

OBTAINING OF NEW MODIFIED ELECTRODES BY ELECTRODEPOSITION OF AZULENE POLYMERIC FILMS

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ABSTRACT

Preliminary assays of the chemical and electrochemical oxidation of azulene-1-azobenzene and 2-[(E)-2-azulen-1-ylvinyl] thiophene were performed. Oligomers of azulene-1-azobenzene and 2-[(E)-2-azulen-1-ylvinyl] thiophene were synthesized by sweeping of potential between -0.1 and 1.8V in 0.1M tetrabutylammonium tetrafluoroborate – acetonitrile (TBATFB-ACN). The redox characterization of the polymeric films was performed in monomer free solution of TBATFB-ACN. The electrodeposition of these monomers occurs by a E(CE)_n mechanism, the initial oxidation of the monomer is followed by chemical (radical-radical) coupling step with another oxidised monomer to form a dihydro dication dimer which loses two protons to form a neutral dimer.

KEYWORDS

Conducting polymers, azulene, modified electrodes, azulene-1-azobenzene, 2-[(E)-2-azulen-1-ylvinyl] thiophene

1. INTRODUCTION

Many electronically conducting polymers have been prepared by electrochemically oxidizing of pyrrol, aniline, thiophene, aminonaphthalene, azulene, benzene, and their derivatives. The dramatic changes in the electronic, magnetic, optical and structural properties of conjugated polymers upon „doping” have been studied extensively, both theoretically and experimentally. A polymer can be made conductive by oxidation (p-doping) and/or, less frequently, reduction (n-doping) either by chemical or electrochemical means to generate the mobile charge carriers. It is well known that doping can improve the performance of light-emitting diodes. Polyazulene has been known to exhibit good electrochemical activities and an excellent reversible doping-undoping behaviour which allowed it to be used as a cathode material in nonaqueous batteries. Due to of some structural characteristics of azulene and its derivatives such as an appreciable dipole moment ($\mu = 0.8 - 1.08$ D), low ionization energy, high electron affinity and a tendency to form stabilized radical cations these materials were

becomed an attractive research target in the area of materials science.

Polythiophenes are one of the most extensively investigated families of conducting polymers. They exhibit high thermal and environmental stability in both the neutral and doped states and their properties could be varied over a wide range of solubility, conductivity, processability and stability depending on their conformational behaviour, the type of substituents attached, and their molecular electronic structure.

Much attention has been paid to the design and synthesis of multicomponent π -conjugated polymers whose electronic properties can be reversibly transmitted upon external stimuli. Incorporation of electroactive unit as a substituent or repeating component in the polymer backbone is one of the successful approaches to prepare new stimuli-responsive conjugated polymers. Despite of remarkable optical and electrochemical properties of azulene there are few reports regarding to azulene-containing conjugated polymers.

Potential applications include field-effect transistors, capacitor coatings, battery electrodes, light-emitting diodes, nonlinear

optical materials, molecular wires, and molecular switches. This paper reports the obtaining of polymeric films by electrochemically oxidizing of *azulene-1-azobenzene* and 2-[(E)-2-azulen-1-ylvinyl] thiophene.

2. EXPERIMENTAL

2.1 Chemicals

The starting materials, *azulene-1-azobenzene* and 2-[(E)-2-azulen-1-ylvinyl] thiophene were synthesized and purified according to the literature method.

Electrolyte support used was 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) from Fluka. Acetonitrile (ACN) from Aldrich was distilled before each experiment and dried over basic alumina (\cong 150 mesh, Aldrich).

2.2. Cyclic Voltammetry

The cyclic voltammetric (CV) measurements were performed in a three electrode cell with a Pt disc (0.07 cm^2) as working electrode (WE), a Pt wire as counter electrode (CE) and a Ag/AgCl as an pseudo reference electrode (calibrated vs ferrocene). The WE was polished mechanically with 0.3 and 0.05 μm alumina powder prior to all measurements.

The polymerization of azulene-1-azobenzene (A1AB) and 2-[(E)-2-azulen-1-ylvinyl] thiophene (A1VT) has been done in ACN containing 0.1 M TBATFB and 10 mM monomer. The polymeric films were characterized in monomer free solutions of 0.1 M TBATFB and the applied potential was controlled with an Autolab (PGSTAT 20) potentiostat. Prior to each measurement the working solution was deaerated with nitrogen for 15 minutes and during the measurement the solution was under atmosphere of nitrogen.

The experimental conditions for growing both PA1AZ and PAVT films were as follows: under potentiodynamic conditions, 20 scans on potential range between -1.0 and 2.0 V for A1AB and between -0.1 and 1 V for A1VT, at 50 mV s^{-1} scan rate for 10 mM azulene-1-azobenzene or 2-[(E)-2-azulen-1-ylvinyl] thiophene, 0.1 M TBATFB in ACN. Both

polymers were then characterized in 0.1 M TBATFB, ACN solution.

3. RESULTS AND DISCUSSION

In order to perform a study of the electropolymerization of azulene-1-azobenzene and 2-[(E)-2-azulen-1-ylvinyl] thiophene cyclic voltammetry was used. In Figure 1 a CV of a polymerization experiment of a PA1AB film from a monomer solution is shown.

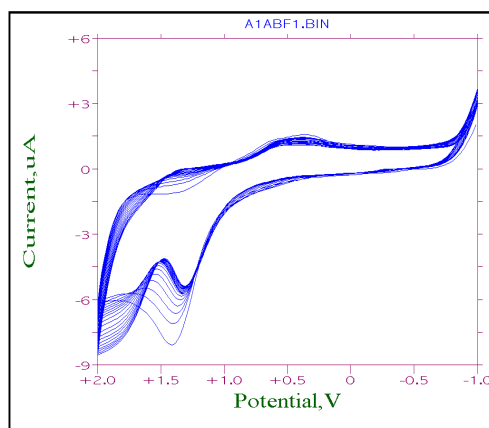


Fig. 1. Successive voltammograms of polymerization of A1AB film from monomer solution

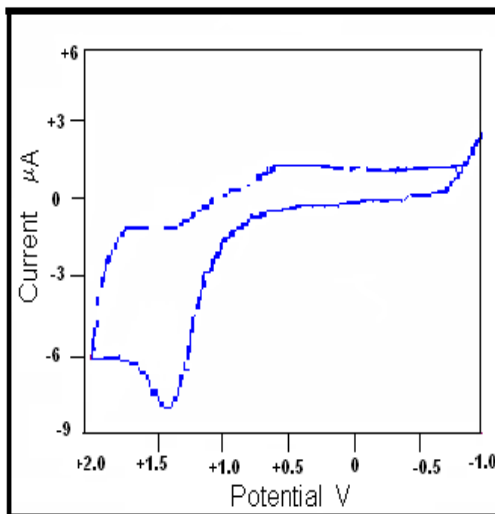


Fig. 2. The CV of the A1AB film in monomer-free solution made as in Fig. 1

In the first cycle, during anodic polymerization by potential cycling, the oxidation peak from

1.85 V corresponds to formation of radical monomer cations. On the reverse scan, the reduction peak corresponding to this oxidation is not always observed. This indicates that in the time scale of the experiment, the intermediate reactive radical monomer cations dimerize in the subsequent chemical reaction. Starting with the second potential scan a current peak at lower potential, 1.4 V than the monomer oxidation peak 1.85 V is observed. This corresponds to oxidation of the formed oligomer chains. On the reverse scan, a peak current due to reduction of the oxidized oligomer species is observed. The polymeric film is growing during subsequent oxidative and reductive potential scans.

The redox peak currents increase until the polymer stops growing on the surface of the electrode. When the monomer is less converted to radical cations in the vicinity of the electrode the current peak corresponding to monomer oxidation more and more is diminished.

Recording a CV of a polymeric film in monomer free electrolyte solution reveals a lot of information concerning that polymer. The electrochemical potential window within which the PA1AB film is active is between 0.6 and 1.5 V. The CV of the PA1AB film from the polymerization in Fig. 1 recorded in monomer free electrolyte solution is shown in Fig. 2.

The redox properties of the PAVT film synthesized in 0.1 M TBATFB in acetonitrile were also studied by cyclic voltammetry. The successive voltammograms of the PAVT film in 10 mM 2-[(E)-2-azulen-1-ylvinyl] thiophene and the dependence of peak current versus square root of scan rate are shown in Fig 3 and respectively Fig. 4.

In order to see if the linear diffusion model is applicable for the oxidation or reduction of polymer films the cyclic voltammograms were recorded at different scan rates for the polymer film in a solution without monomer.

As could be observed in Fig 4, the peak current is directly proportional to the scan rate, this means that the thickness of the film is smaller than the diffusion layer thickness of counter anions which must diffuse in and out during doping and dedoping processes.

The diffusion model applicable to oxidation or reduction of the polymeric films was shown to

depend on the thickness of the film examined. The thickness of the PA1VT film used for this study was about 4 μm .

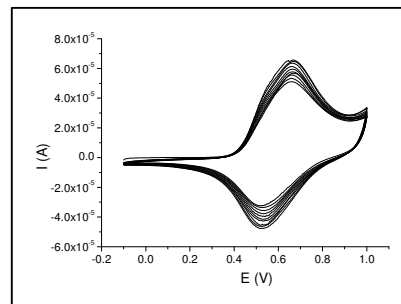


Fig.3 Cyclic voltammograms of 1mM 2-[(E)-2-azulen-1-ylvinyl] thiophene at Pt electrode, TBATFB 0.1M, CAN

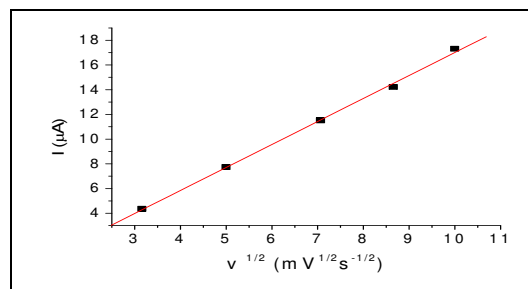


Fig.4 Dependence of peak current on the square root of the scan rate for 1mM 2-[(E)-2-azulen-1-ylvinyl] thiophene)]

The calculated film thickness was defined as:

$$g = (q M_{\text{mon}}) / (n F A \rho)$$

where

- M_{mon} = molar mass of the monomer
- n = the number of electrons taking part in oxidation of one monomer unit
- A = the area of the electrode used in experiment
- ρ = the film density approximated to 1 g/cm^3
- q = total charge used for polymerization
- F = Faraday constant

We decided to use this modified electrode for catalytic purposes. Preliminary studies were performed using the modified electrodes by polymeric films of 2-[(E)-2-azulen-1-ylvinyl] thiophene for hydrogen peroxide determination in order to assemble oxidase based biosensors. In Figure 5 might be seen

that the PA1VT film exhibits an electrocatalytic response to the reduction of H_2O_2 in a 0.1 M phosphate buffer solution, pH = 7.4

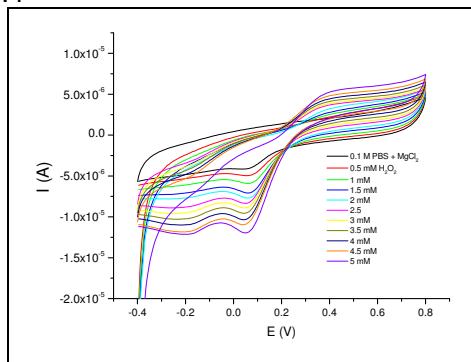


Fig. 5 Cyclic voltammograms of modified electrode by 2-[(E)-2-azulen-1-ylvinyl] thiophene in PBS pH = 7.4, different concentrations of H_2O_2

4. CONCLUSIONS

This paper demonstrates that new conducting polymers were synthesized by electrochemical polymerization. The classic mechanism by anodic coupling is discussed. In the first step the neutral monomer is oxidized to a radical cation, which reacts with other radical cations in the electrolyte solution. If the radical cation is too reactive can react with other nucleophiles before polymerization. If the radical cation is too stable it may have time to diffuse far from the electrode surface before reaction and no polymer film is formed.

The CV responses of these modified electrodes by PA1VT in the presence of H_2O_2 in a 0.1 M phosphate buffer solution at pH = 7.4 suggest that these conducting polymers could have a potential application as biosensors.

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