

New Synthesis Method of Polythiophenes

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ABSTRACT

We report a new procedure for preparation of poly (thiophene), poly (3-methylthiophene), poly (2,2'-bithiophene), cross-linked poly (2-vinylthiophene), poly [(2,2'-dithienyl)-5-5'-diylvinylene], poly [(3,3'-dithienyl)-5,5'-diylvinylene], poly [(1,2-dimethyl-2,2'-dithienyl)-5,5'-diylvinylene], and poly [(3,4-dimethyl-1,3,5-hexatriene-1,6-diyl)bisthiophene] films, where the monomer is polymerized at an interface. Polymeric films are prepared at room temperature by contact between an aqueous solution of HClO_4 9.1 M containing $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ as an oxidant and monomer solution in benzene under N_2 atmosphere. Four-probe electrical conductivity data measured on compressed pellets of the polymers show, $2.5\text{E}-3$, 1.5 , 8 , $1.0\text{E}-5$, 12 , insulating, $1.2\text{E}-2$, $4\text{E}-4 \text{ Scm}^{-1}$, respectively. The FT-IR spectrum of the polymers has been discussed.

Key Words

polythiophenes, conducting polymer, conjugated thiophene, chemical polymerization

INTRODUCTION

Research on electrically conducting polymers recently are focused on the synthesis, characterization and the study of polypyrroles and polythiophenes [1,2,3]. Among the wide variety of conducting polymers those derived from thiophene and substituted thiophenes are depicted to show good stability toward O_2 and moisture in both doped and neutral states [4]. This property is of great interest in the polythiophene (PT) application in electrochromic displays, protection of semiconductors against photocorrosion and energy storage [5].

Two main types of synthesis methods have

been reported for the preparation of the polythiophenes. One of the most widely used is electrochemical polymerization [6,7,8]. The polymers are obtained in their oxidized form and best conductivities of electrochemically synthesized PT lie in the range of $10-100 \text{ Scm}^{-1}$ [4,9]. This is not surprising since electrochemical polymerization was the only way of producing free standing conducting films. In contrast, synthesis of conducting substituted PT via chemical methods, even though it is more convenient and economical, has not been investigated in detail. The other widely used polymerization method is based on a

Grignard coupling reaction, starting with 2,2'-dibromo or 2,2'-diiodothiophene or 3-methylthiophene [10,11]. A one step chemical polymerization and doping of thiophene and derivatives has been reported by using AsF_5 [12] and $\text{Fe}(\text{ClO}_4)_3$ [13] as an oxidant. However, chemical formation of PT films remains a desirable goal.

In this paper, we report a new method of chemical polymerization and in situ doping for the preparation of conductive polythiophenes films. In this method, polymeric films formed at the interface of organic/aqueous solutions.

EXPERIMENTAL

Monomers

Thiophene (Jansenn) was used after distillation. 3-Methylthiophene (3-MeT) was prepared by the Wolff-Kishner reduction of 3-carboxaldehyde thiophene. 2,2'-Bithiophene (BiT) was prepared by the Grignard coupling reaction of the 2-bromothiophene with 2-thienyl magnesium bromide by *anh.* CoCl_2 . 2-Vinylthiophene (2-ViT) was synthesized by Wittig reaction on the 2-carboxaldehyde thiophene.

1,2-(2,2'-dithienyl) ethylene (2DTE), 1,2-(3,3'-dithienyl) ethylene (3DTE), 2,3-(2,2'-dithienyl)-2-butene (DT2B), and 3,4-dimethyl-1,6-(2,2'-dithienyl)-1,3,5-hexatriene (DMDTHT) were synthesized via McMurry's reaction by using Mokaiyama reagent. Thiophene 2- or 3- carboxaldehyde, 2-acetyl thiophene and thienylidene acetone were added, respectively, to a mixture of $\text{TiCl}_4/\text{Zn}/\text{Py}/\text{THF}$ and then refluxed up to 18 hours, under N_2 atmosphere. $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ was prepared from reaction of HClO_4 on the $\text{Fe}(\text{OH})_3$.

Polymers: General procedure

Synthesis of the conducting polymer films carried out in a typical reaction vessel. The bottom of the reaction vessel was covered with 30 ml HClO_4 9.1 M containing an oxidant, such as $\text{Fe}(\text{ClO}_4)_3$.

$9\text{H}_2\text{O}$, AgNO_3 , H_2SeO_3 and $\text{Cu}(\text{ClO}_4)_2$. A definite amount of monomer was dissolved in 10 ml benzene and then floated on the surface of the aqueous solution in the vessel. After a short time the polymeric film formed at the interface of aqueous/organic solutions at diff. temperature under N_2 atmosphere. Polymeric film without air exposure was repeatedly washed with acetone at reflux condition, then dried under dynamic vacuum for 2 hours.

RESULTS AND DISCUSSIONS

Polythiophene (PT)/poly (3-methyl thiophene) (P3MeT)/poly (bithiophene)(PBiT)

These polymer films were chemically synthesized by the reaction of $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ with their monomers, in benzene/ HClO_4 two-phase system. The optimum reaction temperature of the PT and P3MeT were found to be in the range 0-10°C. Rate of films formation was very slow (24h) for the thiophene and 3-MeT, whereas for the BiT the rate was rapid (see Table 2). The facile oxidation of BiT by $\text{Fe}(\text{ClO}_4)_3$, but not sufficiently of thiophene, is consistent with less positive anodic potential of the former (i.e. EPA are 1.32, 2.06 V versus SCE, for BiT and thiophene, respectively). However, the efficiency of this method decreases when the oxidation potential of the monomer increases.

In cases of thiophene and 3-MeT, in addition to $\text{Fe}(\text{ClO}_4)_3$, oxidants such as AgNO_3 , H_2SeO_3 , and $\text{Cu}(\text{ClO}_4)_2$ were also examined at the same conditions. With AgNO_3 and H_2SeO_3 , the reaction proceeded at a much slower rate, while with $\text{Cu}(\text{II})$ it was unsuccessful.

PT and P3MeT, when obtained by chemical oxidative polymerization, are insulating or poor conducting materials [12,13] while the conductivity of the PT, P3MeT, PBiT obtained by this method was $1.2\text{E}-3$, 1.5 and 8 Scm^{-1} , respectively. In comparison with the literature [12,13,14] these results are more interesting.

Figures 1 and 2 show FTIR spectra of the P3MeT and PBiT. The bands at 1330, 1120 are observed in the doped film [15]. The dopant has no

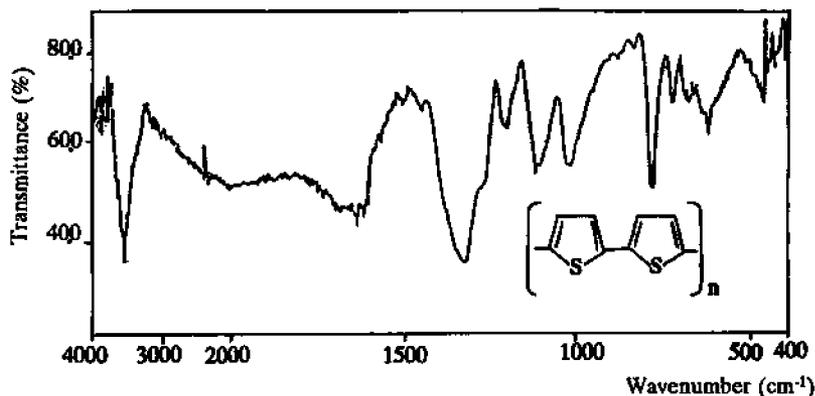


Fig.1. FTIR Spectrum of PBIrT (KBr pellets)

band around 1330 cm^{-1} . This suggests that the band at 1330 cm^{-1} is related to the molecular vibration of the doped polymer. The two bands at 1490 and 1220 cm^{-1} in the PBIrT film are assigned to the ring vibration of 2,5-disubstituted thiophene. Furthermore, the strong band at 790 cm^{-1} is assigned to the C-H deformation vibration of the 2,5-disubstituted thiophene ring. The band at 1110 cm^{-1} is due to the counter ion (ClO_4^-) diffusing from the oxidant into the polymer film. The strong intensity of the 790 cm^{-1} band, which is characteristic of 2,5-disubstituted thiophene rings,

indicates that chemical coupling of thiophene rings occurs preferentially at the 2,5-positions. Broad absorption at 3400 cm^{-1} is due to KBr humidity.

In addition to FTIR, the structures of P3MeT and PBIrT were confirmed by elemental analysis (Table 1), and have the following formula, respectively: $\{\text{C}_5\text{H}_4\text{S}(\text{ClO}_4)_0.25\}_n$ (I), $\{\text{C}_4\text{H}_2\text{S}(\text{ClO}_4)_0.07\}_n$ (II).

Synthesis of conductive cross-linked poly (2-vinylthiophene) has recently been reported through electroinitiation polymerization of 2-ViT

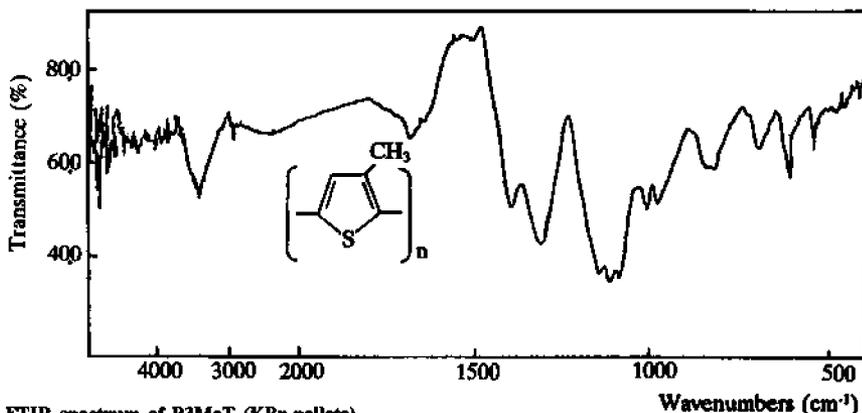
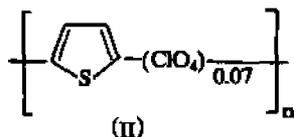
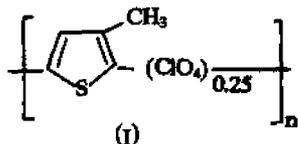


Fig.2. FTIR spectrum of P3MeT (KBr pellets)

Table 1. Elemental analysis of P3MeT and PBiT

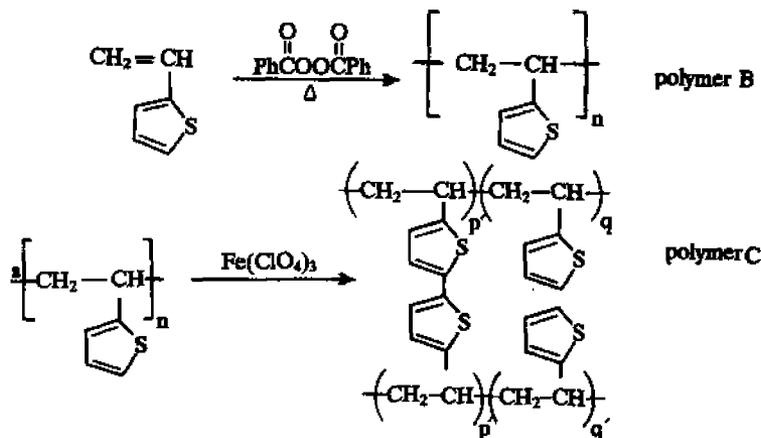
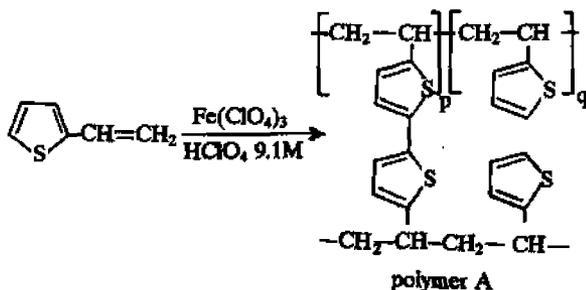
Elements	C	H	S	Cl	
P3MeT	Calc.	49.6	3.3	26.4	7.3
	Found	48.6	3.2	25.8	6.9
PBiT	Calc.	53.9	2.3	35.9	2.8
	Found	53.8	2.8	35.3	2.8



[16].

We now report the direct synthesis of this polymer from chemical oxidation of 2-ViT by general procedure. The product, a black-green film, was insoluble in common solvents. Conductivity was measured by using the four-probe

method and was found to be $1.0E-5 \text{ Scm}^{-1}$ due to the insolubility of this polymer, very few routes for characterization are available. In order to investigate the process through which polymer cross-linked is formed, we prepared an analogous polymer from linear poly (2-vinyl thiophene)(B) by



general polymerization (polymer C).

2-ViT was chemically polymerized in bulk under N_2 atmosphere at $90^\circ C$ using 1% mol benzoyl peroxide as an initiator for 11 h. The product was then dissolved in chloroform, filtered, precipitated in methanol, filtered again and dried under vacuum. Fortunately, most information can be obtained from FTIR spectrum as can be seen in Figure 3. Figures 3,4 and 5 show the FTIR spectra of the polymer A,B and C, respectively. In these spectra, thiophene substitution patterns are evident. Polymer B shows monosubstitution at the 2-position of the thiophene ring. These are the absorption at approximately 690 , 821 and 846 cm^{-1} in Figure 3.

2,5Disubstituted thiophenes show a single absorption at 800 cm^{-1} [17]. Polymers A and C exhibit both mono and disubstitution bands. The 2-monosubstitution bands occur at 690 , 846 cm^{-1} , while the absorption related to 2,5-disubstitution occurs at 801 cm^{-1} . This suggests that polymer A is

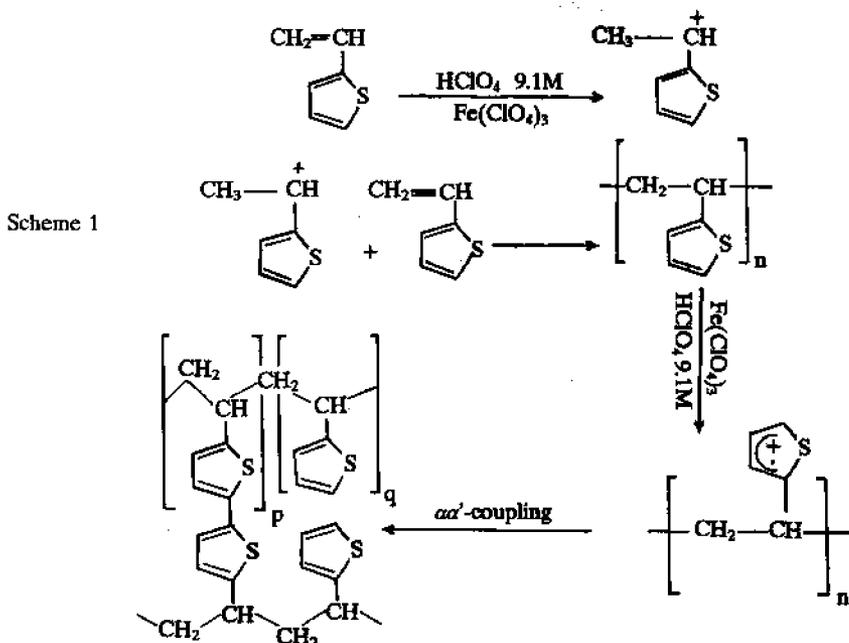
partially cross linked at the 5,5'-positions of the thiophene rings. The proposed mechanism for the formation of cross-linked poly(2-vinylthiophene) is shown in Scheme 1.

First, 2ViT polymerized as cationic form in $HClO_4$ 9.1 M medium to produce polymer A, which is partly disubstituted at the 5-position. The cross-linked process was, in fact, accomplished through oxidation of thiophene ring by $Fe(ClO_4)_3$ to form a radical cation, followed by coupling at the, position and proton elimination, to form polymer A.

The elemental analysis of polymer A confirmed that it is partially cross-linked, $\{C_{6.1}H_{5.8}S(ClO_4)_{0.04}\}_n$, were: C:64.2, H:5.1, S:27.6, Cl:1.2.

Synthesis of Conductive Copolymers

Among the wide variety of organic conducting polymers, doped polyacetylene has highest



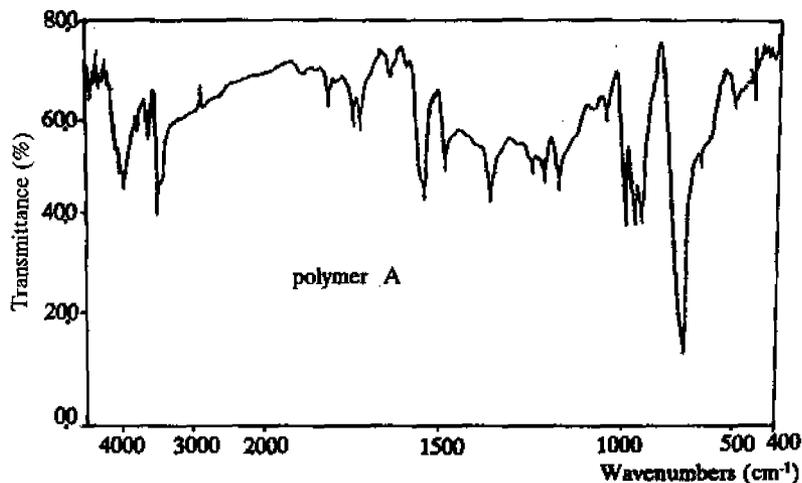


Fig.3. FTIR Spectra of the polymers A (KBr pellets)

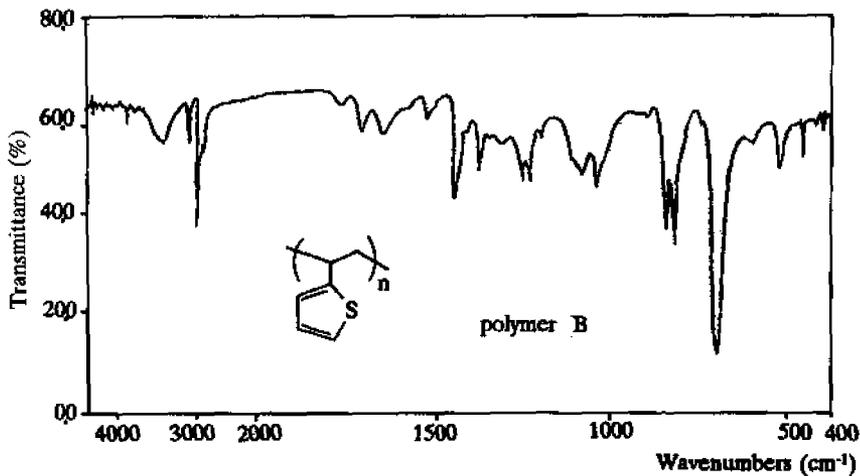


Fig.4. FTIR Spectra of the polymers B (KBr pellets)

conductivity, but it is unstable, whereas those obtained from thiophene and substituted thiophenes show good stability [18]. We have now applied this concept to the synthesis of copolymer of acetylene-thiophene which has high stability.

In this respect, we have synthesized several ethylenic thiophene monomers (1,2,3,4). The mass spectrum of DMDTHT (4) is shown in Figure 6.

The polymeric film of these monomers were obtained in a very short time (5 minutes) in the

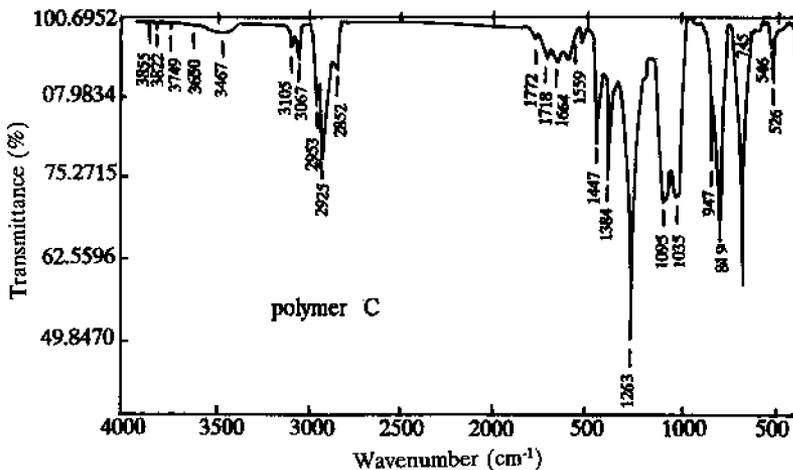


Fig.5. FTIR Spectra of the polymers C (KBr pellets)

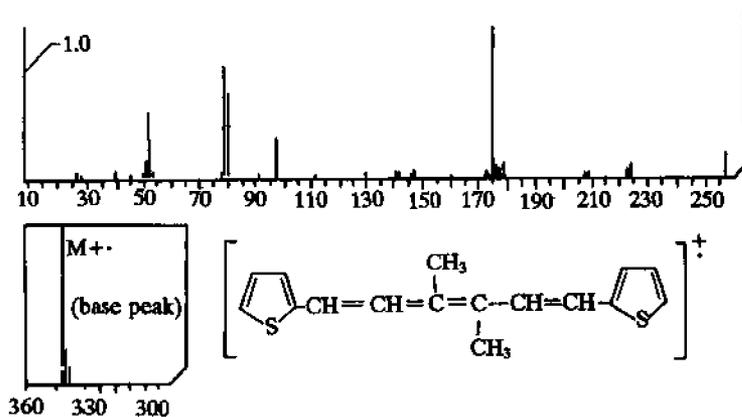


Fig.6. The mass spectrum of DMDTHT (4)

interface of organic/aqueous solutions. In the present experiment, according to the amount of monomer used, thin flexible films or thick dark-green sheets of polymer films were obtained.

The chain of polymers grows via the 5,5'-position of thiophene ring, causing the high conductivity of this polymers, while the P3DTE,

where β linkage is, does not show such conductivity. The measurements of the electrical conductivity were carried out by using the four-probe method on the films (in case of polymer 3 and 4) or on pellets that were made of pressed powdered film. The results of conductivity are shown in Table 2. The electrical conductivity of

polymers can be increased by doping with I_2 .

The FTIR spectra of these polymers are

shown in Figures 7, 8, 9 and 10. The stability of the polymeric samples in air is relatively high for an

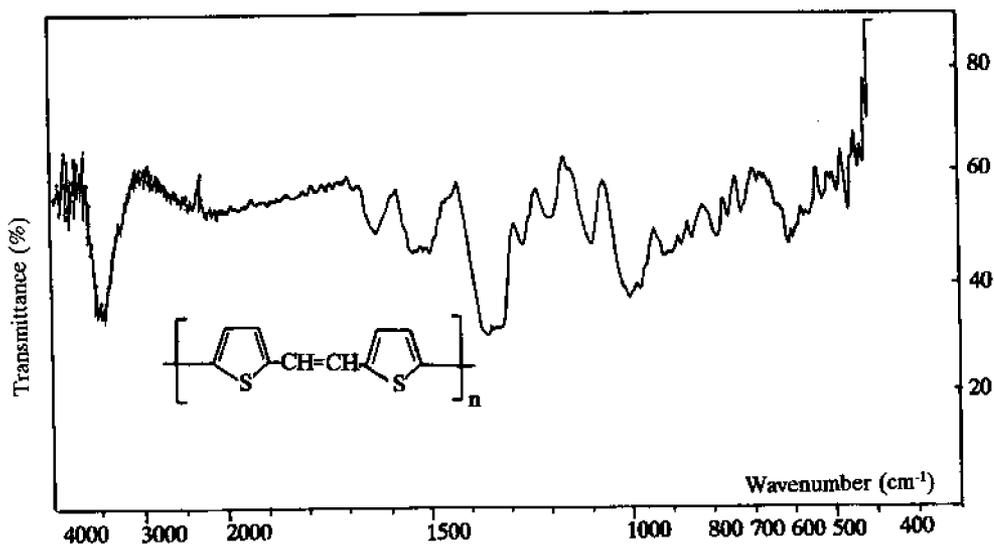


Fig.7. FTIR Spectrum of P2DTE (KBr pellets)

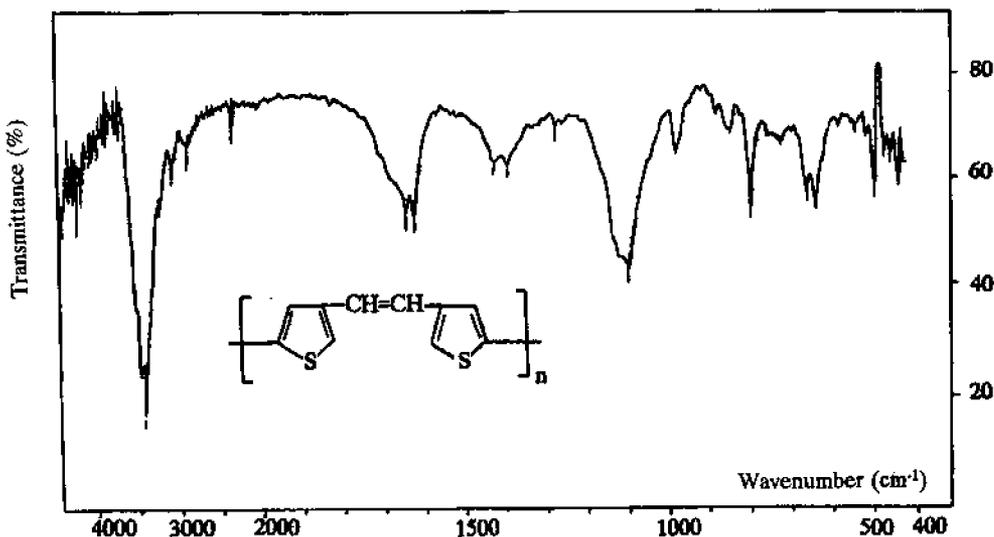


Fig.8. FTIR Spectrum of P3DTE (KBr pellets)

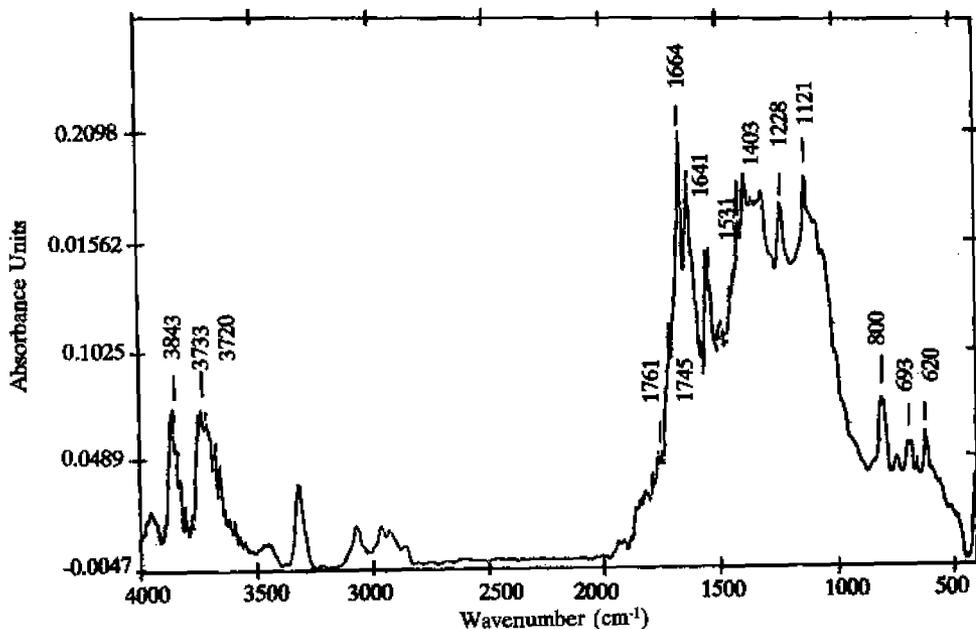


Fig.9. FTIR Spectrum of PDT2B (KBr pellets)

Table 2. The conductivity of polymers and the time of its formation

polymer	Yield (%)	Conductivity S/cm ⁻¹	Time of film formation
PT	35	2.5E-3	20 h.
P3MeT	45	1.5	16 h.
PBiT	95	8	1 h.
PViT (A)	85	1.0E-5	12 h.
P2DTE	100	12	20 min.
P3DTE	100	Insg.	30 min.
PDT2B	100	1.2E-2	5 min.
PDMDTHT	100	4.0E-4	2 min.

extended period of time.

CONCLUSION

We have prepared several conducting polymeric films in a chemical two phase system.

Polymerization of substituted thiophene compound at interface organic phase and HClO_4 9.1M solution containing $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ as oxidant, provides a valuable route to synthesis of conductive films in moderate to high yield.

We expect to develop the range of

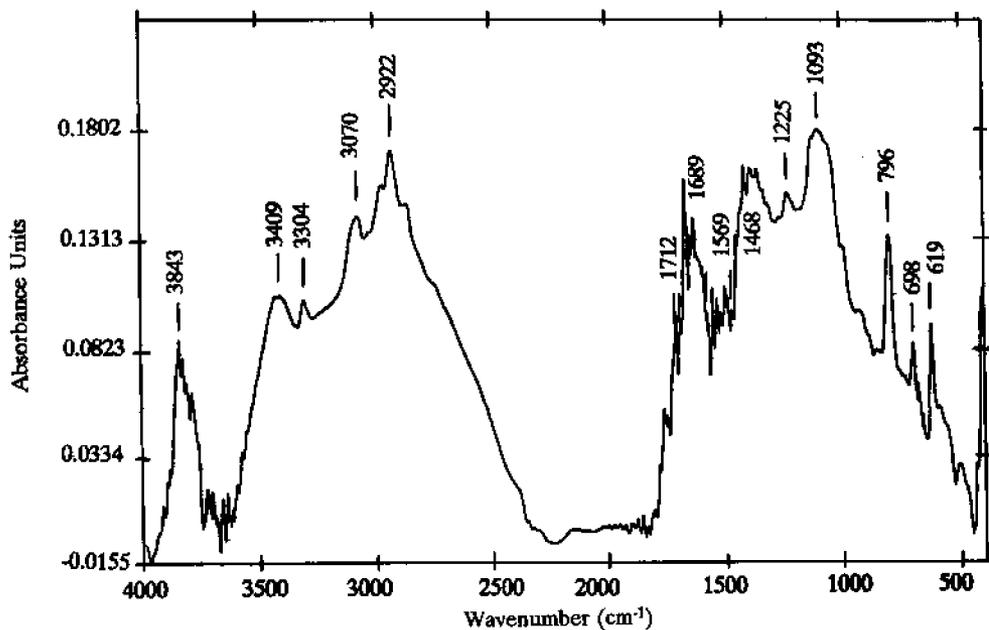
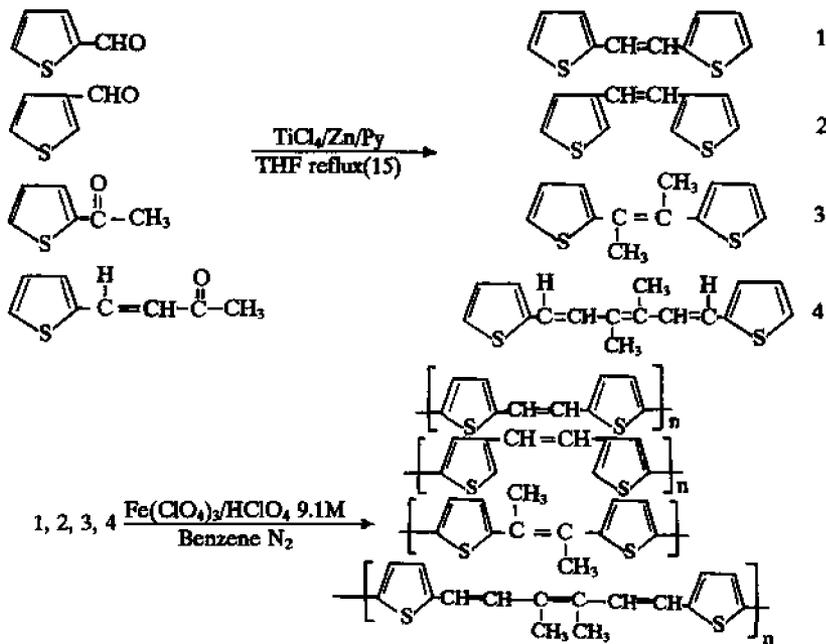


Fig.10. FTIR Spectrum of PDMDTHT (KBr pellets)



conductive polymers by this method. This chemical polymerization reaction is convenient, inexpensive and can be rapid. One of the potential uses of these conducting polymers could be in secondary batteries.

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