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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 ^{1}H 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):

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

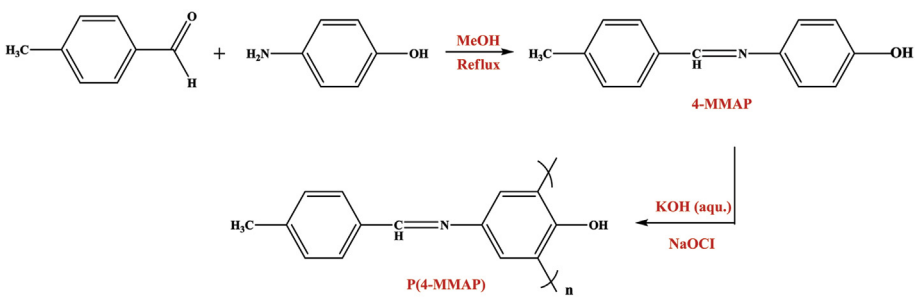
Where w_p and w_m correspond to the polymer and initial monomer mass, respectively.

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).