



Electrochemically Induced Synthesis of Triphenylamine-based Polyhydrazones



P. Data^{a,b,c,1,*}, P. Pander^{a,b}, P. Zassowski^b, V. Mimaite^d, K. Karon^b, M. Lapkowski^{b,c}, J.V. Grazulevicius^d, P. Slepiski^e, K. Darowicki^e

^a Physics Department, Durham University, South Road, Durham, DH1 3LE, United Kingdom

^b Faculty of Chemistry, Silesian University of Technology, M. Strzody 9, 44-100 Gliwice, Poland

^c Center of Polymer and Carbon Materials, Polish Academy of Science, M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland

^d Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254, Kaunas, Lithuania

^e Department of Electrochemistry, Corrosion and Material Engineering, Faculty of Chemistry, Gdansk University of Technology, 11/12 Narutowicza St., 80 233 Gdansk, Poland

ARTICLE INFO

Article history:

Received 2 September 2016

Received in revised form 19 January 2017

Accepted 20 January 2017

Available online 22 January 2017

Keywords:

hydrazone

triphenylamine

spectroelectrochemistry

EPR

DEIS

ABSTRACT

Triphenylamine-based hydrazones were subjected to electropolymerization process that gave well conductive hydrazone based polymers. The first example of polyhydrazone formation during the electrochemical process was shown. The estimation of polymer structure was demonstrated using IR spectroelectrochemistry. The EPR spectroelectrochemistry allowed to explain why in some cases dimer couldn't be formed. The results of electrochemical, spectroelectrochemical investigation of small molecules, as well as their polymers obtained by electropolymerization, are presented. The comparative study of electropolymerization and doping process by IR, EPR, potentiostatic and potentiodynamic UV-Vis-NIR, DEIS spectroelectrochemical techniques was performed to determine the reaction path, charge carriers and conductivity of polymeric layers.

© 2017 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

Hydrazones have been extensively studied in various fields ranging from organic synthesis [1–3], supramolecular chemistry [4–6], medicinal chemistry [7–10]. They have been used as dyes [11,12], hole-transporting materials [13,14], organic nonlinear optical materials [15] in metal and covalent organic frameworks [16–19], dynamic combinatorial chemistry (DCC) [20–22], dye-sensitized solar cells [23] and molecular switches [24]. The modularity, straightforward synthesis, and stability towards hydrolysis of hydrazones can be mentioned as the reasons for their popularity [14]. Hydrazones can be prepared by three main synthetic pathways: coupling between aryl diazonium salts and b-keto esters or acids, which is also known as the Japp–Klingemann reaction [25], coupling between hydrazines and ketones or aldehydes [26] and coupling between aryl halides and non-substituted hydrazones [27]. The readily obtained compounds are usually highly crystalline and precipitate out of

the reaction mixture, which simplifies their purification process. Due to the simplicity of the synthesis and high charge carrier mobilities hydrazones play an important role among organic hole-transporting materials, especially those used in electrophotography [28,29]. Crystalline aromatic hydrazone molecules are not capable of forming thin, neat homogenous layers, and must be used in combination with polymeric hosts in use as the main constituent of electrophotographic devices or active layer in optoelectronic devices. Recently, new monomers [30,31] and polymers [32–34] based on dihydrazone moieties capable of yielding the polymeric hole transport layers were reported. These monomers and polymers exhibit high hole drift mobilities and good film-forming properties. All these polymers were synthesized in the polyaddition reaction with bifunctional nucleophilic linking agents in the presence of a catalyst. Some of them can be chemically cross-linked in the layer by reaction of the hydroxyl groups with polyisocyanates [35]. Such cross-linked systems [30] enable to prepare electrophotographic photoreceptors with high solvent resistance and good mechanical properties [36,37].

In this study, we investigated hydrazone derivatives (Fig. 1) that can be polymerized electrochemically giving conductive polymers. In recent years, many molecules containing hydrazone moiety and having electroactive properties were synthesized. They had

* Corresponding author.

E-mail address: Przemyslaw.Data@dur.ac.uk (P. Data).

¹ ISE member.

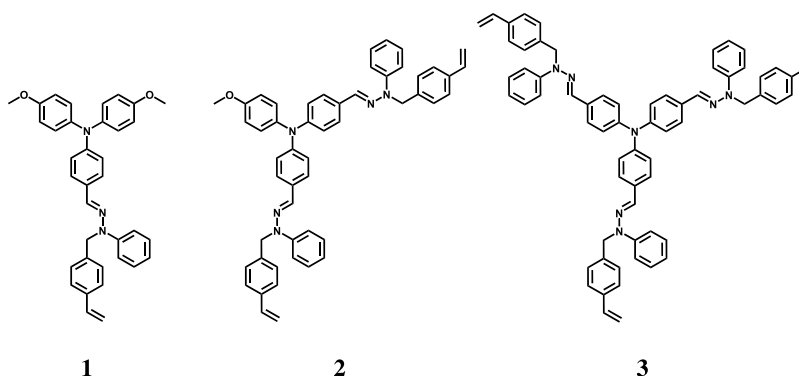


Fig. 1. The chemical structures of investigated compounds.

different electrophores, such phenothiazine [38], triphenylamine [39] or 3,4-ethylenedioxythiophene [40]. To the best of our knowledge, this is the first report on the preparation of conductive polymers by electrochemical polymerization of compounds containing hydrazone moieties. Molecules containing hydrazone moiety substituted by phenylene units are electroactive and have been the subjects of numerous electrochemical studies [41–43]. However, there are no reports of the synthesis of conducting polymers containing hydrazine species.

2. Experimental Section

2.1. Materials

The synthesis of the investigated compounds is reported in the literature [31]. All the solvents used for the measurements were dried and distilled before use. The commercial reagents were used without purification. Electrochemical measurements were done in 1.0 mM concentrations of all compounds for all the cyclic voltammetry measurements. Electrochemical studies were conducted in 0.1 M solutions of Bu_4NBF_4 , 99% (Sigma-Aldrich) in dichloromethane (DCM) solvent, CHROMASOLV[®], 99.9% (Sigma-Aldrich) at room temperature. UV–vis spectroelectrochemical measurements were performed on the ITO (Indium Tin Oxide) quartz glass working electrode coated with polymers.

2.2. Measurements

The electrochemical investigations were carried out using a potentiostats Autolab PGSTAT20 and Metrohm Autolab

PGSTAT100. The cyclic voltammetry (CV) measurements were performed with 1.0 mM solutions of compounds. Electrochemical studies were carried out using 0.1 M solutions of Bu_4NBF_4 in dichloromethane (DCM). The electrochemical cell consisted of 1 mm diameter platinum disk working electrode, Ag/AgCl electrode as a reference electrode and platinum coil as the auxiliary electrode. All electrodes were cleaned before use. The platinum working electrode was polished before use on a polishing pad with 1 μm alumina slurry, then the platinum electrode was rinsed with deionized water and cleaned in an ultrasound bath with deionized water for 15 minutes. After water cleaning the electrode was rinsed with isopropanol (3x), acetone (3x) and dried. The electrode was used directly after cleaning. CV measurements were conducted at room temperature at a potential rate of 50 mV/s and were calibrated against ferrocene/ferrocenium redox couple. UV-Vis-NIR spectroelectrochemical measurements were performed using Indium Tin Oxide (ITO) deposited on quartz glass substrate as the working electrode. Polymeric layers were synthesized on ITO electrode at the conditions similar to that of CV measurements. UV-Vis-NIR spectroscopy and spectroelectrochemistry experiments were performed using QE6500 and NIRQuest detectors (Ocean Optics). IR measurements were carried out using PerkinElmer Spectrum Two FT-IR Spectrometer equipped with UATR attachment with diamond crystal. The in situ IR-ATR-spectroelectrochemical measurements were done using vertical ZnSe crystal that was located between two opposite, large surface area electrodes forming with the crystal walls a thin-layer cavity. Electron paramagnetic resonance (EPR) measurements were performed using a JEOL JES-FA200 spectrometer coupled with an Autolab PGSTAT 100N potentiostat. Measurements were

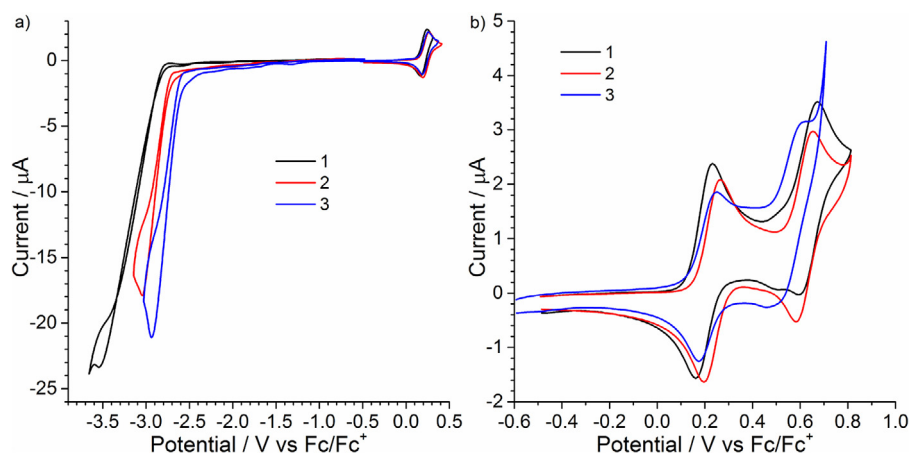


Fig. 2. CV curves of compounds 1–3 at broad oxidation reduction potential range (a) and oxidation range (b). Sample concentration 10^{-3} M, scan rate $0.05 \text{ V}\cdot\text{s}^{-1}$, dichloromethane solution for oxidation and THF for reduction. All potentials vs Fc/Fc^+ redox couple.

Download English Version:

<https://daneshyari.com/en/article/6471354>

Download Persian Version:

<https://daneshyari.com/article/6471354>

[Daneshyari.com](https://daneshyari.com)