



Template-free oxidative synthesis of polyaminonaphthol nanowires



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ABSTRACT

In this study, the polymer was synthesized via template-free oxidative reaction of 3-amino-2-naphthol (AN). For this purpose, bifunctional monomer was polymerized by NaOCl as oxidant in aqueous basic medium to give the corresponding poly (3-amino-2-naphthol) (PAN) with molecular weight ca. 11,100 Da. The chemical and physical properties of PAN were determined by NMR, FT-IR, UV-Vis, gel permeation chromatography (GPC), thermogravimetry (TG), differential scanning calorimetry (DSC), cyclic voltammetry (CV), photoluminescence (PL), dynamic light scattering (DLS), scanning electron microscope (SEM), and transmission electron microscope (TEM). The SEM and TEM analyses indicated to be the resulting polymer has a *nanowire structure*. The reversible *redox behavior* of the polymer was attributed to its electroactive nature. In addition, the kinetic parameters related to the solid state decomposition of the polymer were calculated by several methods based on multiple heating rates.

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1. Introduction

In the period from 1959 until today, in order to optimize the reaction conditions of oxidative polymerization products, different oxidizers and catalysts have been used. Thanks to the differences in materials used in oxidative polymerization reactions, various synthesis methods have emerged. These include; *i*-polymerization reactions carried out with strong Lewis acids (such as FeCl₃, AlCl₃ and CuCl) [1–3], *ii*-oxidative polymerization reactions performed using a suitable oxidant in the presence of transition metal catalysts [4–8], *iii*-enzymatic polymerization reactions carried out in the presence of oxidoreductase enzymes such as horse radish peroxidase or soybean peroxidase [9–11], and *iv*-oxidative polycondensation reaction carried out by a mild oxidant (O₂, NaOCl, H₂O₂, etc.) [12–16]. The internal

resonance energy of polyphenols increases due to the shifts in chain length of flexible π -electrons in the conjugated bond system. This situation makes such compounds more durable against the impact of high energy, heat, radiation and gamma rays, differing from oligomers. Also, the active –OH groups in polyphenols provide high solubility for industrial production. However, due to the high polarity of –OH groups, polyphenols form quality and precision thin films on metal, glass and other substrates. Considering these qualities, some representatives of polyphenols have been successfully used to produce photoresist that is resistant to plasma, instead of bakelite [6,17]. The composites of oligonaphthol and its epoxy derivatives are used for producing graphite material [18,19]. Composites with polyphenylene of polyphenols are successfully used in the manufacture of plastic materials resistant to temperature and chemical reactions [20]. One of the important features of polyphenols is that some of their derivatives are biologically active. Oligooxyquinoline, among oligophenols, occupies an

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important and diverse place. On one hand, oligophenols have the feature of releasing atomic oxygen under certain conditions; on the other hand, they have high antimicrobial properties since it contains triple nitrogen bonds in the oligoquinoline rings. The numbers of polyphenols synthesized are very high today. However, the physical and chemical properties of polyphenols which contain other reactive groups, ($-\text{NH}_2$, $-\text{HC}=\text{N}-$, $-\text{CHO}$, $-\text{COOH}$, etc.) in addition to the $-\text{OH}$ group is unknown. Therefore the properties of phenols which contain multiple active groups constitute a topic of current interest. As can be seen from the literature data discussed above, the conjugated oligophenol systems have a wider application area in terms of their technological features. In recent years, because of expanding usage in solar concentrators, fiber optic sensors and plastic brightener applications, fluorescence polymers have attracted more attention [21–23]. It is known that many fluorescent dyes contain units of 2-naphthol. Accordingly fluorescence polymers with naphthol chromophoric units could be used in the areas mentioned above. Some dihydroxynaphthalenes were polymerized by Yamamoto et al. using horseradish peroxidase enzyme [24]. They analyzed the photoluminescence characteristics of the resulting polymers. In addition, 1,5-dihydroxynaphthalene monomer was electropolymerized by Lu et al. They reported that naphthalene polymer exhibited high conductivity, and fluorescence properties [25]. Thus, the literature review has shown that the oxidative polycondensation (OP) reaction is vital for oligophenol synthesis. This reaction has a simple and cheap synthetic pathway, and is based on high productivity, with less hazardous waste. Here, we aimed to complete the oxidative polymerization of a bifunctional monomer in an aqueous basic medium by suitable oxidants and reported the regio-selective synthesis of the resulting polymer and its *nanowire structure*. Optical, electrochemical, and thermal properties of the product were also investigated.

2. Experimental

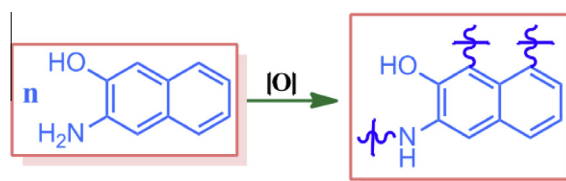
2.1. Materials

In this study the regio-selective synthesis of polyaminonaphthol was carried out in an aqueous basic medium and the synthesis, characterization and some physical and thermal properties, as well as solid state degradation kinetics, were also investigated. The monohydroxyaminonaphthol monomer, 3-amino-2-naphthol (AN) (99%, ACS reagent), sodium hypochloride, hydrogen peroxide (30% aqueous solution), potassium hydroxide ($\geq 85\%$, ACS reagent, pellets) and hydrochloric acid (37%, AR grade) used in OP were purchased from Merck Chem. Co., (Germany). Hydrochloric acid was used for neutralization of the resulting polymer. Acetonitrile (ACN), methanol, ethanol, chloroform, acetone, tetrahydrofuran (THF), dimethylsulfoxide (DMSO), dichloromethane and other solvents were purchased from Merck Chem. Co., (Germany) and then used for solubility and removing remaining monomer. The monohydroxyaminonaphthol monomer was oxidatively polymerized in optimal reaction conditions by using various

oxidants such as NaOCl, H_2O_2 and air. The structure of polyhydroxyaminonaphthol was confirmed with UV–Vis, FT-IR, ^1H NMR measurements. The resulting polyaminonaphthol particles were characterized by SEM and TEM images and GPC, DLS, PL and CV analyses. Thermal analysis of polyaminonaphthol was determined from TG/DTA and DSC measurements. Finally, the kinetic triplets such as the activation energy E , the exponential factors A , and reaction order n related to the solid state degradation kinetics were obtained for the resulting polyaminonaphthol.

2.2. Synthesis and optimum reaction conditions of the resulting polymer

PAN was synthesized in the presence of various oxidants such as NaOCl (30%), H_2O_2 (30%) and air by OP in aqueous basic media (Scheme 1) [26,27]. The AN monomer (0.16 g, 0.001 mol) was dissolved in aqueous KOH solution (10%, 0.001 mol) into a 50 mL three neck flask. The reaction was carried out in a refluxing system with a thermometer, magnetic stirrer and a dropping funnel containing a solution of NaOCl or H_2O_2 . In experiments conducted with air, the CO_2 in the air was neutralized by the collection unit containing a 20% solution of KOH before releasing the reaction medium. After completion of the reaction, the mixture was cooled to room temperature and then neutralized with the equimolar amount of HCl. The precipitated product was separated by filtration and washed 3 times with 50 mL of hot water. The resulting polymer was dried at 110°C in the oven. The yield of the polymerization reaction performed with NaOCl as oxidant in the aqueous basic medium was increased parallel to the increase in temperature and the reaction reached the maximum yield level at 80°C . In addition, it was obviously observed that expanding the time slot at 80°C increased the yield. Based on these data, the optimal reaction conditions of PAN at 80°C for 10 h were $[\text{AN}]_0 = [\text{KOH}]_0 = 0.025 \text{ mol L}^{-1}$ and $[\text{NaOCl}]_0 = 0.06 \text{ mol L}^{-1}$. However, it was observed that the yield in OP performed by H_2O_2 , decreased at all temperatures above 70°C . Also in experiments performed at these temperatures, the highest yield is limited to 10 h. In addition Table 1 indicates that the amount of used NaOCl oxidant and KOH significantly affect the yield of polymerization. Accordingly, the optimum reaction conditions of PAN with regard to H_2O_2 as oxidant, at 70°C for 10 h were determined to be $2[\text{AN}]_0 = [\text{KOH}]_0 = 0.05 \text{ mol L}^{-1}$ and $[\text{H}_2\text{O}_2]_0 = 0.1 \text{ mol L}^{-1}$. Finally, the yield level of OP performed with air as oxidant was examined according to the temperature and time slot. Accordingly the optimal reaction conditions for 5 h at 60°C is $2[\text{AN}]_0 = [\text{KOH}]_0 = 0.05 \text{ mol L}^{-1}$ and air = 8.5 L s^{-1} .



Scheme 1. Synthetic route for PAN.

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