

## Kinetic study of 3,6-dimethylthieno[3,2-*b*]thiophene electropolymerisation

S.B. SAIDMAN<sup>1,\*</sup>, R.O. GARAY<sup>2</sup> and J.B. BESSONE<sup>1</sup>

<sup>1</sup>*Instituto de Ingeniería Electroquímica y Corrosión (INIEC), Universidad Nacional del Sur, Bahía Blanca, Argentina*

<sup>2</sup>*Instituto de Investigaciones en Química Orgánica (INIQO), Universidad Nacional del Sur, Bahía Blanca, Argentina*  
(\*author for correspondence, e-mail: ssaidman@criba.edu.ar)

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### Abstract

A systematic investigation was carried out by means of cyclic voltammetry, chronoamperometry and chronopotentiometry on 3,6-dimethylthieno[3,2-*b*]thiophene (DMTT) electropolymerisation on vitreous carbon in acetonitrile (ACN) containing 0.1 M LiClO<sub>4</sub>. The electrochemical doping–undoping process was reversible and the coulombic efficiency over a charge–discharge cycle was ca. 100%. The electropolymerisation mechanism was unchanged by the presence of methyl groups. When an aluminium electrode was used, poly(DMTT) deposition could only be performed in the potentiostatic mode. In this case, electropolymerisation hindered the pitting process on Al, which was initiated in the early stages of anodisation.

### 1. Introduction

Polymers with good cyclability and colour change upon electrochemical reaction have possible uses in rechargeable batteries and electrochromic displays. Thus, fused-ring systems containing thiophene units have been electropolymerized under various conditions due to their conducting, optical and catalytic properties [1].

Thienothiophenes are much easier to oxidise than thiophene itself due to the larger  $\pi$ -electron delocalisation in the fused-ring structure [2]. Hence, the corresponding polymers can be driven to a reduced state by setting the electrode potential to more negative values. Electropolymerisation of thieno[3,2-*b*]thiophene was reported by Danieli et al. [3]. Electrochemical characterisation by cyclic voltammetry showed that the polymer, which has low conductivity, could be repeatedly transformed between the doped and the undoped species. The polymer is expected to consist mainly of  $\alpha,\alpha'$ -linked units since  $\alpha$ -substituted derivatives do not yield polymeric products [2]. The reactivity of the starting monomer, which is influenced by the substituents steric and electronic properties, affects the resulting polymer quality. Among others, alkyl groups are common substituents at the  $\beta$ -position of thiophene rings. The positively charged polymer chain is stabilised due to the inductive effect of the alkyl groups [1, 4]. Also, the 3,4-substitution in the thiophene ring facilitates the formation of linear polymer chains, which should lead to increased conjugation length, and also lowers the oxidation potential at which the monomer polymerises [5]. Thus, the substitution of the thieno[3,2-*b*]thiophene

may result in new possibilities for the modification of the polymer properties. Consequently, we performed a systematic investigation by means of cyclic voltammetry, chronoamperometry and chronopotentiometry of 3,6-dimethyl thieno[3,2-*b*]thiophene (DMTT) electropolymerisation in acetonitrile (ACN) electrolyte.

There has been an increasing interest lately in the use of conducting polymers as anti-corrosion coatings. Therefore, a first attempt to deposit poly(DMTT) on aluminium was performed. In spite of the fact that aluminium is an electroactive metal and that anodic electropolymerisation thereon is consequently very difficult, polymer coatings have already been achieved from other monomer solutions in aqueous and non-aqueous electrolytes [6–10].

### 2. Experimental details

Vitreous carbon or aluminium (99.999%, Aldrich Chemical Company) rods embedded in a teflon holder with an exposed area of 0.070 cm<sup>2</sup> were used as working electrodes. The electrodes were polished with 1000 emery paper, 1 and 0.3  $\mu$ m grit alumina suspensions, then cleaned with triple distilled water and wiped with filter paper. A monomer modified carbon paste electrode was also used. Carbon paste was prepared by hand mixing 1.00 g of graphite (Graphite extrapure, Merck), 0.4 ml of paraffin-oil (Uvasol, Merck) and 0.16 g of sodium dodecyl sulphate. The auxiliary electrode was a large Pt sheet. The reference electrode was an Ag/AgCl (Metrohm) with a standard potential of 0.100 V vs NHE