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Polyazomethines derived from polynuclear dihydroxyquinones and siloxane diamines

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ABSTRACT

New polyazomethines have been synthesized based on polynuclear dihydroxy quinones (5,8-dihydroxy-1,4-naphthoquinone and 1,4-dihydroxyanthraquinone) and siloxane diamines differing by the siloxane sequence length (1,3-bis(3-aminopropyl)tetramethyldisiloxane and α,ω-bis(3-aminopropyl)oligodimethylsiloxane having about 12 siloxane units/sequence). The structures were verified by spectral analyses. Solubility tests, GPC and viscosity measurements were performed. Some properties of the resulted polymers were investigated by thermal (TGA and DSC), electrical, spectral (UV–Vis) and electrochemical (differential pulse voltammetry) methods.

1. Introduction

Quinones are ubiquitous in electron transfer chemistry and biochemistry. Thus, in electrochemistry, p-benzoquinone commonly serves as aqueous redox indicator. Due to their ability to bind two protons and two electrons, quinones have many different states in terms of protonation and redox potential [1]. Hydroxyquinones are of high importance, since many of these compounds can be find in large amounts in many vegetal species [2]. Dihydroxyquinones are of interest for chemistry and biochemistry having important applications as a family of pharmaceutically active and biologically relevant chromophores. They are used as an analytical tool for the determination of metals and preparation of the metal complexes [3], as well as in many aspects of electrochemistry [4]. Quinizarine behaves as a reversible redox system, and is strongly adsorbed on mercury [5,6]. Electrochemical literature reflects a growing interest in the study of the redox behavior of electroactive monolayers such as those formed by anthraquinone derivatives strongly adsorpted at mercury or carbon electrodes [7,8]. The redox behavior of the naphthazarine in relation to the scavenging activity for superoxide and hydroxyl radicals, generated in inorganic and biological systems have been explored. A strongly colored metal chelating ligand system is obtained with naphtazarine. Naphtazarine and its derivatives were used as biologically active substance by mixing with a polymer to obtain a coating composition for an implantable medical device [9].

Taking into account those above presented, the idea of this paper is to incorporate such dihydroxyquinones in polymer systems, namely polyazomethines. Polyazomethines are largely used as chelating agents or as semiconductor materials [10–13]. The properties of the azomethines and their polymers depend in great measure on the kind of amine and carbonylic compounds from which they were obtained [14]. The literature is poorly regarding siloxane azomethines synthesis [15], even though the siloxane

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presence can induce some useful properties such as solubility or high gas permeability. A series of polyazomethines containing pyridine ring and oligosiloxane moieties has been synthesized as macromolecular tridentate ligands, and complexed with cobalt in order to obtain highly oxygen permselective membranes [16–18]. 5,5′-Methylene-bis-salicylaldehyde was also used as a carbonylic compound to obtain chelating polyazomethines by the reaction with siloxane diamines [19]. The using of the quinone (known as freely diffusing electron transfer mediator in analytical sensors) as a carbonylic partner would permit to obtain a new combination of interesting properties. It has been reported the immobilization of 1,8-dihydroxyanthraquinone on the silica gel in order to act as tridentate ligand for metals. For anchoring 1,8-dihydroxyanthraquinone, silica gel was first reacted with (3-aminopropyl)triethoxysilane and thereafter with the quinone. The resulting chelating matrix having three O (suitably oriented for chelating) and one N donor sites proved to have high sorption capacity for Cd(II), Pb(II) and Zn(II) [20]. It has already been reported the synthesis of polysiloxanes bearing pendant quinone moiety as polymers having redox activity [1].

In the present study, new polyazomethines have been synthesized based on 5,8-dihydroxy-1,4-naphthoquinone (naphtazarine), and 1,4-dihydroxyanthraquinone (quinizarine) and siloxane diamines. Some of the features induced by the presence of the quinone moiety have been investigated. The paper originality consists in obtaining such structures that, on our knowledge, are no reported in literature until now, and evaluation of the developed properties: thermal, spectral, redox.

2. Experimental part

2.1. Materials

5,8-Dihydroxy-1,4-naphthoquinone (naphtazarin), DHNQ, $M = 190.15$, m.p. = 220–230 °C and 1,4-dihydroxyanthraquinone (quinizarine), DHAQ, $M = 240.22$, m.p. = 195–198 °C, purchased from Aldrich were used as received.

1,3-Bis(3-aminopropyl)tetramethyldisiloxane, (AP_0), supplied by Fluka (b.p. = 142 °C/11.5 mmHg, $d_4^{20} = 0.905$) was used as received. α,ω-Bis(3-aminopropyl)oligodimethylsiloxane (AP) having an average number molecular weight of 1120 (determined on the basis of ^{1}H NMR spectrum) was synthesized according to the known procedure [19] by the bulk equilibration reaction of octamethylcyclotetrasiloxane (D_4) with 1,3-bis(aminopropyl)tetramethyldisiloxane in the presence of the base, tetramethylammonium hydroxide (TMAH), as a catalyst. The equilibrium cycles were removed from the reaction mixture by vacuum distillation, at 150 °C/5 mmHg.

Solvents: dimethylformamide (DMF), tetrahydrofuran (THF) supplied by Fluka and petroleum ether supplied by Chimopar, Romania were used as received.

2.2. Measurements

Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Vertex 70 FT-IR instrument. Analyses were performed in the transmission mode in the range 400–4000 cm^{-1} at room temperature with a resolution of 2 cm^{-1} and accumulation of 32 scans. The samples were incorporated in dry KBr and processed as pellets in order to be analyzed.

The ^{1}H NMR spectra were recorded on a BRUKER Avance DRX 400 spectrometer, using DMSO-d6 as a solvent.

Electronic absorption spectra were obtained by using an Analytik SPECORD 200 spectrophotometer with quartz cells of 1 cm thickness in DMF as a solvent.

Thermogravimetric measurements were performed with STA 490C apparatus produced by Netzsch-Germany, in static air atmosphere, in the temperature range 25–1000 °C, and a heating rate of 10 K min^{-1}. The DSC curves were recorded by the DSC 204 F1 Phoenix apparatus produced by Netzsch-Germany, in Ar flow, and using the temperature program: $25\,^\circ\mathrm{C} \to -70\,^\circ\mathrm{C}$ — isotherm 20 min $\to -70\,^\circ\mathrm{C} \xrightarrow{10\ \mathrm{K/min}} 150\,^\circ\mathrm{C}$ in Ar stream. The glass transition temperature was determined as the midpoint of the heat capacity change in the heating scan.

The reduced viscosities were determined based on the measurements of the polymer solution (about 0.5% w/v) in DMF at 25 °C by using an Ubbelohde Suspended Level Viscometer.

Gel permeation chromatographic analysis (GPC) was carried out on a PL-EMD 950 Evaporative Mass Detector instrument by using DMF as eluant after calibration with standard polystyrene samples.

Electrical measurements were performed on polymer films having thickness of about 10^{-3} cm ($0.80–1.08 \times 10^{-3}$ cm) laid down on glass plates by spin coating. The Van der Paw method (the method of the four probes) was applied to measure the electrical resistivity.

The redox activity of the synthesized quinoneimine-containing polymers was investigated by cyclic voltammetry in differential pulse regime (5 impulse/s) with the impulse amplitude of 25 mV by using a Polarograph PA-3. The scan rates: $v = 50$ mV/s. DMF was used as a solvent and 1 M solution of $NaClO_4$ as the electrolyte. The working electrode has been prepared from carbon fiber UMV-1800 °C (5 mm length, 30 μm in diameter). The reference electrode: Ag/AgCl sat.

2.3. Synthesis of polyazomethines

The reactions were carried out in a two-necked, flat-bottom flask, equipped with reflux condenser having a Dean-Stark trap attached, drying tube, nitrogen inlet and magnetic stirrer, and heated in a silicone oil bath.

For a typical procedure 2.0 g (8.3 mmol) DHAQ was solved in 20 ml freshly dried DMF. Then 5 ml dried toluene and a solution consisting in 2.3 ml AP_0 (8.3 mmol) solved in 20 ml DMF was slowly added. The colour of the reaction mixture quickly changed from orange to brown-mauve. The mixture was stirred at 100 °C 48 h. The polymer was laid down as a sticky precipitate on the glass walls. The polymer was isolated by the solvent removing, washed with water, and petroleum ether and dried in vacuum at 50 °C.