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Regioselectively functionalized synthesis of poly(amino naphthalene disulfonic acid)

Fatih Doğan[a,b], İsmet Kaya[a,*], Kevser Temizkan[a]

[a] Polymer Synthesis and Analysis Laboratory, Department of Chemistry, Çanakkale Onsekiz Mart University, Çanakkale 17020, Turkey
[b] Faculty of Education, Secondary Science and Mathematics Education, Çanakkale Onsekiz Mart University, 17100 Çanakkale, Turkey

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ABSTRACT

Here, we reported the regioselective formation of poly(amino naphthalene disulfonic acid) (PANDA) nanoparticles by a template-free polymerization process in an aqueous alkaline medium. The NMR, FT-IR, UV–vis, gel permeation chromatography (GPC), thermogravimetry (TG), differential scanning calorimetry (DSC), cyclic voltammetry (CV), photoluminescence (PL), dynamic light scattering (DLS), X-Ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and conductivity techniques were used to investigate the structure characterization in addition to the chemical and physical properties of PANDA polymer-based nanoparticle with molecular weight ca. 14000 Da. Polymer-based nanoparticle showed a reversible redox behavior because of its electroactive nature. PANDA, also, emitted a yellow light while ANDA typically emitted a blue light in DMSO. PANDA displayed an uncommon high photoluminescence quantum efficiency of approximately 30%. The kinetic parameters related to the solid state thermal decomposition of the poly-nanoparticles were calculated from isoconversional methods based on multiple heating rates by TG-DTG/DTA curves.

1. Introduction

Conducting polymer systems (CPSs) have attracted much attention due to their conductive adhesive, optical and electrochemical properties, especially thermal stability and low-cost production [1–4]. The multifunctional conductive polymers (MFCPs) among CPSs are generally accepted to be insoluble in most common organic and aqueous solvents because of their conjugated structure [5,6]. Therefore, MFCPs have a low processability in the multidiscipline areas due to their stiffness. So many efforts have been carried out to improve the processability and limited usage of the pristine MFCPs because solubility is decreased with the increase in the number of high polarity functional groups. The solubility can be achieved either with ring systems substituted by alkoxy, alkyl, acyl halide and alkyl sulfonate groups or by changing the synthesis method [7–9]. Oxidative polycondensation (OP) procedure is a general way to synthesis soluble CPSs by various oxidants. OP, compared with other synthetic pathway, has some important advantages like use of simple structured oxidants, providing high productivity with less hazardous waste, and yielding soluble MFCPs.

Here, we present functionally regio-selective synthesis of a multifunctional monomer by OP in present of a suitable oxidant in an aqueous basic medium. To our knowledge, with this study, the facile and template-free oxidative synthesis of MFCP with four-functional groups has been carried out for the first time. Optical, electrochemical, and thermal properties of the resulting product were also investigated. The product was characterized by NMR, FT-IR, UV–vis, GPC, SEM, TEM analyses. In addition, the thermokinetics related to the solid state decomposition were determined by isoconversional procedures based on multiple heating rates.

2. Materials and methods

2.1. Materials

In this study, we aimed to synthesize a high-quality conjugated polymer and then achieved the regio-selectively functionalized synthesis of fluorescent polyaminonaphthol disulfonic acid nanoparticles in an aqueous medium. The monohydroxyaminonaphthol disulfonate monomer, 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid disodium salt (H-Acid disodium salt), potassium hydroxide and hydrochloric acid were purchased from Merck Chem. Co. (Germany) and then used in OP. Acetonitrile (ACN), methanol, ethanol, chloroform, acetone, tetrahydrofuran, dimethyl sulfoxide (DMSO) dichloromethane and other all solvents were

* Corresponding author.
E-mail addresses: kayaismet@hotmail.com, ikaya@comu.edu.tr (İ. Kaya).

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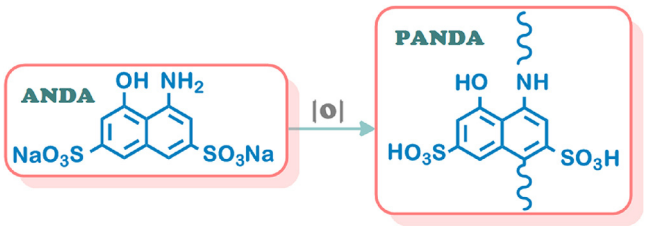


Scheme 1. Synthetic pathway for PANDA.

purchased from Merck Chem. Co. (Germany) for solubility testes and removing remaining monomer.

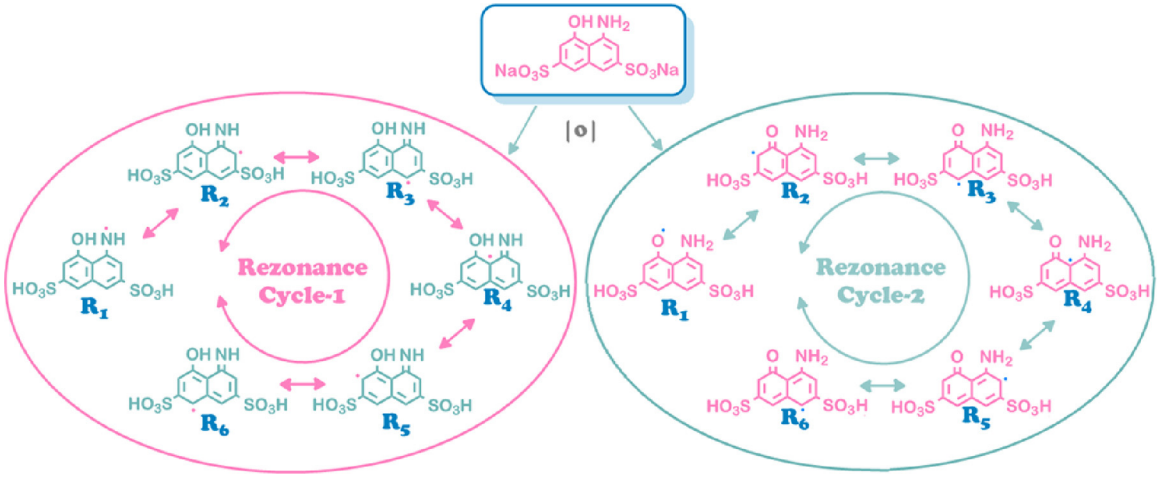
2.2. Regioselectively synthesis of PANDA

Here, PANDA was oxidatively synthesized in optimal reaction conditions by using a green chemical method (Scheme 1). PANDA was prepared by dissolving of monomer (ANDA) (0.36 g, 0.001 mol) in aqueous KOH solution (10%, 0.001 mol) into a 50 mL three neck flask. Air was passed at a flow rate of 8.5 L s^{-1} with constant stirring. In experiments the CO_2 in the air was neutralized by KOH solution of 20% before releasing the reaction medium. The black colored polymer were filtered, successively washed 3 times with 50 mL of hot water and finally dried at 60 °C in vacuum oven. The percentage yield for PANDA was found to be 82%. The yield level of OP was examined according to the temperature and time slot. The yield of the polymerization reaction was slightly increased with an increasing in temperature and then reached the maximum yield level at 60 °C for 10 h. In subsequent experiments above so-called temperature the yield decreased due to depolymerization reactions. In addition the amount of KOH used in OP significantly affects the yield of polymerization. Accordingly, the optimal reaction conditions for 10 hours at 60 °C was found as $[ANDA]_0 = [KOH]_0 = 0.03$ mol L^{-1} and air = 8.5 L sn^{-1} with 82% yield level. Scheme 1 shows functional group-selective polymerization of a tetra functional monomer. Resonance structures of ANDA compound are given in Scheme 2.

FT-IR: 3207(Ar-OH, intramolecular hydrogen bonding), 1699 (C=N), 1412 (Ar), 1356 (C-N), 1226 (C-O), 1096 (SO_3), 861 cm^{-1} (CH for substituted naphthalene ring). ^{1}H NMR (DMSO-d_6): δ ppm, 7.19 (s, Hc, 1H), 7.07 (s, Hd, 1H), 6.94 (s, Hf, 1H). Elemental analysis results for monomer: Calculated (found, %) C: 33.06 (33.00), H: 1.93 (1.90), N: 3.86 (3.75), S: 17.63 (17.55). Elemental analysis results for polymer: Calculated (found, %) C: 37.86 (37.60), H: 2.21 (2.25), N: 4.42 (4.50), S: 20.19 (19.85).

2.3. Solubility and characterization techniques

The PANDA compound was dark black color in powder form. The solubility tests were performed by using solution/polymer systems (1 mg/1 mL) at room temperature. It was completely soluble in organic solvents with high solubility parameters such as DMF, THF and DMSO because of relatively low molecular weight. However, polymer-based nanoparticle did not dissolve or partially dissolved in solvents with low solubility parameters like ethanol, acetonitrile and toluene. FT-IR spectra were measured by PerkinElmer Spectrum One FT-IR system and recorded using universal ATR sampling accessory in the mid IR region between 4000 cm^{-1} and 400 cm^{-1}. UV–vis spectra were recorded within the wavelengths of 200–800 cm^{-1} by Analytik jena Specord 210 Plus. NMR spectra of the samples were monitored in a Bruker Avance DPX-400 MHz instrument using DMSO-$_{d6}$ as solvent at 298 K. Elemental analyses of compounds were carried out with a LECO CHNS 932. 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 of Malvern Viscotek GPC Dual 270 max. For GPC investigations a medium 300 × 8.00 mm Dual column Addition 1 g/L of lithium bromide in DMF (1 mL/min) was used as solvent. Light Scattering Detector (LS) and a refractive index detector (RID) and polystyrene standards were used to analyze the products at 55 °C. Cycle voltammogram (CV) measurements were carried out by a device CHI 660C Electrochemical Analyzer (CH Instruments, Texas, USA) at various potential scan rates, along with a voltammetry cell under argon inert atmosphere at room temperature in acetonitrile/DMSO solution (v/v, 1/4). The Ferrocene/Ferrocenium (Fc/Fc^+) couple was used to calibrate the electrochemical potential of silver electrode. A Dynamic Light Scattering (DLS) instrument (Malvern CGS-3) was used to determine the sizes and the polydispersity value of poly- polynanoparticle. The surface morphology of polymer-based nanoparticle was recorded by using a Jeol JSM-7100F Schottky field emission scanning electron microscope. All the TEM images was investigated by using a Jeol JEM 1400 Plus transmission electron microscope. An atomic force microscopy (AFM) Alpha 300 A (WITec, Ulm, Germany) were used to determine the topography and 3D images of polymer-based nanoparticle films at room temperature. X-ray diffractograms were recorded by using a PANalytical empyrean model X-ray diffractometer instrument with CuK_α radiation at a wavelength of 1.54 A° over a 2θ range from 5° to 90° with the scan speed of 4°/min. Photoluminesans (PL) measurements were carried out by using Shimadzu RF-5301PC



Scheme 2. Resonance structure of 4-amino-5-hydroxy-2,7-naphthalenedisulfonic acid.