



A novel shape-controlled synthesis of bifunctional organic polymeric nanoparticles



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ABSTRACT

A novel shape-controlled bifunctional organic nanoparticle was reported using the facile synthesis of self-stabilized monohydroxy amino naphthol nanoparticles. For this purpose, bifunctional monomer was polymerized by NaOCl as oxidant in aqueous alkaline medium at 70 °C. These poly-nanoparticles with molecular weight ca. 5000 Da was obtained by template-free oxidative polymerization (OP) process. The structure of polymer was confirmed by NMR, FT-IR, UV–Vis and X-RD measurements. The chemical and physical properties of polymer were determined size exclusion chromatography (SEC), thermogravimetry (TG), differential scanning calorimetry (DSC), cyclic voltammetry (CV), photoluminescence (PL), dynamic light scattering (DLS), scanning electron microscope (SEM), transmission electron microscope (TEM) and conductivity techniques. The SEM analysis of polymer indicated to be had a nanoparticle 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 poly-nanoparticles were calculated by non-isothermal methods based on multiple heating rates.

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1. Introduction

There are many polyaromatic compounds such as polypyrrole [1], polypyrene [2], polyaminoanthraquinone [3], polynaphthalene [4], poly (aromatic ethers) [5], polyquinoline [6], polyphenol [7,8] and polyaniline [9] classes. They are used in various fields, as promising new materials because of their interesting electrical, optical, magnetic, and chemical properties. Among these polyaromatics, polynaphthalenes have especially attracted increasing interest due to their interesting intrinsic properties. With adding to various functional groups such as amine (–NH₂) or hydroxyl (–OH) to their structures, they are also profited to new properties. Because of functional groups, these types of compounds are used as an antimicrobial agent, semi-conductive, graphite, photoresist, antistatic and electroactive materials. However, although many studies on the polynaphthalenes with only one functional group have been reported so far, to the best of our knowledge, a properties of a 4,1-linked polynaphthalene (with more than one functional group) bearing both amine (–NH₂) and hydroxyl (–OH) groups into polymer backbone has not been reported until now. On the other

hand, there are very suitable synthetic routes such as the electrochemical methods, vapour deposition methods or reduction of metal salts in the presence of various stabilizers to prepare polymeric nanoparticles (PNPs). In addition, the stabilizers in such synthetic routes play a crucial role in controlling the morphology of nanoparticles. However, the hard works are recently carried out to obtain PNPs from the functional aromatic polymer by suitable synthetic routes [10–14]. In such studies, it is also investigated the important potential applications for expanding the usage of PNPs [15–17].

In this study, we easily prepared nanoparticles with ellipsoidal shapes via OP without using any external template, surfactants, stabilizers or functional dopants. The photophysical, electrochemical, thermal and morphological properties of the nanoparticle polymer were investigated with various techniques such as UV–Vis, CV, TGA, DSC, SEM and TEM.

2. Experimental

2.1. Chemicals

All solvents and 4-amino-1-naphthol (ANAP) were purchased from Merck Chem. Co. (Germany) and used as received. Sodium

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hypochlorite (30% aqueous solution) was obtained from Paksoy Chemical Co. (Turkey).

2.2. Synthesis of nanoparticles

The nanoparticles of poly(4-amino-1-naphthol) (PANAP) were synthesized in an aqueous alkaline medium as described in follow [18]: 4-amino-1-naphthol (1 mmol) and 20 mL of aqueous solution containing KOH (10%, 0.001 mol) were mixed in a 100 mL three-necked round bottom flask fitted with condenser, thermometer, and magnetic stirrer at room temperature for 1 h. The reaction mixture was heated up to 70 °C under reflux. A solution of NaOCl (30%) was added into the drop by drop for 30 min. After stirring for 5 h the color of reaction medium converted into black. Reaction mixture was neutralized by equivalent amount of HCl solution (10%, 0.001 mol) at room temperature. The resulting polymer was precipitated as black-colored particles. In order to separate the unreacted monomer, mineral salts and oxidant, the particles was filtered and washed by acetonitrile (MeCN) (30 mL) and hot water (30 mL) and then dried in a vacuum oven at 55 °C for 24 h (yield: 89%). The synthetic pathway is outlined in Scheme 1.

FT-IR: 3337 (Ar–NH₂), 1661 (C=O), 1575 (Aromatic, –C=C), 1282 (C–O–C), 787, 680 cm⁻¹ (CH for substituted naphthalene ring). ¹H NMR (DMSO-d₆): δ ppm, 8.05 (d, Ha, 1H), 7.88 (d, Hb, 1H), 7.10 (d, Hc, 1H), 7.97 (t, Hd, 1H), 6.69 (s, He, 2H).

2.3. Characterization techniques

Infrared spectra were measured by PerkinElmer Spectrum One FT-IR system and recorded by solid sample in powder form at room conditions using universal ATR sampling accessory within the wavelengths of 4000–650 cm⁻¹. UV–Vis spectra of monomer and polymer were measured in AnalytikJena Specord 210 Plus at 25 °C by using DMSO as solvent. ¹H NMR spectra (Bruker Avance DPX-400 and 100.6 MHz) were obtained by using d₆-DMSO as a solvent at room temperature. The SEC analyses were performed by using a Shimadzu 10AVp series HPLC-SEC system calibrated with a mixture of polystyrene standards. The analyses were carried by DMF/MeOH (v/v, 4/1) as eluent at a flow rate of 0.4 mL/min out at room temperature. Polystyrene standards were used because they are similar in terms of aromaticity with bifunctional organic polymeric nanoparticles. Electrochemical properties of nanoparticles were explored with a CHI 660C Electrochemical Analyzer (CH Instruments, Texas, USA) in 0.1 mol L⁻¹ tetrabutylammoniumhexafluorophosphate as supporting electrolyte. The voltametric measurements were performed in a dry box under argon gas atmosphere at room temperature. A glassy carbon working electrode (GCE) and an Ag wire were used as reference electrodes. Platinum wire was used as a counter electrode. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital

(LUMO) energy levels were calculated from oxidation and reduction onset values [19]. A Dynamic Light Scattering (DLS), (Malvern CGS-3) was used to determine the size and polydispersity value of the polymer particles. The solid-state conductivity measurements of nanoparticles pressed by using a hydraulic press were performed on a Keithley 2400 electrometer. The fluorescence measurements were determined by a Shimadzu RF-5301PC spectrofluorophotometer. A Bruker AXS Diffractometer instrument was used to obtain X-ray spectra of nanoparticles. Scanning electron microscopy (SEM) photographs of resulting nanoparticles were recorded using a Philips XL-305 FEG SEM instrument. Jeol 1400 plus model transmission electron microscopy (TEM) was used to determine the particle images. The samples were suspended in methanol and ultrasonically dispersed. 2 mL of this suspension were dried on a metal discs with carbon tape and carbon film 300 mesh Cu for SEM and TEM analyses, respectively. The TG/DTG-DTA thermograms were recorded using a PerkinElmer Diamond Thermal Analysis in dynamic nitrogen atmosphere at a flow rate of 100 mL min⁻¹ up to 1273 K. The heating rates were chosen as 5, 10, 15 and 20 °C/min and sample sizes ranged in mass from 8 to 10 mg. A platinum crucible was used as sample container. DSC measurements were performed between 25 and 420 °C (in N₂, heating rate 10 °C/min) using a PerkinElmer Pyris Sapphire DSC instrument.

3. Results and discussion

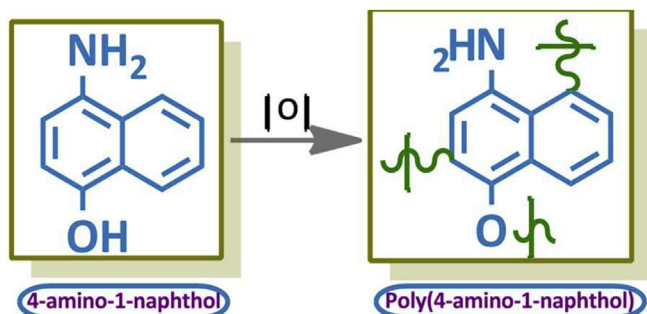
3.1. Solubility and spectral characterization

The solubility of nanoparticles was determined by using 1 mg sample and 1 mL solvent at room temperature. The nanoparticles were obtained in the black-colored powder form. They were insoluble in apolar organic solvents such as heptane and hexane while it was completely soluble in DMF and DMSO. It was also partly soluble in methanol, ethanol, acetone, and THF. The SEC chromatogram exhibited a typical mono-modal particle size distribution with a number-average molecular weight (*M_n*) of 5000 Da and polydispersity (*PD* = *M_w*/*M_n*) value of 1.2, respectively. Accordingly the nanoparticles exhibited a relatively high molecular weight including nearly 32–39 repeated units. It is well known that phenol polymers consist of a mixture of phenylene (Ph) and/or oxyphenylene (Ox) units. A comparison of the spectral data such as UV–Vis, FT-IR and ¹H-NMR provides valuable information on the chemical composition of nanoparticles.

Fig. 1 depicts UV–Vis. spectra (a) and Touch curve (b). From the UV–Vis spectra, the wavelengths of maximum absorption are observed at 337 nm for monomer and 379 nm for resulting nanoparticles. The absorption of resulting polymer is shifted to longer wavelengths because of conjugation. Equation (1) was used to determine the absorption coefficient of organic polymeric systems [20].

$$\alpha hv = A(hv - E_g)^n \quad (1)$$

where α is a linear absorption coefficient, A is an energy-independent constant, v is frequency, h is Planck constant, and E_g is energy band gap between the valence and the conduction band. n is a constant which depends on the type of optical transitions. For a direct allowed transition, direct forbidden transition, indirect allowed transition and indirect forbidden transition n is, respectively 1/2, 3/2, 2 and 3. From the linear dependence of $\ln(\alpha hv)$ vs. $\ln(hv - E_g)$ n was found to be about 2, showing that nanoparticles had an allowed indirect transition. The optical band gap was also determined to be 2.36 eV from the linear extrapolation of the curve (Fig. 1). FT-IR and ¹H NMR analyses were used to identify the structure of nanoparticles. Fig. 2 displays the representative FT-IR



Scheme 1. Synthetic method for the preparation of nanoparticles.

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