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STUDIES ON THE CONDUCTING POLYMER OF THIOPHENE

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ABSTRACT

Thiophene during chemical peroxidation catalysed by Cu^{2+} undergoes simultaneous polymerization and oxidation. The polymer is characterised by chemical analysis, solution viscosity, Infra-red and UV-visible spectra. UV-visible spectra indicate the presence of a band due to $\pi - \pi^*$ transition and an exciton band due to interband transition. The polymer is thermally stable and the temperature dependence of electrical conuctivity is used to understand the conduction mechanism which is found to 'hopping' charge from state to state.

INTRODUCTION

The origin of the intensive research efforts aiming the synthesis of poly(thiophene) is in keeping with the emergence of the widespread interest for conducting polymers in the early part of the 1980s[1,2]. The poly(thiophene) and derivatives of poly(thiophene) are essentially prepared by chemical and electrochemical methods. Recently, Perrine et al[3] reported the synthesis and the occurrence of natural quaterthienyl (compounds containing four bonded thiophene rings). These are branched quaterthienyl However, it is the linear chain quaterthienyl which is found to be conducting when doped[4]. The chemical peroxidation method and simultaneous doping has the advantage of being a simple method for the synthesis of poly(thiophene). In this communication, we report the studies on the poly(thiophene) prepared by chemical peroxidation of thiophene with special reference to the mechanism of conduction in poly(thiophene).

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EXPERIMENTAL

Preparation of polymer[5,6]

0.012 mol thiophene and 0.01 mol perchloric acid were mixed in 25 ml acetonitrile. The mixture was cooled. To this mixture 10 ml of 0.56 M aqueous solution of ammonium persulphate containing 0.05 g of copper sulphate was added dropwise while stirring the solution in an inert atmosphere (N_2 gas was passed continuously during polymerization). The mixture was diluted and filtered. The soiled powder obtained after filtration was dried in hot air oven.

Elemental analysis

C, H elemental analyses were carried out by Regional Sophisticated Instrumentation Centre, CDRI, Lucknow on Carlo Erba Strum DP200 C,H,N element analyser.

Sulphur was qualitatively tested in the sample by converting into sulphate.

The presence of counter ion ClO_4^- was confirmed by perchlorate test[7].

Intrinsic Viscosity

Solution viscosity of poly(thiophene) as prepared sample is measured in DMF by Ostwald-Ubbelhode dilution viscometer at 28°C. Solution viscosity at different concentrations is used to determine the intrinsic viscosity by the usual graphical method (by plotting η_{sp}/c as a function of c). However, in these measurements, the standard deviation increases with a decrease in concentration. Therefore, in order to improve the reliability of measurement, the extrapolation of the usual equation η_{sp}/c Vs c ($y = ax \pm b$) is replaced with the extrapolation of the linear transformation[8] using $G = AF + B$, where

$$F = \frac{x}{\alpha - x} \quad \text{and } G = \frac{y}{\alpha - x}$$

and $= x_m + x_M$ (index m and M denote the lowest and the highest value of the independent variable x (concentration variable). The suggested transformation results in approximately uniform error distribution and renders extrapolation feasible ($[\eta]$ (usual graphical method) = 0.224 dlg^{-1} and by refined graphical method $[\eta] = 0.20$ dlg^{-1}).

Infra-red spectra

Infra-red spectra is recorded on a Perkin Elmer 577 spectrophotometer using KBr pellet technique at CDRI, Lucknow, India in the range 400-4000 cm^{-1}.

UV-visible spectra

The UV-visible spectra of the polymer were recorded in DMF, DMSO, NMP, Acetone, using UV-240 Shimadzu Automatic Recording double beam spectrophotometer at room temperature in the range 190-700 nm.

Thermal Gravimetric Analyis

The thermal gravimetric analysis was carried out on a Perkin Elmer TGS2 Thermal analyser system in nitrogen atmosphere at Regional Sophisticated Instrumentation Centre, Nagpur University, with a heating rate 15 K min^{-1}.

Electrical Conductivity Measurements

Powder sample pellets were used for electrical conductivity measurements using a Systronics Direct Reading LCR Bridge Model 926 as a function of temperature at a heating rate 1 K min^{-1}. Measured resistance was converted to conductance using cell dimensions.

RESULTS AND DISCUSSION

Characterization

The elemental analysis of the polymer gave C = 44.06% (44.85) and H = 2.32% (1.87). The theoratical values (in bracket) have been calculated by considering quaterthienyl unit with one counter ClO_4^- ion.

The IR absorption spectra of poly(thiophene) obtained by chemical peroxidation of thiophene, shown in Fig. 1. The group frequency C = S shows an intense bond at 1640$cm^{-1}$and the figure displays four strong absorption bands at 1330, 1210, 1115 and 1040cm^{-1} which are characteristic bands of the doped poly(thiophene)[9]. The band at 785 cm is assigned to the out-of-plane C-H vibration characteristic of 2,5-disubstituted thiolylene[9]. The skeleton vibration assigned to C-S band occurs in the region 600-700 cm^{-1} and due to ClO_4^- at 1105 and 630 cm^{-1}. The former is masked by the doped thiophene bands[10].

UV-visible spectra

The UV-visible spectra for poly(thiophene) perchlorate has been investigated in different solvents in order to identify the bands. The UV-visible spectral bands are recorded in Table 1. The absorption spectra are characterized by at least two bands in different solvents.

The band between 500-600 nm is an exciton band[11]. The exciton band exhibits bathochromic shift with an increase in the dielectric constant of the solvent. It has been reported[12] that the direction of

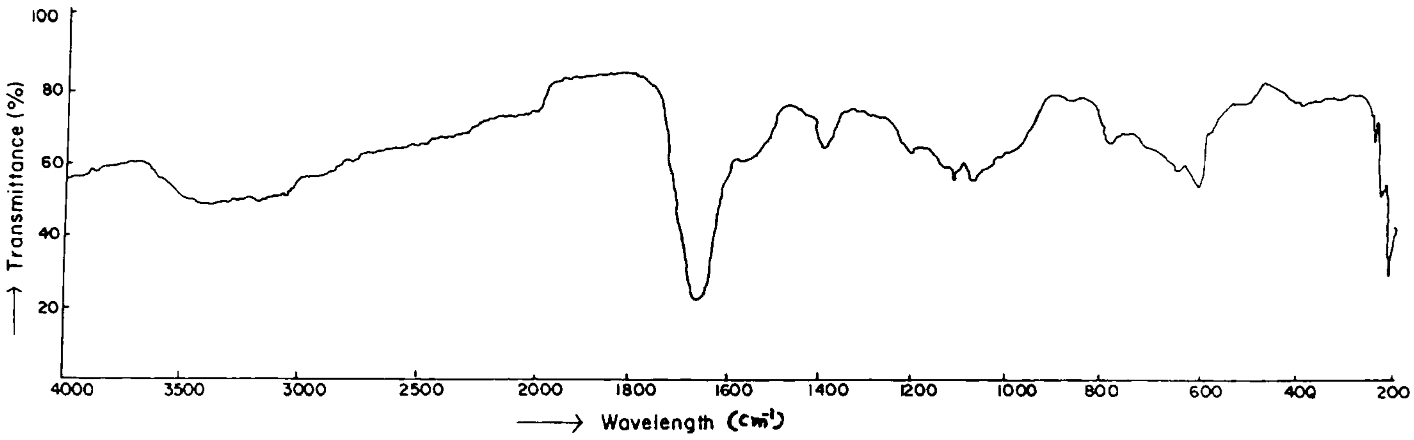


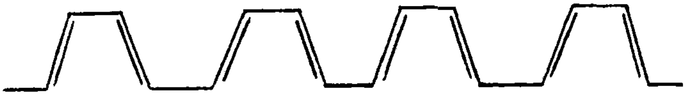
Fig. 1. IR Spectra of poly(thiophene) perchlorate

TABLE-1

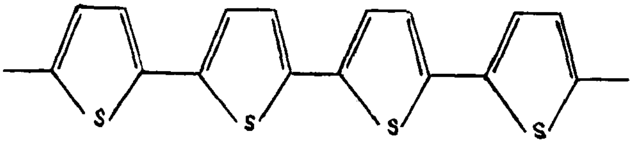
UV-visible absorption bands of poly(thiphene) percholarate in different solvents

Solvent (Dielectric constant)	λ max., nm (eV)	Transition
a) DMSO	370 (3.36)	π - π*
(46.68)	650 (1.91)	π_β--π_α (Exciton band)
b) DMF	380 (3.27)	π - π*
(36.71)	460 (2.71)	-
	590 (2.11)	π_β--π_α (Exciton band)
c) NMP	390 (3.19)	π - π*
(32.0)	470 (2.64)	-
	590 (2.11)	π_β--π_α (Exciton band)
d) Acetone	330 (3.77)	-
	370 (3.36)	π - π*

the shift depends upon the relative magnitude of the dipole moment of the solute molecules in the excited and ground electronic states, respectively. When the solute molecules are excited, they find themselves in the environment of the solute molecules oriented according to the ground state condition or excited state is a charged state. Thus, a bathochromic shift of the exciton band in a solvent of higher dielectric constant shows that the dipole moment of the solute in the excited state is higher than in the ground state. Poly(thiophene) can be viewed[13] as an Sp^2 p_x carbon chain, in which structure is analogous to that of Cis - (CH)$_x$, is stabilized by hetero atom. The structure can be represented by

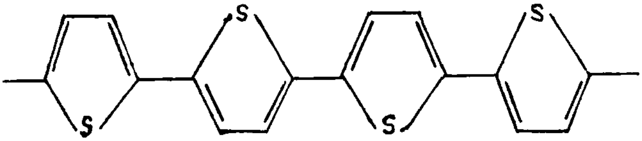


Cis-(CH)$_x$



poly(thiophene)

However, the more stable form is trans-form as



The poly(thiophene) differ from $(CH)_x$ by its non-degenerate ground state related to the non-energetic equivalence of its two limiting mesomeric forms, aromatic (benzenoid type) and quinoid. The transition, aromatic to quinoid is thus assigned to this exciton band, since the transition will enhance the dipole moment in excited state in the same direction. Thus, exciton band is due to $^{\pi}$Aromatic $-^{\pi}$ Quinoid transition wherein π aromatic HOMO, is the electronic state extended over the aromatic rings and π_Q is strongly localized to quinoid ring.

The 370-390 band is assigned to $\pi \longrightarrow \pi^*$ transition. In this transition the dipole moment on excitation will be larger than in the ground state and will cause a hypsochromic shift in a solvent of higher dielectric constant as observed from Table 1.

Thermogravimetric Analysis

TGA of polymer sample as prepared by chemical peroxidation of thiophene, in nitrogen is shown in Fig. 2 and indicates that the sample degrades in two steps. The first mass loss starts at 140°C and continues up to 380°C (Mass loss 36.11%) and the second stage of decomposition is in the temperature range 400-860°C (Mass loss 51.53%). The initial mass loss of 36.11% may be due to the loss of low molecular mass oligomer such as bithiophene (Theoretical mass loss due to bithiophene 39%) and loss of counter ion. The second stage mass loss may be due to the pyrolysis with evolution of H_2S or decomposition to and volatolization of bithiophene formed during the degradation of poly(thiophene)[13] . The activation energy of the thermal degradation and decomposition of poly(thiophene) in N_2 was calculated using Sharp-Wentworth method[14] and is found to be 55 and 93 KJ mol^{-1} for first and second stages of degradation, respectively.

The TG analysis show that the product consist of bithiophene which could have been formed during peroxidation of thiophene as intermediate. The bithiophene may be formed through α , α'-coupling, α - β coupling or β-β'- coupling. Thus, there will be three isomeric bithophene intermediates during polymerization either at α-position or β -position. However, the relative reactivities are in the ratio of 95/5.[15] Thus, the addition to β-position will be very less and the product may have low molecular mass oligomer with a short chain length. The addition to α will lead to high molecular mass linear product. Thus, the polymer will be a mixture of isomeric bithiophene low molecular mass oligomer and linear chain polymer. The bithiophene and low molecular mass oligomers will volatalize at low temperature range (200-400°C) causing the loss in the first stage.

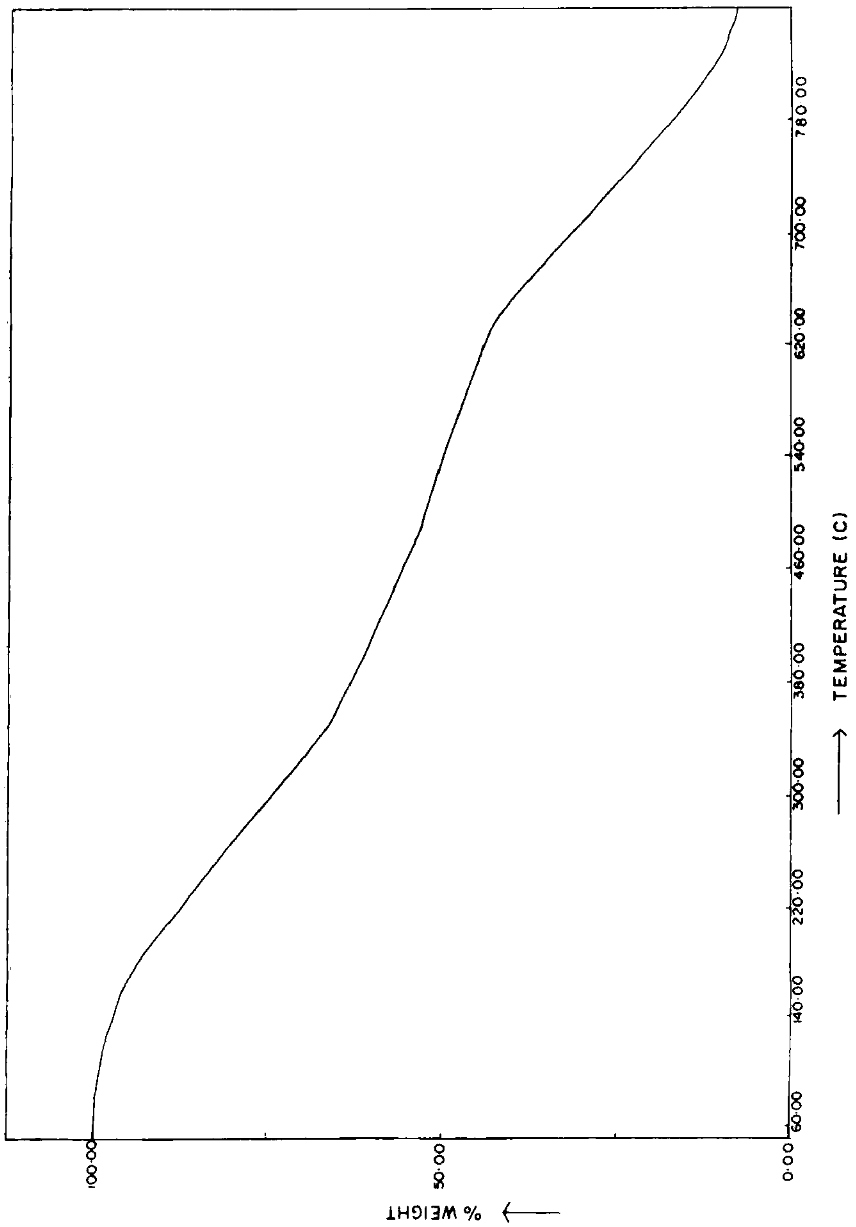


Fig. 2 - TG Curve of poly (thiophene) perchlorate

The results of the chemical anslysis and TG indicate that the chemical peroxidation of thiophene leading to polymerization proceeds via formation of three isomeric bithiophenes. Only α-α' coupling of bithiophene leads to a linear chain polymer and have a linear quaterthienyl unit which has no ring attached to more than two others and one counter ClO_4^- ion attached to the linear quaterthienyl unit[4].

Electrical conductivity

The temperature dependence of the electrical conductivity data (in the middle range of temperature) fit the Arrhenius type equation (1)

$$\sigma(T) = \sigma_0 \exp(-E_a/2kT) \qquad ...(1)$$

in the temperature range investigated. The measured values are plotted semilogarithmically as a function of the reciprocal of temperature in K as shown in Fig. 3. The conductivity increases with temperture and the activation energy of conductivity is 0.06 eV (compare with E_a = 0.04 eV for Pyrrole)[16] and σ_0 = 1.67 x 10^{-6} ohm^{-1} cm^{-1}. The low coinductivity is due to the occurrence of three isomeric bithiophenes. The low reactivity of β-coupled thiophene[13] allows their insertion in polymer backbone causing low conductivity and decrease in chain length thereby decreasing mean conjugation length in the polymer. This α-β link in a chain modifies the electronic charge distribution which promotes branching and generate distortion in adjacent chain[13]. Thus, morphological disorder decreases and the conductivity also decreases. From the studies on poly(pyrrole) it has been established that in chemical peroxidation of heterocyclic compounds, a positive hole like state is created and as a result polaronic energy bands are formed. These polarons act as a charge carriers. Thus, conducting state in conducting organic polymers is described with a polaron lattice model giving rise to metallic band structure. However, the conduction of these polarons is influenced by dopant level, protonation, morphology of the polymer; orientation of the conducting species and the crystalline or amorphous state of the polymer.

In order to understand mechanism of conduction over the entire range of temperature, the temperature dependence of conduction data are plotted to various models for conduction of charged species in solids. By analysing the data, it is found that in the entire temperature range, the electrical conductivity can be expressed as

$$\sigma(T) \alpha \exp[(-T_0/T)^{1/2}] \qquad ...(2)$$

Thus, when ln σ (T) is plotted as a function of $T^{-1/2}$, the data fitted to a steraight line as shown in Fig. 4.

The equation (2) suggests[11,17] the relevance of variable range hopping (VRH) of polaron charge between the nearest neighbouring chains. Thus in poly(thiophene) it can be said that charge polaron is localized to

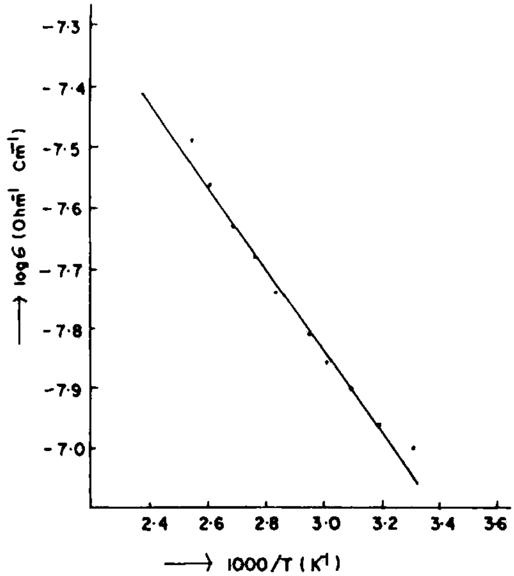


Fig.3 Conductivity of poly (thiophene) perchlorate as a function of temperature

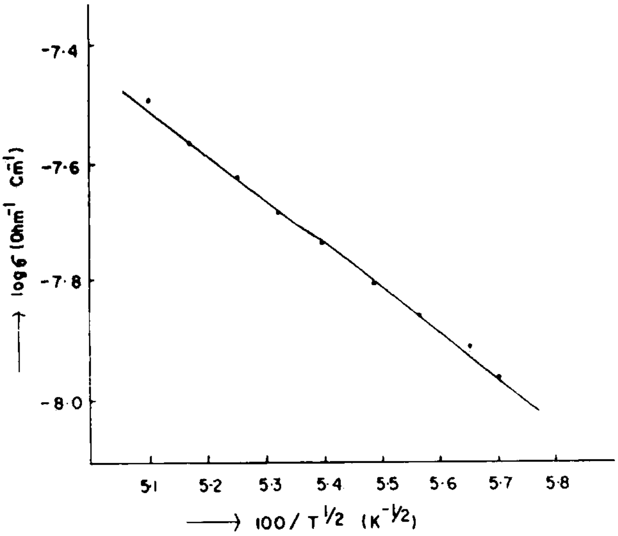


Fig.4 Temperature dependence of the conductivity of poly (thiophene) perchlorate

individual chains or states and the charge motion is explained by variable range hopping mechanism.

Conclusion

In chemical peroxidation of thiophene three isomeric bithiophenes are formed. The polymer sample prepared is thus a mixture of branched chain oligomers and the linear chain polymer whose unit is a linear quaterthienyl in which each thiophene ring is connected with one counter ion ClO_4^-. The temperature dependence of conductivity shows that the charged polarons are localized to individual chains and they hop from one stage to another (variable range hopping of polarons from one chain to another).

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