



## Multi-response behavior of aminosulfonaphthole system



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### ABSTRACT

Here, we report regioselectively functionalized synthesis, as well as photo physical, electrochemical, and thermal, of a novel water-soluble conjugated polymer. For this purpose, horseradish peroxidase (HRP)-catalyzed polymerization of a multifunctional monomer, 7-amino-4-hydroxy-2-naphthalene sulfonic acid (AHNAPSA) was carried out by using hydrogen peroxide as the oxidant at room temperature for 24 h under air. The structure of poly(7-amino-4-hydroxy-2-naphthalene sulfonic acid), (PAHNAPSA) was identified by using nuclear magnetic resonance, infrared and ultraviolet-visible. Further characterization was performed by means of gel permeation chromatography (GPC), thermogravimetry (TG), differential scanning calorimetry (DSC), cyclic voltammetry (CV), photoluminescence (PL), dynamic light scattering (DLS) and solid state conductivity measurements. The spectral analysis results exhibited functional group selective polymerization of the monomer containing a multi-active center. Solvent effects on the optical, electrochemical and photo physical properties of PAHNAPSA were investigated by using five different solvents. PAHNAPSA presented an irreversible redox characterization at different scan rates. Optical band gap of PAHNAPSA is also found in the range of 3.18 eV to 3.55 eV. The fluorescence measurements were utilized to investigate the photochemical behaviors of PAHNAPSA in selected polar solvents. Accordingly, PAHNAPSA surprisingly presented multicolor emission behavior with relatively high quantum yield in all selected solvents. In addition, PAHNAPSA presented a reversible pH-responsive behavior and also had high selectivity and sensitivity towards chromium ions. Finally, the kinetic parameters associated with the solid state thermal degradation of PAHNAPSA were calculated from isoconversional methods. The TG/DTG analysis showed that PAHNAPSA followed a diffusion controlled degradation mechanism in N<sub>2</sub>.

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### 1. Introduction

In recent years, conducting polyarene systems (CPS) have received much attention in various fields as advanced functional materials because of their interesting optical, electronic and thermal characteristics [1–4]. Among CPS, water-soluble conjugated polymers (WSCPs) have attracted particular interest not only due to their specific applications, such as monitoring drug delivery, anticancer therapy, polymer light-emitting diodes (PLEDs), organic photovoltaics (OPVs), polymer solar cells (PSCs), as well as organic field effect transistors (OFETs) in cross-disciplinary areas of chemistry, material and biological sciences, but also their soluble behavior in environmentally-friendly solvents. WSCPs have several advantages compared to conventional CPS, like using a green process, producing more stable devices under ambient con-

ditions in the fabrication process and highly sensitive detection of biomacromolecules (DNA, RNA, and proteins) in biological applications. Palladium-catalyzed coupling reactions [5,6] and FeCl<sub>3</sub> oxidative polymerization reactions [7] are the most common routes employed for the synthesis of WSCPs. However, it is quite challenging to synthesize special WSCPs by the above routes including different polyarene systems due to the limited types of backbones. Therefore, a new WSCP is usually constructed by substituting different side-chains bearing amine (-NH<sub>2</sub>), hydroxyl (-OH), sulfonyl (-SO<sub>3</sub>H) or carboxyl (-COOH) groups responsible for dissolving in aqueous solution to its backbone. We here present a new polyarene system without side-chains different from traditional backbone structures like poly (fluorene) and poly(thiophene). Thus, we aimed to develop the potential applications of this new polyarene in various disciplines, due to the fluorescent probe properties, high emission quantum yields and reversible P<sup>H</sup>-responsive behavior as well as end groups capable of selective reactions. The new system consisting of aminosulfonaphthole backbone was easily prepared via template-free one-step enzymatic polymerization

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process. UV–vis, CV, TGA, DSC, DMA, and PL techniques were then used to characterize the photo physical, electrochemical and thermal properties of the new system. Finally, the kinetic parameters relating to the solid state decomposition of the system were determined by isoconversional methods based on the multiple heating rates.

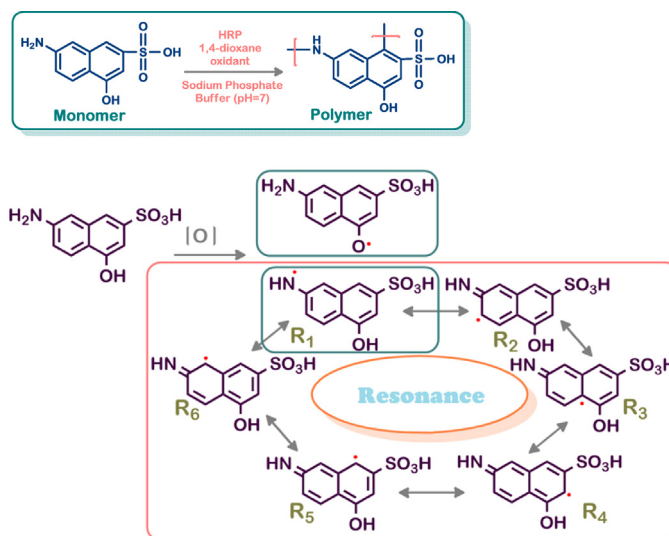
## 2. Experimental

### 2.1. Materials

HRP was purchased from Sigma-Aldrich Chemical Company as a solid powder (259 purpurogallin units/mg solid and  $RZ = 3.0$ ) and used to catalyze the polymerization of aminosulfonaphthole in dioxane/sodium phosphate buffer mixture at room-temperature. Monomer, 7-amino-4-hydroxy-2-naphthalenesulfonic acid, was purchased from Sigma-Aldrich Chemical Company and used as received. All other chemicals and  $H_2O_2$  (30% w/w solution in water) were also obtained from Sigma-Aldrich and used without further purification.

### 2.2. Techniques

A PerkinElmer Spectrum One FT-IR system was used to determine the chemical structure of the polyarene system. Measurements were performed in solid powder form at room temperature using universal ATR sampling accessory within the wavelengths of  $4000\text{--}650\text{ cm}^{-1}$ . UV–visible spectroscopy, was used to study the electronic transition in the UV–vis region of the resulting polymer. Measurements were performed by an AnalytikJena Specord 210 Plus with wavelength range of  $190\text{--}900\text{ nm}$  in doubly distilled and deionized water and selected solvents such as DMF, DMSO, EtOH and acetonitrile at  $25^\circ\text{C}$ .  $^1\text{H}$  NMR spectrum of the resulting polymer (Bruker Avance DPX-400 and  $100.6\text{ MHz}$ ) was recorded by using deuterated DMSO as solvent and Tetramethylsilane (TMS) as internal standard at room temperature. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and polydispersity index (PDI) were determined by Gel Permeation Chromatography-Light Scattering (GPC-LS) device by Malvern Viscotek GPC Dual 270 max. For GPC investigations a medium  $300 \times 8.00\text{ mm}$  Dual column Light Scattering Detector (LS) and a refractive index detector (RID) were used to analyze the products at  $55^\circ\text{C}$ . LiBr (40 mM) was added to the DMF mobile phase to dissociate molecular aggregates of polymer during GPC analysis. Thermal analysis was performed using a thermogravimetric analyzer, PerkinElmer Diamond Thermal Analysis, and a differential scanning calorimeter, PerkinElmer Pyris Sapphire DSC. The flow rate of nitrogen was  $200\text{ mL min}^{-1}$  and the sample size was  $10\text{ mg}$  for DSC. The heating rate was  $10^\circ\text{C min}^{-1}$ . DSC measurement was performed in the temperature range of  $25\text{--}420^\circ\text{C}$ . The TG-DTA analyses were carried out at heating rates of 5, 10, 15, and  $20^\circ\text{C min}^{-1}$  in a platinum crucible under nitrogen atmosphere. The solid state conductivity measurements were performed by a Keithley 2400 electrometer, using four-point probe technique. The resulting polymer was pressed in pellet form with the  $1600\text{ kg/cm}^2$  hydraulic pressure. Doping procedures were carried out by exposure of the precipitated solid to iodine vapor in a desiccator at room temperature for 24 h [8,9]. Electrochemical properties of the resulting polymer were investigated using a CH instruments 660C electrochemical workstation (CH Instruments, Texas, USA) in  $0.1\text{ mol L}^{-1}$  lithium perchlorate as the supporting electrolyte. All cyclic voltammetry (CV) measurements were carried out in a dry electrochemical cell under argon gas atmosphere at  $25^\circ\text{C}$ . The electrochemical cell is composed of an Ag wire pseudo-reference electrode (RE), Pt wire as counter electrode (CE), and platinum



**Scheme 1.** Synthetic pathway and possible coupling modes of AHNAPSA.

working electrode (WE). The experiments were carried out in selected solvents at different scan rates. The potentials were calibrated to the ferrocene redox couple ( $E^{1/2}$ ) ( $\text{Fc}/\text{Fc}^+$ )  $0.39\text{ V}$  versus  $\text{Ag}/\text{Ag}^+$ . All potentials were reported versus  $\text{Ag}/\text{Ag}^+$ . The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels were determined from oxidation and reduction onset values [10]. Fluorescence measurements of PAHNAPSA were carried out by using a Shimadzu RF-5301PC spectrofluorophotometer in selected solvent at the same concentration and the visible colors of the homogenous solutions were recorded. The size and polydispersity value of the polymer particles in water was determined by Dynamic Light Scattering (DLS), using Malvern CGS-3. DMA tests were performed with a Perkin Elmer Pyris Diamond DMA 115 V using single cantilever bending mode at a heating rate of  $3^\circ\text{C min}^{-1}$  in the range  $20\text{--}350^\circ\text{C}$ .

### 2.3. Polymerization

A typical procedure of enzymatic polymerization is performed as described [11]. Monomer of  $7.5\text{ mmol}$  and  $10\text{ mg}$  HRP were added to  $35\text{ mL}$  dioxane solution containing  $15\text{ mL}$  sodium phosphate buffer ( $\text{pH}: 7$ ) in a  $100\text{ mL}$  three-necked round bottom flask at room temperature.  $H_2O_2$  solution of 30% was added dropwise to the reaction mixture over a period of 5 h. This process performed to avoid from denaturation of HRP-enzyme. After vigorously stirring for 10 h, black precipitate was collected by filtration, washed periodically with ether ( $3 \times 30\text{ mL}$ ) to remove unreacted monomer and then dried in a vacuum oven at  $55^\circ\text{C}$  for 24 h. The yield of polymer was found as 92%. The synthetic pathway is outlined in Scheme 1.

## 3. Results and discussion

### 3.1. The structure characterization of the polymer

The solubility tests of PAHNAPSA were determined by using  $1\text{ mg}$  sample and  $1\text{ mL}$  solvent at room temperature. The polymer was soluble in polar solvents like DMF, DMSO,  $H_2O$ , and  $H_2SO_4$ . The product was insoluble in toluene, hexane, and benzene while it was partly soluble in ethanol, acetone, chloroform and THF. Structurally, WSCPs generally consist of  $\pi$ -conjugated backbones and charged side-chains. The main optical properties, such as absorption and emission spectra were determined by WSCP backbones. The charged side-chains have capability to dissolve in aqueous

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