

# Electrosynthesis of Highly Conducting Polythiophene Thin Film in Perchloric Acid

## Key Words:

electropolymerization, polythiophene, conductive polymers, thiophene, electrochemical oxidation

*A. Entezami and N. Arsalani*

Department of Organic Chemistry, Faculty of Chemistry, Tabriz University, Iran

## ABSTRACT

Electroactive/conductive polymer film can be generated on an electrode surface by the oxidation of thiophene in highly concentrated perchloric acid. The mechanism of electropolymerization has been proposed in acid perchloric solution.

## INTRODUCTION

The electrochemical oxidation of thiophene in organic solvents leads to the formation of electrically conducting polythiophene film on the electrode surface [1]. Thin film of polythiophene, when supported by an electrode surface, can be electrochemically cycled between the oxidized conducting state and the neutral insulating state [2]. In this paper, we report the electrochemical polymerization of thiophene in concentrated perchloric acid. The electrochemical oxidation of thiophene in acid media leads to the formation of polythiophene. We have shown that polythiophene prepared in concentrated perchloric acid has similar behaviour as polythiophene obtained in organic media.

## EXPERIMENTAL

All compounds were obtained from commercial sources. Polythiophenes were synthesized in a three electrode, single compartment cell.

Platinum disc (0.5 cm<sup>2</sup>), platinum wire, and saturated calomel (SCE) were used as the working, counter, and reference electrodes, respectively. The solutions were typically 0.02 M thiophene in concentration perchloric acid. The solution was bubbled with nitrogen for 10 - 15 min. Polymers were grown on platinum disc electrode under scan potential in the range of 0.00 - 1.10 volts in 9.1 M HClO<sub>4</sub> and under potentiostatic condition (0.75 V) in 11.6 M HClO<sub>4</sub>. After the polymerization, the anode was rinsed with HClO<sub>4</sub>

with the same concentration and transferred to another three - electrode cell containing 9.1 or 11.6 M HClO<sub>4</sub>. Cyclic voltametric experiments were performed with Polarecord E 506 combined with VA - Scanner E 612 and 7015 A X - Y Recorder Hewlett Packard. Coulostat E 254 Metrohm Herisau was used for polythiophene film at fixed potential. UV spectra were acquired with Model 2100 Shimadzu.

## RESULTS AND DISCUSSION

The cyclic voltamogram of a film from polythiophene in 9.1 M HClO<sub>4</sub> at a different sweep rate, clearly shows that the polymer can be oxidized ( $E_{pa} = 0.30$  V) and reduced ( $E_{pc} = 0.20$  V), (Figure 1(A)). In cyclic voltammetry in the range 0 - 1.1 V an irreversible oxidation peak of thiophene is observed at 0.98 V. The maximum of current,  $I_p$ , linearly varies with the sweep  $v$  (Figure 1(B)). This behaviour is characteristic of an electroactive film grafted on an electrode where diffusion phenomena do not exist. The oxidation or doping of the polymer (evolving from a red state to a blue state) corresponds to the transfer of one charge from the electrode to the polymer, and then to the migration of this charge by a hopping mechanism to the film - electrolytic media interface. An anion, present in the solution, must then migrate inside the polymer in order to ensure electroneutrality. This phenomenon repeats until all electroactive sites are oxidized. This process is accompanied by a volume expansion of the polymer. Where as Tourillon has been able to show that, in the case of polymethylthiophene, the thickness varies from 160 nm in the

neutral undoped state to 200 nm in the oxidized doped state [3]. These oxido-reduction processes of polymer are fully reversible. The cyclic voltammogram for a film of polythiophene were generated via oxidation of thiophene at fixed potential (750 mV) in 11.6 M HClO<sub>4</sub>, shows that the polymer can be oxidized (E<sub>pa</sub> = 0.45 V) and reduced (E<sub>pc</sub> = 0.32 V),

(Figure 2). The shift of E<sub>pa</sub> in Figures 1(A) and 2, relates to the characteristic of film on the electrode surface. This characteristic is due to the different step of growing chains of polymer and concentration of reactants media. One of the most important aspects of this reaction is that it has electrochemical stoichiometry and occurs via a nucleation and phase growth mechanism akin to the deposition of metal on to a foreign substrate [4, 5]. In different media the apparent stoichiometry for the film forming reaction is in the range 2.06 - 2.5 Farads / mole of monomer (for example, pyrrole, thiophene, azulene, carbazole), [6].

The polymerization is very complicated and the mechanism has been described with pyrrole and with azulene [6]. The initial step involves the oxidation of the monomer, and the polymerization reaction proceeds when and only when the potential is sufficiently high to oxidize the monomer. Thus at the anode, the concentration of monomer is low. These conditions favor the radical cation dimerization process. The initial combination product of two radical cations is the dication of the dihydrodimer which subsequently deprotonates to produce the aromatic dimer. The dimer is next oxidized, coupled, and deprotonated to produce the next higher homologue. The reaction is an extension of the ECE mechanism (i.e., a sequence of steps where by an electron transfer event (E) is followed by a chemical reaction (C) and a subsequent electron transfer reaction (E), and the E (CE)<sub>n</sub> is suggested. Oxidation of the polymer and incorporation of counter anions result in the polymer-anion composite film [7].

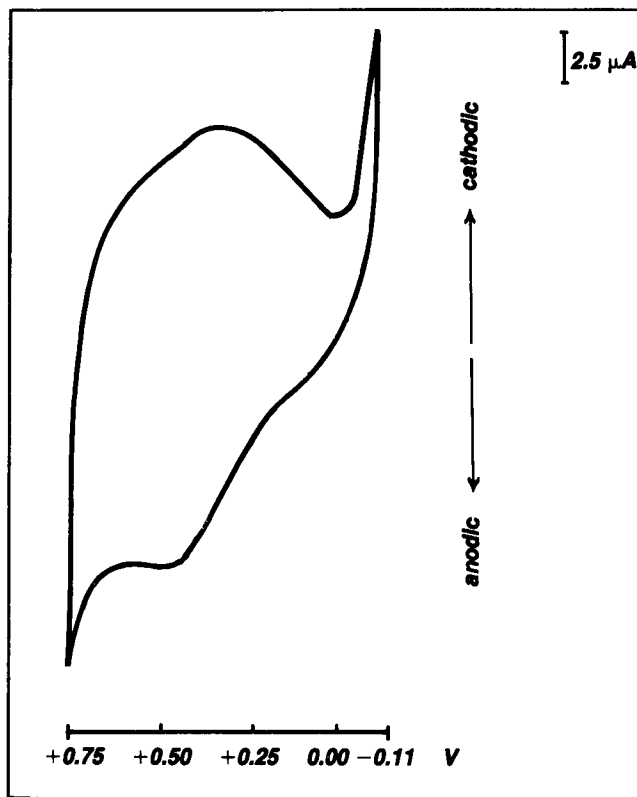


Figure 2: Cyclic voltammogram of polythiophene-Pt, prepared in perchloric acid (11.6 M) by potentiostat, sweep rate 50  $\frac{mv}{s}$ .

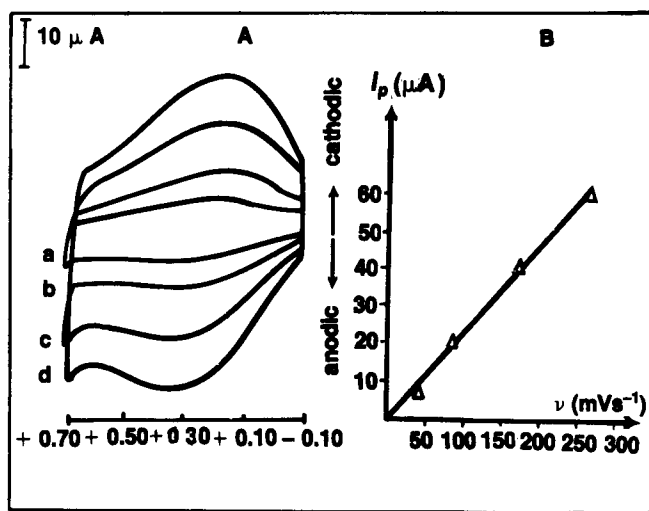


Figure 1: (A) variation of the current  $I_p$  with the sweep rate: (a) 50  $\frac{mv}{s}$  (b) 100  $\frac{mv}{s}$  (c) 200  $\frac{mv}{s}$  (d) 300  $\frac{mv}{s}$ . (B) Linear relationship between  $I_p$  and  $v$ .

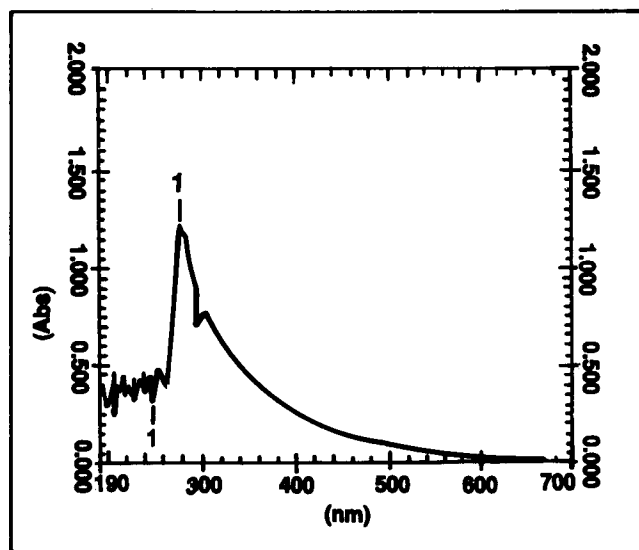
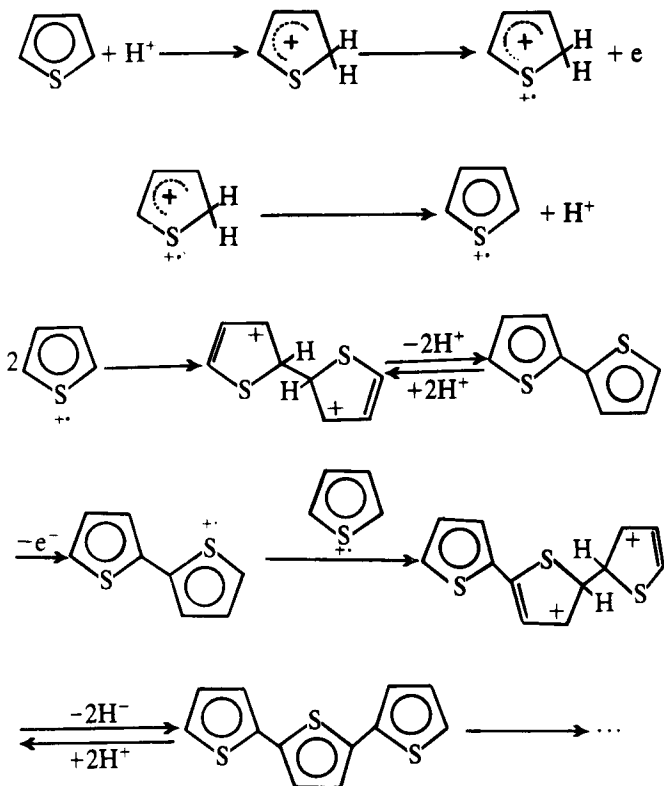


Figure 3: U.V. spectra of protonated thiophene in perchloric acid (9.1 M).

The final step in the reaction is also not clear, however, there is some reaction with moisture to produce oxygenated material. In the case of polythiophene obtained in concentrated perchloric acid, the mechanism of elec-

tropolymerization is only different in the initiation step. At first the thiophene in concentrated perchloric acid is protonated as can be seen in UV spectra (Figure 3). Then protonated thiophene is electro-oxidized to its radical dications at the electrode surface (E). This species is very unstable, deprotonated rapidly and forms corresponding cation radical (C). This cation radical, similar to the mechanism of electropolymerization discussed above, is coupled and then deprotonated to produce the aromatic dimer (C). The dimer then is electrooxidized on the electrode surface (E). Since the film forming reaction can be described as a cascade to ECCE reactions, the general term EC (CE)<sub>n</sub> has been proposed (see Scheme 1).



Scheme 1

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