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# Structure-Conductivity-Relationship in Current Conducting Polymers of Thiophenes

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A series of conducting polymers of thiophene and β-substituted thiophenes have been prepared by electrochemical oxidation and polymerization of these monomers in the form of polythiophene films. It has been observed that chemical or electrochemical doping has considerably increases the electrical conductivity of their polythiophenes through manifold of magnitude ranging from insulator ($\sim 10^{-10}\ \Omega^{-1}\ cm^{-1}$) to semi-conductor and finally to metal ($\sim 10^{+2}\ \Omega^{-1}\ cm^{-1}$). The electrochemical properties of monomers expressed in terms of peak oxidation potentials (Epa) are found to depend on nature of substituents which is indicated by the linear correlation ($r = 0.92$) between Epa and Hammett substituent constants (σ). Also, as a result of polymerization, polythiophenes have been found to have relatively less Epa and high conductivity. A linear correlation between Epa and σ ($r = 0.96$) has also indicated the dependence of electrical properties of the polymers on the nature of substituents. A combination of these two results have proved that a better conducting polymer of desired conductance can be synthesized by suitable introduction of substituent group in thiophene. It is found that free α-position and nature of substituents at β-position, respectively, are responsible for chain growth and variation in conductivity. However, it has also been found that viscous solvent modifies the electrochemical characteristics, which is indicated by the shifts of the oxidation peak towards more positive potential side.

**Key Words: Polythiophene, Conducting polymers, Substituent constants, Doping.**

## INTRODUCTION

Among the conducting polymers[1,2] those of acetylene doped with halogens are the most studied. Later on many other conducting polymers[3-12] have been reported among which some of conducting polymers like polyacetylene, poly(*p*-phenylene) and polypyrrole show reversibility of the doping-undoping process, while polythiophenes are the good polymers which are chemically as well as electrochemically stable in air in both their doped and undoped states.

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In due course of time attempts have been made to discover highly conducting polymeric systems like poly(*p*-phenylene)[4,5] consisting of a linear sequence of phenyl rings with a nonacetylenic complex structure having metallic properties. The discovery of conducting poly(*p*-phenylene) and polyacetylene complexes with both *n*- and *p*-type dopants have provided the basis for device applications as in Schottky barrier photocells[13].

Polymerization of thiophene through 2- and 5-positions with preservation of aromatic nucleus has been reported and dominance of $\alpha$-$\alpha'$-linkage in polythiophenes has been confirmed by $^{13}C$ nuclear magnetic resonance spectrum analysis[14,15]. The contribution of substituent groups at $\beta$-position has been reported to bring remarkable change but no general correlation between nature, number and position of substituents with the electrochemical properties of these polymers has been proposed. It has been observed that in case of pyrrole and polyazulene the solvent has a very strong influence on the outcome of the electro-oxidation reaction. Film formation can be minimized by enhancing the nucleophilic character of the solvent[7]. Electroactive and electrochromic films of electro-polymerized polyazulene and polythiophene have been found to be surprisingly insensitive to common solvents and temperature[5,9].

Thus, basic objective of the present investigation is to explore the importance of $\beta$-position and nature of substituents in modifying the electrochemical characteristics in thiophenes. Impact of $\pi$-electron system on the electrochemical properties of their polymers in various solvents will also be explored in the form of general structure-conductivity-relationship (SCR).

## EXPERIMENTAL

Thiophene and its substituted derivatives were obtained from Sigma Chemical Co. and were used without further purification. $LiCl_4$, $CH_3CN$ and other chemicals were obtained from Flucka AG Buchs Switzerland.

The polymers of thiophene have been obtained on a Pt electrode which is suitable for the grafting of films[12]. The medium for electrolysis consisted of $N(Bu)_4Cl_4$, acetonitrile and thiophene. Other solvents, such as, THF, $CH_2Cl_2$ or supporting salts; such as, $N(Bu)_4$ $BF_4$ and $LiClO_4$, can also be used.

These polymers have then been electrochemically characterized in various media:$CH_3CN$, THF, $H_2O$ and glycol with the anions $BF_4^-$, $ClO_4^-$, *etc.* It is observed that these anions have no influence on electrochemical characteristics. The film density has been measured using flotation technique.

## RESULTS AND DISCUSSION

Table-1 shows that as a result of substitution of electron repelling groups on position 3 and/or 4, oxidation potentials of corresponding polymer decrease. The variation in the oxidation potential values with the change in the structure of monomer units has been observed.

TABLE-1
OXIDATION POTENTIALS OF THIOPHENE AND DERIVATIVES ($E_{ox}^{mon}$) AND ($E_{ox}^{poly}$) OXIDATION VALUES OF CORRESPONDING POLYMERS

| Polymer | $E_{ox}^{mon}$/V(SCE) | $E_{ox}^{poly}$/V(SCE) |
|---|---|---|
| Thiophene (T) | 1.65 | 1.10 |
| 2,2'-Bithiophene (2,2'-bT) | 1.20 | 0.70 |
| 3-Methylthiophene (3-MeT) | 1.35 | 0.77 |
| 3-Bromothiophene (3-BrT) | 1.85 | 1.35 |
| 3,4-Dibromothiophene (3,4 BrT) | 2.00 | 1.45 |
| 3,4-Dimethylthiophene [3,4-$(Me)_2$T] | 1.25 | 0.98 |
| 3,4-Methylethylthiophene (3,4-MeEtT) | 1.26 | 1.06 |
| 3,4-Diethylthiophene (3,4-EtT) | 1.23 | 1.10 |
| 3-Thiomethylthiophene (3-$SCH_3$T) | 1.30 | 0.72 |

The oxidation or doping of the polymer (evolving from a red state to a deep blue state) corresponds to the transfer of one charge from the electrode to the polymer, producing a hole and then to the migration of this charge to the film-electrolytic medium interface. An anion, present in the medium, must then migrate in inside the polymer maintaining electroneutrality. This phenomenon repeats itself until all electroactive sites are oxidized. This process is followed by a volume expansion of the polymer. The voltamperometric behaviour of 250 nm thick film of poly(3-methylthiophene) (PMeT) in $CH_3CN$-$LiClO_4$ medium at a sweep rate of 50 mV $s^{-1}$ clearly indicated that polymer can be oxidized and reduced.

The reeducation or undoping of the polymer is more complex and extends over a large potential range, from +0.82 to -0.10 V/SCE in the case of polymethyl thiophene. Similar observations have also been found with polyacetylene, polypyrrole and polyaniline[16].

The result that the charge involved: $Q_{ox}$ = 6.85 mC/cm$^2$ and $Q_{red}$ = 6.84 mC/cm$^2$, for 255 nm thick film, indicates that oxide-reduction processes of polythiophenes are fully chemically reversible. On the other hand, it is possible to determine, from the i=f(V) characteristic, if 255 nm film is entirely electroactive or not. Using the preceding parameters and supposing a one-electron reaction, the electroactive site concentration calculated is $6.90 \times 10^{-8}$ mol/cm$^3$. The film density being about 1.1 g cm$^{-3}$ (obtained by flotation technique) and the molar mass 96 g, the 250 nm thick film would correspond to $5 \times 10^{-7}$ mol cm$^{-3}$. The oxido-reduction curve showing the variation of potential, E/V (SCE) against -current, i/mA cm$^{-2}$ (Fig. 1, Tables 2 and 3) for polymethyl thiophene in two electrolytic mediums consists of two parts '1' and '2', the curve '1' occurring in acetonitrile medium and '2' in glycol medium. When a positive charge is developed in every 4 monomeric units, as shown by the 25 % dopling level, it is found that the whole film becomes electroactive (Fig. 1).

There are two parameters which decide the electrochemical properties of polymer films: the nature of anion and the nature of solvent[17]. It is obvious from results obtained (Fig. 2) that the solvent modifies the electrochemical characteristics of the polymer indicating their relation to the swelling property and to the polarity of

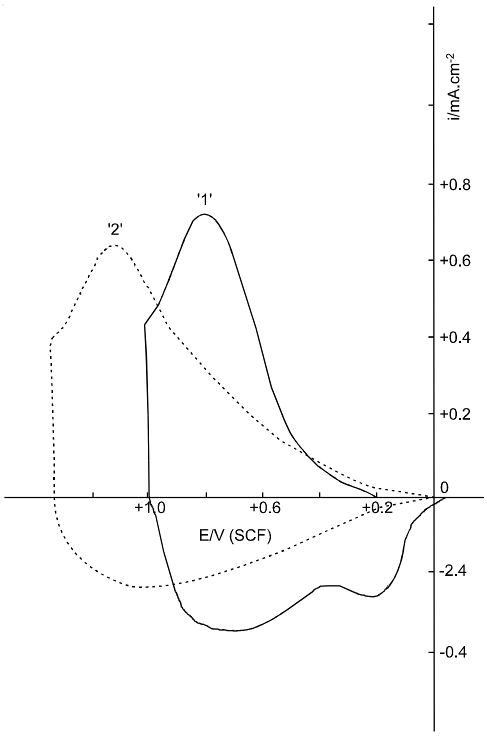

Fig.1. Dependence of the oxide-reduction curve for PMeT with the electrolytic medium. (Sweep rate) $V_B$ = 50m V/s ('1') $CH_3CN + 10^{-1}$ mol $L^{-1}$ $LiClO_4$: ('2') glycol + $10^{-1}$ mol $L^{-1}$ $LiClO_4$

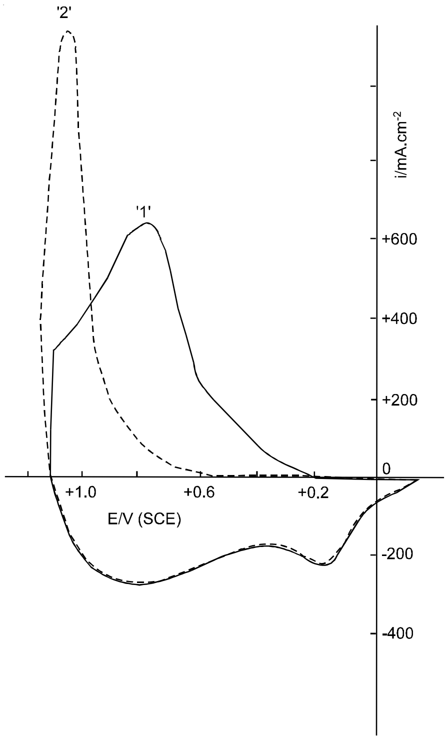

Fig. 2. Effect of solvent on electrochemical properties. Electrolytic medium : ('1') $CH_3CN + 10^{-1}$ mol $L^{-1}$ $LiClO_4$, $V_B$ = 50 mV/s and i-E curve after a polarization at -0.2 V/SCE

TABLE-2
VOLTAMPEROMETRIC DATA OF POLYTHIOPHENE FILM IN ELECTROLYTIC MEDIUM:$CH_3CN + 10^{-1}$ mol $L^{-1}$ $LiClO_4$

| E/V(SCE) | i/m A.com$^{-2}$ | E/V(SCE) | i/mA.cm$^{-2}$ |
|---|---|---|---|
| 0.00 | 0.00 | -0.06 | 0.00 |
| 0.10 | 0.00 | 0.00 | -0.03 |
| 0.20 | 0.00 | 0.10 | -0.14 |
| 0.30 | 0.03 | 0.20 | -0.26 |
| 0.40 | 0.07 | 0.30 | -0.23 |
| 0.50 | 0.16 | 0.40 | -0.29 |
| 0.60 | 0.35 | 0.50 | -0.33 |
| 0.70 | 0.56 | 0.60 | -0.35 |
| 0.80 | 0.72 | 0.70 | -0.34 |
| 0.90 | 0.64 | 0.80 | -0.26 |
| 1.00 | 0.47 | 0.90 | 0.00 |
| 1.03 | 0.45 | 0.99 | - |
| 0.99 | 0.00 | - | |

TABLE-3
VOLTAMPEROMETRIC DATA OF POLYTHIOPHENE FILM IN ELECTROLYTIC MEDIUM:GLYCOL + $10^{-1}$ mol $L^{-1}$ $LiClO_4$

| E/V(SCE) | i/m A.$cm^{-2}$ | E/V(SCE) | i/mA.$cm^{-2}$ |
|---|---|---|---|
| 0.00 | 0.00 | 0.0 | 0.00 |
| 0.10 | 0.01 | 0.1 | -0.02 |
| 0.20 | 0.02 | 0.2 | -0.03 |
| 0.30 | 0.04 | 0.3 | -0.06 |
| 0.40 | 0.07 | 0.4 | -0.10 |
| 0.50 | 0.12 | 0.5 | -0.12 |
| 0.60 | 0.18 | 0.6 | -0.16 |
| 0.70 | 0.23 | 0.7 | -0.18 |
| 0.80 | 0.32 | 0.8 | -0.21 |
| 0.90 | 0.38 | 0.9 | -0.23 |
| 1.00 | 0.52 | 1.0 | -0.24 |
| 1.10 | 0.64 | 1.1 | -0.23 |
| 1.20 | 0.59 | 1.2 | -0.17 |
| 1.30 | 0.43 | 1.3 | 0.05 |
| 1.34 | 0.39 | - | - |

solvent. When acetonitrile is replaced by the comparatively viscous glycol the current which is a function of potential [i= f (V)], a modified curve is observed (Fig. 2). The curve '2', (Fig. 2) is shifted towards more positive potential side and the peak becomes larger than that found with acetonitrile (curve '1', Fig. 2) which may be due to the higher viscosity of glycol than water, an astonishing result was obtained, the film could be oxidized and reduced and the oxidation peak was almost constant in energy and in intensity. However, the reduction range revealed only one maximum; the brown coloured film existing then in a intermediate electronic state, between the blue doped form and the red undoped form. The porous fibvillar structure of the film was accounted for the swelling in an aqueous medium.

The values of oxidation potential of thiophene and related derivatives ($E_{ox}^{mon}$) and their polymers ($E_{ox}^{poly}$) show significant differences, such that, later have values lower than those of the former substances. A linear correlation has been expected between these parameters. This indicates that β-substituted thiophene monomers as well as their respective polymers must contain a related system of π-electrons. These conclusions have been supported from a linear relationship (Fig. 3) between peak oxidation potentials (Epa) of thiophene polymers and Hammett substituent constants (σ). This indicates that electrochemical properties in β-substituted thiophene polymers depend on nature of substituents, the π-electron system in polymers and the π-electron system in monomer units. From the comparison of the curves Epa *versus* σ for monomers (Fig. 3, curve '1', r = 0.92) and that for polymers (Fig. 3, curve '2', r = 0.96), it is concluded that polymers exhibit better electrochemical properties (r = 0.96) than those indicated by monomers (r = 0.92).

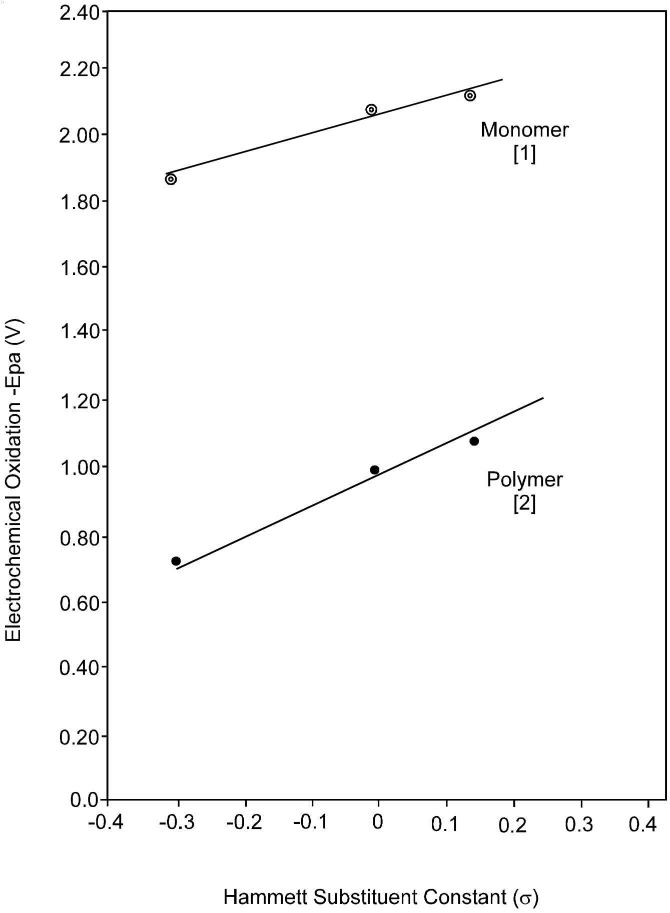

Fig. 3. A correlation between peak oxidation potentials (Epa) and Hammett substituent constants (σ). [1] For monomers (r = 0.92) [2] For polymers (r = 0.96)

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