

SYNTHESIS OF POLYTHIOPHENE: n-TYPE AND p-TYPE DOPING AND COMPENSATION

S PITCHUMANI, M VIJAYAN and V KRISHNAN

Central Electrochemical Research Institute, Karaikudi-623 006, INDIA

[Received: 1987 July; Accepted: 1988 February]

The synthesis of polythiophene leading to the formation of n-type polythiophene, p-type polythiophene and neutral polythiophene has been investigated through electropolymerization with different dopant ions. The influence of doping level over conductivity of the polymer matrix has also been studied which reveals that a preselected room temperature conductivity can easily be imparted to the parent polymer chain. It has also been found that the compensation of one type of conductivity over other occurs during the process of dedoping and redoping.

Key words: Polythiophene, electropolymerization, n- and p- type doping

INTRODUCTION

Conducting polymers are new class of synthetic metals with growing increase in its membership [1]. Such a growth can well be appreciated by virtue of the fact that these polymers can be used in place of traditional semiconductor and metallic electrodes for a number of electrochemical applications such as in energy storage [2] and modified electrodes [3]. With the thorough understanding of the development of earlier members of this class namely polyacetylene [4] and poly p-phenylene [5], whose preparative routes are predominantly conventional chemical routes, heterocyclic polymers have emerged as alternative candidates with their electrochemical preparative routes [6,7]. Besides heterocyclic polymers are more stable in atmosphere than these well understood potential member of the family, namely polyacetylene. To understand its utility in the use as electroactive material, particularly in energy storage devices, the relationship between the dopant level and conductivity becomes important besides the type of conductivity that may be imparted to the parent polymer matrix. Electropolymerization with its ease of adoption is extended here in the studies of the synthesis of polythiophene exhibiting different types of conductivity about which this present paper deals with.

EXPERIMENTAL

Materials

Thiophene, acetonitrile, tetrabutylammonium tetrafluoroborate, sodium perchlorate and potassium hexafluoroarsenate were all purified and used as per the standard procedure.

Electropolymerization

A two electrode cell containing thiophene and any one of the electrolytes such as $(C_4H_9)_4 NBF_4$, $NaClO_4$ or $KAsF_6$ dissolved in acetonitrile was used. A platinum or stainless steel plate was used as anode and a platinum cathode was placed opposite to the anode very closely. Electropolymerization was carried out by impressing a current as per the previously standardised method [8].

Electrochemical dedoping

The prepared polymer film was dedoped by the immediate reversal of the polarity after electropolymerization as described earlier [8].

The voltage applied between the anode and the cathode increased during this process and settled down after some time.

Electrochemical redoping

The dedoped polymer was again doped with respective counter ions

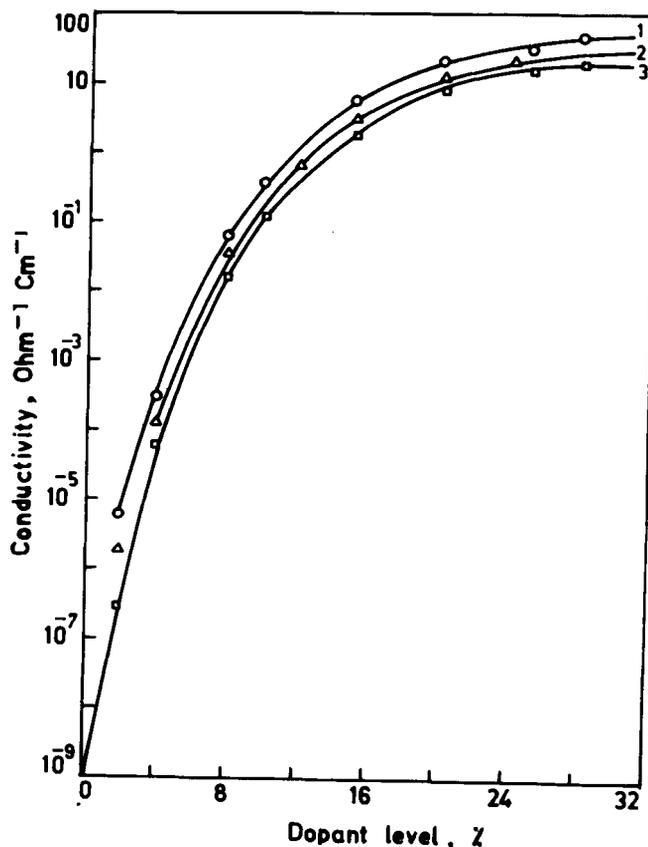


Fig.1: Electrical conductivity as a function of dopant level. 1 = BF_4^- , 2 = AsF_6^- , 3 = ClO_4^-

as described earlier [8] in the same electrolytic cell.

The doping levels were estimated by the weight increase method [8] and the products were analysed through IR spectral data.

RESULTS AND DISCUSSION

The growth of polythiophene film through electropolymerization is readily seen within a few minutes of the application of current. The grown polymer film has been washed repeatedly with acetonitrile and when subjected to IR spectral analysis, showed characteristic bands at 3300 cm^{-1} , 1300 cm^{-1} , 1080 cm^{-1} , and 790 cm^{-1} due to thiophene unit [7] via CH bending and stretching, heterocyclic vibration. The dopant ions are identified with characteristic bands at 1100 cm^{-1} and 625 cm^{-1} for ClO_4^- at 1050 cm^{-1} and 520 cm^{-1} for BF_4^- and 696 cm^{-1} for AsF_6^- [9]. The polymer films thus synthesised show good electrical conductivity, indicating that polymerization has been accompanied by simultaneous doping.

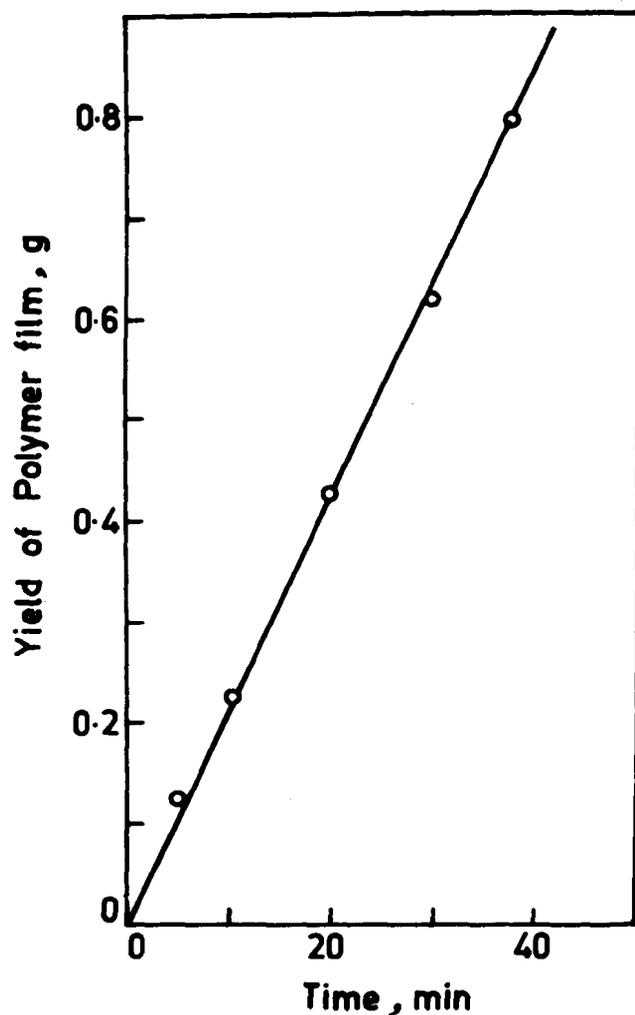


Fig. 2: Polymer yield as a function of time for electropolymerization of thiophene using NaClO_4 in CH_3CN

Fig. 1 shows the influence of dopant concentration over the conductivity of the resultant polymer films with different counter ions. The film bearing BF_4^- ions shows a better conductivity than the polymer films synthesised with other counter ions. The dependence of the conductivity over the dopant concentration clearly shows that the required level of doping can easily be imparted to the polymer matrix by carefully adjusting the supporting electrolyte concentration. The maximum doping level that is obtainable is around 30%. Fig. 2 shows a linear relationship between time of polymerization and the yield of the resultant p-type polythiophene which suggests the possibility of preparing polymer films of desired thickness.

Fig. 3 shows the course of dedoping of polythiophene films with different counter ions and redoping in the cell after a certain saturation point. The saturation point indicates the state of polythiophene as neutral, carrying no counter ions and dedoping can be utilized to synthesise neutral polythiophene. The increase in conductivity

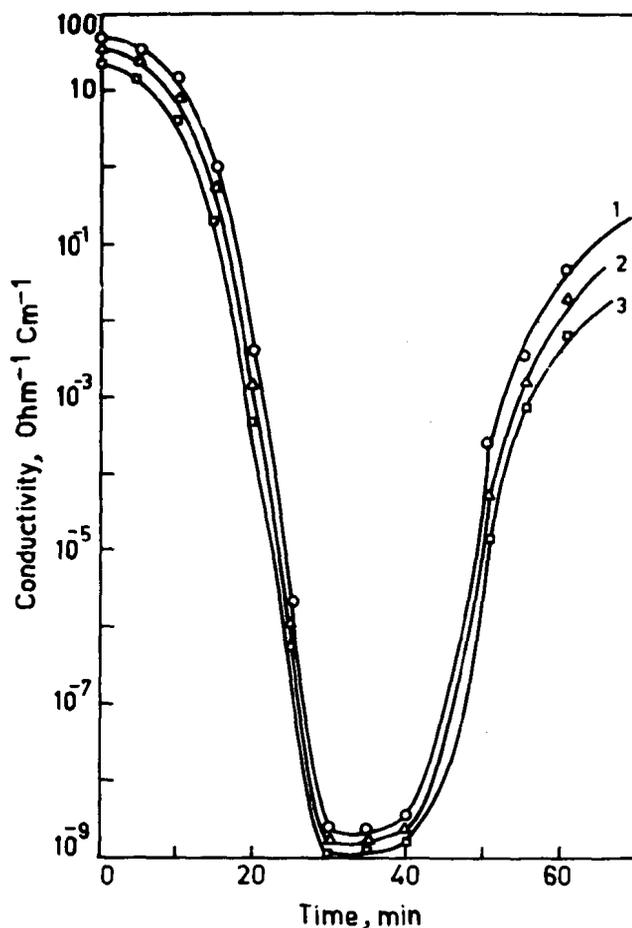


Fig. 3: Compensation curves for polythiophene dedoping and redoping 1 = $(\text{C}_4\text{H}_5)_4\text{NBF}_4$; 2 = KAsF_6 ; 3 = NaClO_4