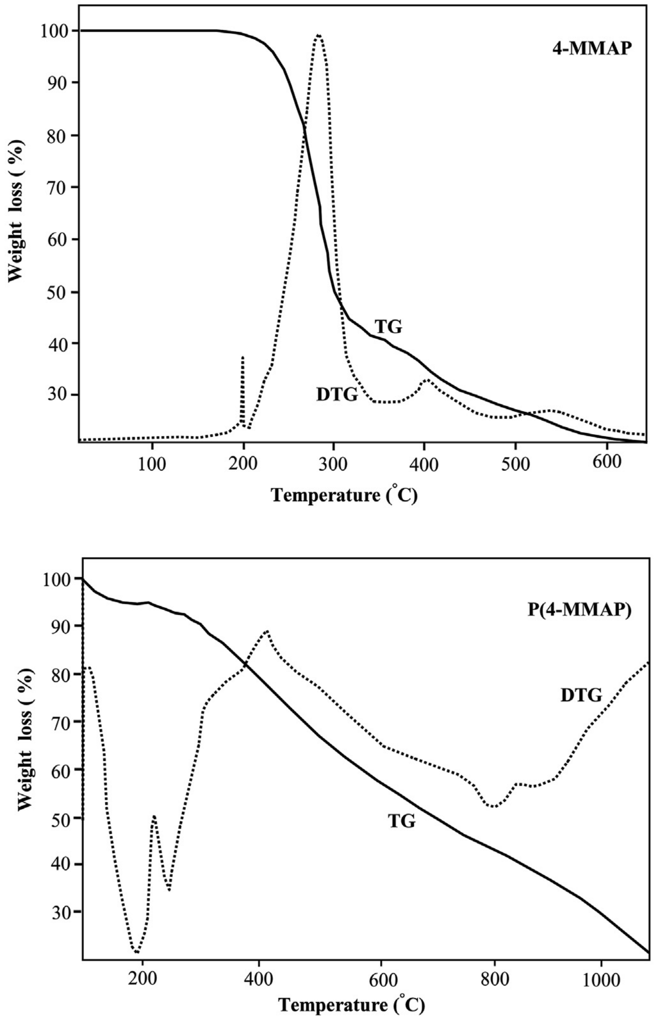


Fig. 5. TG ( ) and DTG ( ) curves of 4-MMAP and P(4-MMAP).

aliphatic –C–H bending vibrations (1370 cm^{-1}) support the results obtained from the thermal analysis curves. In the third degradation step of P(4-MMAP), the 18.6% weight loss can be attributed to the degradation of the phenol group in the temperature range 767–1000 °C. This was also proven by the preservation of the peaks belonging to –OH, C–O vibrations and aromatic –C═C– stretching around 800 °C.

3.8. Doping with iodine

It has been reported in the literature that the doping process of the Schiff base polymers occurs with the coordination of the highly electronegative N atoms of the polymers with iodine molecules [21,32].

The conductivity values calculated using resistivity values measured of the P(4-MMAP) before and after doping with iodine vapor for up to 48 h were monitored for the temperatures of 20, 40 and 60 °C (Fig. 6). While the initial conductivity of the polymer was 5×10^{-11} Scm^{-1}, the conductivity values were measured to be 7.30×10^{-6}, 15.5×10^{-6} and 7.8×10^{-5} Scm^{-1} after doping for 48 h at 20, 40 and 60 °C, respectively. It can be seen from figure that the conductivity of the P(4-MMAP) increased remarkably with the increase in doping time at each temperature, but then stabilized. The increase in the conductivity with temperature is typical for conductive polymers, and this situation is defined as 'thermally activated behavior', in the literature [33]. It can be explained by the increase in the charge transfer efficiency between the polymer chains and the mobility of I_3 dopant anions with temperature [16,33].

3.9. Antimicrobial properties

Schiff base monomers and polymers containing active hydroxyl groups are known to inhibit enzyme production [34]. The inactivating process takes place by inhibiting free OH groups which is necessary to show the activity of the enzyme due to having both N and O donor structures [34]. For this reason, the usability of 4-MMAP and P(4-MMAP) as antimicrobial agents was investigated. The bactericide and fungicide activities of them were tested against six bacteria and two yeasts using the conventional well diffusion method [25]. *S. lutea, E. aerogenes, E. coli, E. faecalis, K. pneumonia and B. subtilis* as well as *C. albicans* and *S. cerevisiae* were selected as the bacteria and yeasts, respectively and the test results are presented in Table 3. As can be seen from the table, 4-MMAP showed strong antibacterial activity against all the tested bacteria, apart from *E. coli*. Whereas, P(4-MMAP) was active against the following bacteria: *S. lutea*, *K. pneumoniae* and *B. subtilis*. Additionally, it was detected that 4-MMAP demonstrated antifungal activity against *S. cerevisia*, while P(4-MMAP) did not show any activity against the

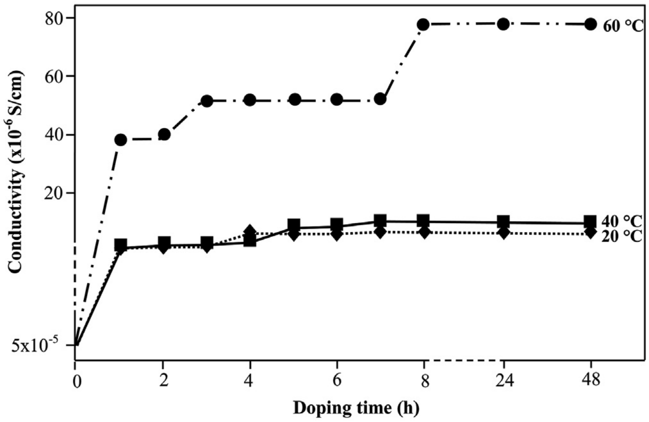


Fig. 6. The change in conductivity of P(4-MMAP) as function of temperature and time during doping with iodine.

Table 3
Antimicrobial behavior of 4-MMAP and P(4-MMAP) in the presence of bacteria and yeasts.

Microorganism	Inhibition zone (mm)			
	4-MMAP		P(4-MMAP)	
	100 μg	200 μg	100 μg	200 μg
S. lutea ATCC 9341NA	17	25	12	20
E. aerogenes ATCC 13048	9	12	–	–
E. coli ATCC 39628	–	–	–	–
E. faecalis ATCC 29212	12	12	–	–
K. pneumonia[a]	15	25	12	15
B. subtilis ATCC 6633	–	12	16	20
C. albicans[a]	–	–	–	–
S. cerevisiae	10	14	–	–

[a] Clinical isolate.

two tested yeasts. When Table 3 is examined, it is seen that antimicrobial activity of monomer is generally better than polymer (except *B. subtilis*). This case may be explained by the extension of the conjugation in the polymeric structure which make difficult permeation through the lipid layer of cell.

In additionally, inhibition zones increase with increasing amount of tested sample and this case is in agreement with the literature [20,33]. When the antimicrobial activity results of the monomer and polymer were compared to findings reported in the literature [34], it was observed that the synthesized compounds exhibited good antibacterial activity and they have potential usage as antibacterial agent.

4. Conclusions

Our results showed that P(4-MMAP) could be synthesized from 4-MMAP in an alkaline medium by oxidative polycondensation reaction using NaOCl, H_2O_2 and O_2 as the oxidants. It was observed that the oxidant type, polymerization temperature and time were parameters that affected the yield and molecular weight of the polymer. The solubility of the P(4-MMAP) in polar aprotic solvents such as DMF, DMSO, NMP and ethyl acetate makes it possible to investigate different properties such as catalyst and antimicrobial activity of the polymer and the use of the polymer in different fields such as synthesis of copolymer and resin as well as various analytical applications. The thermal analysis results of the polymer confirmed that it was suitable for use in materials requiring high thermal stability. Additionally, the conductivity of P(4-MMAP) after doping with iodine showed that the polymer could be used as a semiconductive material. According to the antimicrobial test results, P(4-MMAP) also has potential to be used as an antibacterial agent.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.06.028.

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