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Electrosynthesis and study of some physical properties of conductive and solid-state gas sensing polydiphenylamine

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ABSTRACT

Polydiphenylamine was prepared using electrochemical oxidation of the corresponding monomer diphenylamine in an acetonitrile solution containing sodium perchlorate ($NaClO_4$) and characterized spectroscopically. First, some physical characterization using infrared (FTIR) measurement shows that this material has a polymeric structure. Moreover, Differential Scanning Calorimetry (DSC) and thermal gravimetric analysis (TAG) showed a good stability at temperatures above 200 °C. Second, the electrical conductivity and dielectric properties of polydiphenylamine were studied as guides for sensing performance using impedance spectroscopy technique in the frequency range 5 Hz–13 MHz at various temperatures (118–150 °C).

DC conductivity is thermally activated with activation energy around 0.65 eV. On the other hand AC conductivity is investigated through Jonscher law. The imaginary part of the complex impedance has a maximum whose relaxation frequency increases with temperature according to Arrhenius law. Finally, Values of dielectric constants ε_1 and ε_2 were calculated.

1. Introduction

During these last years, much work has been devoted to the synthesis of the conductive polymers [1]. These materials have the advantages of being lightweight, easy to implement and inexpensive in comparison with conventional semiconductors such as silicon and germanium. The abundance of organic resources is a potential argument for their use and enhancement in solid-state gas sensors domain, electronics and optoelectronics fields.

Several conductive polymers have been studied such as polyacetylene [2–4], the polyaniline [5–7], poly-thiophene [8,9] and poly-pyrroles [10,11]. The common property of these materials is the combination pi–sigma that sprawled along the molecule. Previous studies have shown that the mechanism is connected to the conduction of the π bond delocalization throughout the chain of the molecule [12–14]. The synthesis of π-conjugated polymers by different methods and under different conditions may be at the origin of several interesting physico-chemical properties.

Several methods have been used for the synthesis of these organic semiconductors [15–21].

Among them, the electrochemical technique [22–25] leads to the synthesis of π conjugated polymers, which is simple, cost effective technique. Also, this process can control the length of the polymer chain with a good choice of potential and lasted polymerization as well as the use of appropriate doping of the polymers during the synthesis.

This work aims to prepare the polydiphenylamine by a simple electrochemical root using a starting solution containing acetonitrile and sodium perchlorate as supporting electrolyte. Some physical properties have been carried out. Particular attention is paid on both thermal stability in terms of thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) as well as electrical properties using conductivity at various temperatures.

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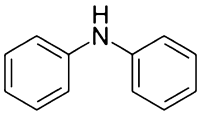

Fig. 1. Semi structural formula of diphenylamine.

2. Experimental details

2.1. Polydiphenylamine preparation

Polydiphenylamine (PDPA) was electro-synthesized potentiodynamically by means of cyclic potential between 0.0 and 1.5 V in a solution containing diphenylamine (Fig. 1) (varying concentrations specified for each reported result) and sodium perchlorate ($NaClO_4$, 0.1 M). The polymer film was grown on a Pt electrode. A Pt wire served as a counter electrode and all potentials are quoted against an ECS reference electrode. Prior to the polymerization, the solution was degassed using nitrogen as inert gas.

The electrolysis of an agitation power of monomer was carried out at constant potential in a nitrogen stream using the PGP potensiosat 201 provided with a load. During the electrolysis, the charge integrator is programmed to pass an electron per molecule.

After the electrolysis, a step regarding extracting, purifying and drying is necessary to obtain the polymer in powder form.

2.2. Characterization techniques

IR transmission spectra were performed in order to confirm the polymerization of diphenylamine monomer using a Mattson Cygnus 100 (FT-IR) spectrophotometer. The Differential Scanning Calorimetry (DSC) and the thermo-gravimetric analysis (TGA) were performed using a Du Pont thermal analyzer, 3D surface topography of all obtained films was performed in taping mode by an atomic force microscopy (VEECO digital instrument).

The electrical conductivity measurements of the polymer have been obtained by means of an automatically controlled HP4192A analyzer working at 120 frequencies, log-scaled between 5 Hz and 13 MHz whose principle set up is displayed in Fig. 2. In electrical measurements, a sinusoidal signal of 50 mV has been applied.

These measurements were carried out on a thickness wafer of 0.93 mm and 13 mm as diameter. Finally, the electrodes were painted on both ends of the sample with silver paste, Fig. 3. To avoid the problems of thermal stability, the electrical measurements were limited to 150 °C (Fig. 4).

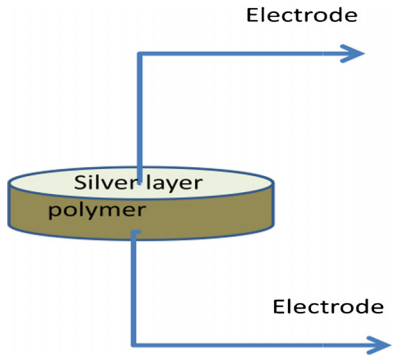

Fig. 3. Configuration of Ag/polymer/Ag samples for the electrical measurements.

3. Results and discussion

3.1. Cyclic potential

Fig. 3a and b shows the cyclic voltammograms recorded in 10^{-1} M $NaClO_4$ during the electrochemical oxidation of 10^{-3} M and 10^{-2} M of diphenylamine (DPA) on a platinum substrate. The working electrode was immersed in this solution at a controlled potential of 0 V in order to avoid the initial oxidation of the monomer species. Then, the potential was cycled between 0 and 1.3 V at a constant speed rate of 10 mV s^{-1}. These scans show the maximum current is reached at 0.88 V for 10^{-3} M diphenylamine concentration whereas this maximum is shifted to 0.9 V for 10^{-2} M concentration. This red shift is related to the difference of DPA concentration. In addition, during the reverse scan any reversible reduction of oxidized.

DPA species is not observed. From the first scan, it is assumed that there is the existence of a rapid chemical reaction coupled to the electrochemical one. This effect becomes obvious in the voltammogram of the most concentrated solution. This result suggests the presence of a mechanism of polymerization from the monomer (DPA) to the polymer (PDPA). Since the scanning is performed in the oxidation direction, at the anode, which is seat oxidation, it is likely to pass from two monomers neutral into two radical cations, which form the dimer. In the second step, the formation of radical cations based on monomers and dimers gives the associated polymer the polydiphenylamine (PDPA) by symproportionation reaction. This phenomenon is also observed in a substrate monomer based on DPA such as 2-aminodiphenylamine [26] and 4-aminodiphenylamine reported previously [27,28].

Moreover, the effect of the monomer concentration on the peak oxidation can be seen in terms of current and potential. The intensity decreases with the order of the cycle but remains non-zero.

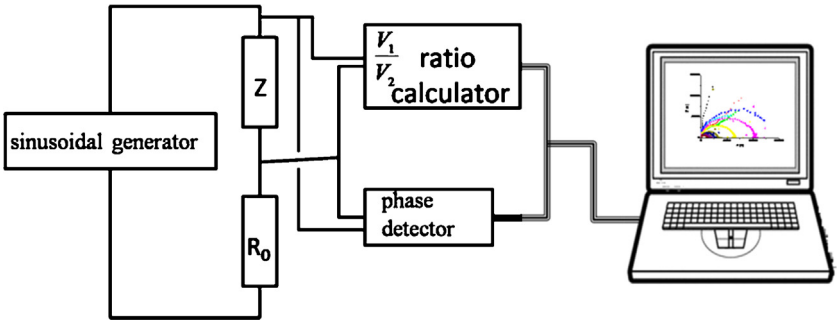

Fig. 2. Schematic principle of mounting impedance measurement.