Electrochemical Synthesis and Properties of Poly(3-methylthiophene): Novel Synthesis of Poly(3-methylthiophene) with Pentachlorostannate and Hexachloroantimonate

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ABSTRACT: Poly(3-methylthiophene) (P3-MeT) doped with different anions were prepared electrochemically in the presence of tetraalkylammonium salts. The new poly(3-methylthiophene) $SnCl_5^-$ and $SbCl_6^-$ (P3-MeT $SnCl_5$ and P3-MeT $SbCl_6$) were prepared electrochemically using tetra-*n*-butylammonium pentachlorostannate and tetra-*n*-butylammonium hexachloroantimonate as the supporting electrolytes. The effect of current density, salt concentration, reaction temperature, and the nature of solvents on the polymer yield and polymer conductivities have been investigated. Cyclic voltammetry of poly(3-methylthiophene) has been examined at platinum electrode in 1,2-dichloroethane medium containing n-Bu_4NSnCl_5, Bu_4NSbCl_6, and Bu_4NClO_4 as the supporting electrolytes in the range of -1.0 to 1.7 V versus SCE in the presence and absence of 3-methylthiophene. Electrical conductivity, magnetic susceptibility measurements, and structural determination by elemental analysis and infrared studies were also made. Scanning electron microscopy revealed a globular, branched, fibrous and a spongy, fibrous morphology of poly(3-methylthiophene) $SnCl_5^-$, ClO_4^-, and $SbCl_6^-$, respectively. The thermal analysis of the polymers was also investigated. Possible causes for the observed lower conductivity of these polymers have also been discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 91–102, 1999

Key words: poly(3-methylthiophene); tetra-*n*-alkylammonium salts; electrochemical synthesis; cyclic voltammetry; conductivity measurements; thermogravimetric analysis

INTRODUCTION

There has been a rapid development in the preparation and properties of organic conducting polymers over the last few years.[1–10] Special attention of researchers is directed towards polymers based on aniline and five-membered heterocyclic compounds, such as pyrrole and thiophene.[11] An important step in the development of conjugated polyheterocycles occurred in 1979 when it was shown that highly conducting and homogeneous, free-standing films of polypyrrole could be produced by oxidative electropolymerization of pyrrole.[12] Among these numerous conducting polymers, polythiophenes have rapidly become the subject of considerable interest. Polythiophenes have attracted the attention as a part in several reviews, detailing their electropolymerization,[13–17] electrochemistry, environmental stabil-

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Table I   Yield, Magnetic Susceptibility, and Conductivity of Poly(3-methylthiophene) Obtained in Different Solvents and Electrolytes by the Electrochemical Method

Sl. No.	Solvent	Electrolyte[a]	Magnetic Susceptibility (emu/two-ring unit)	μ_{eff} (BM)	Yield (mg)	Conductivity (S cm^{-1})
1	1,2-Dichloroethane	TBAPCS	0.403×10^{-3}	0.969	240	3.32×10^{-4}
2	1,2-Dichloroethane	TBAP	0.299×10^{-3}	0.835	325	2.90×10^{-4}
3	1,2-Dichloroethane	TBAP[b]	5.264×10^{-3}	3.502	210	15.60×10^{-3}
4	1,2-Dichloroethane	TBATFB	3.444×10^{-3}	2.830	120	5.20×10^{-3}
5	1,2-Dichloroethane	TBAHFP	1.006×10^{-3}	1.531	150	8.68×10^{-5}
6	1,2-Dichloroethane	TBAHFP[b]	1.305×10^{-3}	1.779	165	4.09×10^{-7}
7	1,2-Dichloroethane	TBAHCA	0.647×10^{-3}	1.228	160	3.71×10^{-4}
8	1,2-Dichloroethane	TBAHCA[c]	1.141×10^{-3}	1.631	150	2.52×10^{-5}
9	Acetonitrile	TBAPCS	0.357×10^{-3}	0.912	160	1.13×10^{-4}
10	Acetonitrile	TBAP	4.059×10^{-3}	3.075	120	2.66×10^{-5}
11	Acetonitrile	TBAHFP	0.611×10^{-3}	1.193	300	1.29×10^{-5}
12	Dichloromethane	TBAPCS	0.139×10^{-3}	0.570	232	2.85×10^{-5}
13	Dichloromethane	TBAHCA	0.376×10^{-3}	0.936	120	4.10×10^{-5}
14	Nitrobenzene	TBAPCS	3.606×10^{-3}	2.899	226	0.86×10^{-4}

cd = 3.2 mA cm^{-2}; t = 15 ± 2°C; volume of reaction mixture-100 mL; electrolysis time = 5 h at Pt (6.25 cm^2) electrode.

[a] TBAPCS is tetra-*n*-butylammonium pentachlorostannate; TBAP, tetra-*n*-butylammonium perchlorate; TBATFB, tetra-*n*-butylammonium tetrafluoroborate; TBAHFP, tetra-*n*-butylammonium hexafluorophosphate; TBAHCA, tetra-*n*-butylammonium hexachloroantimonate.

[b] At the Ni electrode.

[c] At the stainless steel electrode (6.25 cm^2).

ity, and optical properties. Conducting polymers find importance as an interesting class of synthetic metals that are useful in a wide variety of technological avenues, such as the electroactive material in batteries, photoelectrochemical solar cells, and various electronic devices.[18–20]

Poly(3-methylthiophene) (P3-MeT) has been prepared electrochemically by oxidative polymerization of 3-methylthiophene using different electrolytes, such as Et_4NPF_6,[21] $Bu_4NCF_3SO_3H$,[22] Bu_4NClO_4,[23] Et_4NBF_4,[24] Bu_4NPF_6,[11] $HClO_4$,[25] and borontrifluoride ethyl ether.[26] In the present study, P3-MeT has been obtained incorporating Bu_4NSnCl_5 and Bu_4NSbCl_6 as a novel dopant in the polymer matrix.

The objectives of the present study are as follows:

(1) the synthesis of P3-MeTSnCl$_5$ and P3-MeTSbCl$_6$ by electropolymerization of 3-MeT using *n*-Bu$_4$NSnCl$_5$ and Bu$_4$NSbCl$_6$ galvanostatically;

(2) characterization of the P3-MeT by infrared, thermogravimetric, cyclicvoltammetry, magnetic susceptibility, electrical conductivity measurements, and scanning electron microscopy;

(3) elucidating the constituents of the P3-MeT salts; and

(4) the effect of dopant concentration, current densities, reaction temperature, and the nature of the solvent on the polymer yield and conductivity.

EXPERIMENTAL

3-Methylthiophene (Aldrich, bp 113°C), 1,2-dichloroethane (Glaxo), dichloromethane (CDH),

Table II   Yield and Conductivity of Poly(3-methylthiophene) Doped with SnCl$_5^-$ Formed in 1,2-Dichloroethane at Different Current Densities and Temperature

Sl. No.	Current Densities (mA cm^{-2})	Reaction Temperature ± 2°C	Yield (mg)	Conductivity ($\times 10^{-4}$ S cm^{-1})
1	1.6	15	160	1.56
2	2.4	15	182	2.90
3	3.2	15	240	3.32
4	4.0	15	282	3.80
5	3.2	05	302	4.25
6	3.2	10	284	3.53
7	3.2	30	210	2.97
8	3.2	40	150	1.35

3-Methylthiophene (0.1*M*) and *n*-Bu$_4$NSnCl$_5$, 0.01*M*; volume of reaction mixture, 100 mL; electrolysis time, 5 h at Pt (6.25 cm^2) electrode.
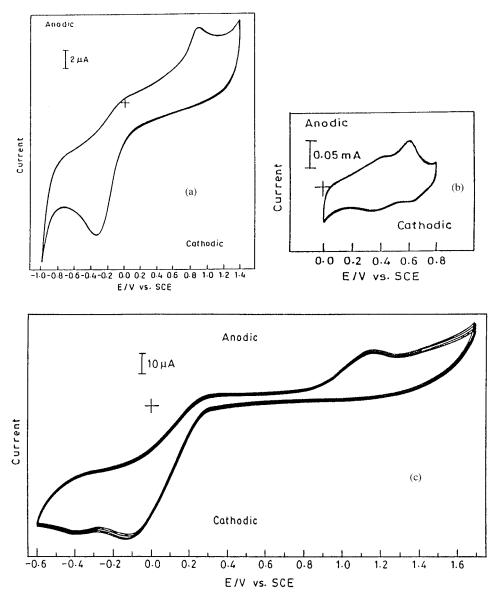
Figure 1 Cyclic voltammogram of 3-methylthiophene on a platinum microelectrode (0.16 cm^2) in 1,2-dichloroethane containing (a) 3-MeT (0.001M) and Bu$_4$NClO$_4$ (0.001M) at 100 mVs^{-1}, (b) 3-MeT (0.1M) and Bu$_4$NSnCl$_5$ (0.02M) at 50 mVs^{-1}, and (c) 3-MeT (0.01M) and Bu$_4$NSbCl$_6$ (0.005M) at 50 mVs^{-1}.

acetonitrile (BDH), and nitrobenzene (E. Merck) were used after distillation. Tetra-n-butylammonium salts were commercial products. However, tetra-n-butylammonium pentachlorostannate[27] and tetra-n-butylammonium hexachloroantimonate,[28,29] were prepared by the reported procedure and purified by recrystallization. The melting point of tetraalkylammonium salts and their concentration in 1,2-dichloroethane, used as the supporting electrolyte in electrochemical polymerization, are given as follows: n-Bu$_4$NClO$_4$

(Fluka), mp 210°C (0.1M); n-Bu$_4$NBF$_4$ (Aldrich), mp 160°C (0.02M); n-Bu$_4$NPF$_6$ (Aldrich), mp 244°C (0.02M); n-Bu$_4$NSnCl$_5$, mp 206°C (0.01M); and n-Bu$_4$NSbCl$_6$, mp 200°C (0.005M).

Electropolymerization

A typical electropolymerization was carried out in a simple one-compartment cell, which accommodates platinum foils (6.25 cm^2) as the anode and cathode. A solution of 3-methylthiophene (0.1M)

and *n*-butylammonium pentachlorostannate (0.01*M*) in 1,2-dichloroethane (100 mL) was kept in the cell at 15 ± 2°C under a nitrogen atmosphere. The electrolysis was performed at a constant current (I = 20 mA; cd = 3.2 mA cm^{-2}) with the help of a DC-regulated power supply without stirring. The electrolysis was continued for 5 h, and then it was terminated. During electrolysis, the colored polymer mass covered the anode surface heavily, and the same was removed by a sharp blade at the interval of 20–30 min.

The polymer mass was filtered, washed thoroughly with distilled water, and dried at a controlled temperature of 70°C for 4–5 h. The polymer mass was pressed (~ 10 Pascal) to form pellet for measuring its conductivity. The presence of counterions in the polymer chain was confirmed by the usual analytical method. Conductivity of the polymer samples were measured by using a Keithley electrometer. Magnetic susceptibility was determined by Gouy's methods at room temperature using mercury tetra thiocyanato cobalt (II), Hg[Co(CNS)$_4$], as a reference material. Cyclic voltammograms were recorded with an EG&G Parc Model-362 scanning potentiostat and a Servogor-733 *x*-*y*(*t*) recorder. Potential was measured with reference to saturated calomelelectrode (SCE). Thermogravimetric analysis (TGA) was carried out on STA-1500. A scanning electron micrograph (JSM-840-A) of the polymer was obtained with the film deposited on the platinum sheet. C, H, and N analysis of the polymer samples were taken by a microanalytical technique using a Perkin–Elmer 240C instrument. Infrared (IR) measurements were carried out with a JASCO-FTIR-5300 IR spectrophotometer using a KBr pellet. The IR spectral data of poly(3-methyl thiophene) are given as follows.

Poly(3-methylthiophene) ClO$_4^-$, IR (KBr, cm^{-1}): 1478, 1438, 1378, 1300, 1110, 1000, 920, 780, 680; poly(3-methylthiophene) BF$_4^-$, IR (KBr, cm^{-1}): 1480, 1430, 1378, 1050, 808, 780, 755, 680; poly(3-methylthiophene) Pf$_6^-$, IR (KBr, cm^{-1}): 1478, 1439, 838, 740, 705; poly(3-methylthiophene) SbCl$_6^-$, IR (KBr, cm^{-1}): 1489, 1420, 825, 775, 702; poly(3-methylthiophene) SnCl$_5^-$, IR (KBr, cm^{-1}): 1495, 1440, 830, 788, 701.

RESULTS AND DISCUSSION

Poly(3-methylthiophene) with various dopants, namely, ClO$_4^-$, BF$_4^-$, PF$_6^-$, SnCl$_5^-$, and SbCl$_6^-$ was obtained by the anodic polymerization of 3-methyl-
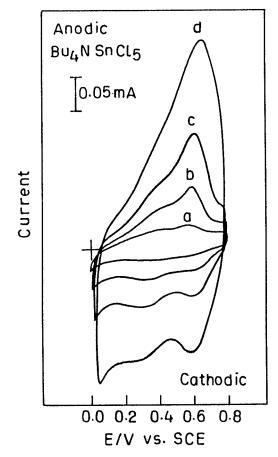

Figure 2 Cyclic voltammograms of 3-methylthiophene (0.1*M*) in 1,2-dichloroethane containing tetra-*n*-butyl ammonium pentachlorostannate (0.02*M*) on a platinum microelectrode with different scan rates of (a) 20, (b) 50, (c) 100, and (d) 200 mVs^{-1}.

thiophene in different solvents and electrolytes. P3-MeT doped with SnCl$_5^-$ and SbCl$_6^-$ are novel polymers reported here for the first time. The yield and electrical conductivity of the polymers under various polymerization conditions are given in Table I. The result shows that the yield and conductivity of the polymers varied with the nature of the solvent and electrolytes due to possible variation in the chain length of polymer. The oxidation level and nature of anion produces variation in the electrical conductivity. The results in the Table I suggest that the size of the counterion affects the electrical conductivity. The lower conductivity may be due to a lower level of oxidation. In general, the role of the anion in the electrical conductivity of the oxidized polymer film depends upon different parameters, like polarizability, ionization potential, basicity, size of anion, and rotational/vibrational dynamic of the anion. Hence, a correlation is not simple and
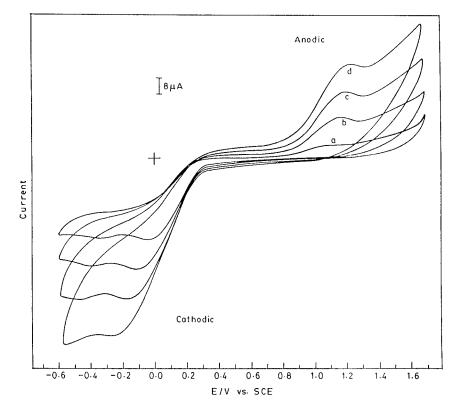
Figure 3 Cyclic voltammograms of 3-methylthiophene (0.01M) in 1,2-dichloroethane containing tetra-n-butyl ammonium hexachloroantimonate (0.005M) on a platinum microelectrode with different scan rates of (a) 20, (b) 50, (c) 100, and (d) 200 mVs^{-1}.

has to be worked out with these properties of the anion. Magnetic susceptibility per two ring unit mole and magnetic moment data are also recorded in Table I. The variation in magnetic susceptibility of the polymers may be due to a change in the unpaired spin concentration in the polymer chain units. Mizoguchi[30] proposed that the polaron–polaron reaction or polaron ionization to bipolaron (spinless charge defects) could change the spin concentration in the polymer sample and, hence, the magnetic susceptibility. In π-conjugated systems, polarons probably interact with each other or with neighboring chains, leading to spinless charged states or hole states. The state may be free or delocalized, depending on the coulomb interaction between the interacting moieties.

Table III   Cyclic Voltammetric Results: Polymerization of 3-Methylthiophene in 1,2-Dichloroethane Containing n-Bu$_4$NSnCl$_5$, n-Bu$_4$NSbCl$_6$, and Polymer Film in the Same Solvent Containing n-Bu$_4$NClO$_4$ (0.05) Without 3-Methylthiophene

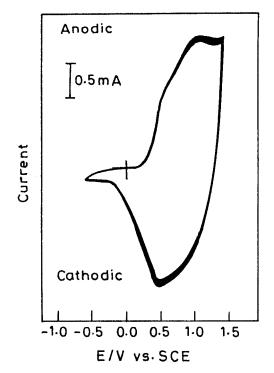| Sl. No.	S.R. (mVs^{-1})	n-Bu$_4$NSnCl$_5$ (0.02M)					n-Bu$_4$NSbCl$_6$ (0.005M)					n-Bu$_4$NClO$_4$ (0.05M)				
		Epa (mV)	Epc (mV)	Ipa (mA)	Ipc (mA)	Ipa–Ipc	Epa (mV)	Epc (mV)	Ipa (μA)	Ipc (μA)	Ipa–Ipc	Epa (mV)	Epc (mV)	Ipa (mA)	Ipc (μA)	Ipa–Ipc
1	20	560	600	0.035	0.015	2.3	1060	−30	64	400	0.16	750	650	0.40	0.40	1.0
2	50	580	600	0.090	0.038	2.3	1150	−110	200	560	0.35	900	600	0.90	0.85	1.05
3	100	600	600	0.165	0.070	2.3	1190	−170	328	704	0.46	1050	550	1.80	1.55	1.16
4	200	640	590	0.305	0.150	2.0	1220	−270	464	880	0.52	—	—	—	—	—

Figure 4 Cyclic voltammograms of poly(3-methylthiophene) film on a platinum microelectrode in 1,2-dichloroethane containing tetra-*n*-butyl ammonium perchlorate (0.05*M*) at 100 mVs⁻¹.

Figure 6 Cyclic voltammograms of poly(3-methylthiophene) film on a platinum microelectrode containing 1,2-dichloroethane tetra-*n*-butylammonium perchlorate (0.05*M*) at different scan rates of (a) 20, (b) 50, and (c) 100 mVs⁻¹.

Effect of Current Density and Reaction Temperature

The yield of the anodically polymerized polymer mass was found to increase with an increase of current densities. Similarly, the conductivity was also observed to increase with the increase in current density. The conductivity of the polymer obtained at cd, 1.6 mA cm⁻² was found to be lower than those obtained at higher current density (Table II). Structural changes in the polymer due
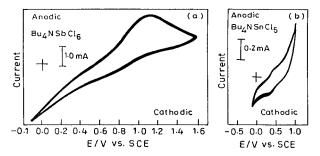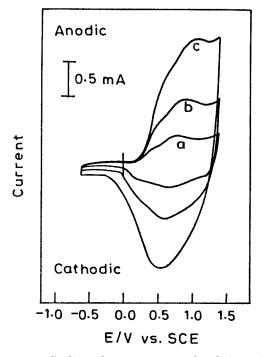

Figure 5 Cyclic voltammograms of poly(3-methylthiophene) film on a platinum microelectrode in 1,2-dichloroethane containing (a) Bu₄NSbCl₆ (0.005*M*) and (b) Bu₄NSnCl₅ (0.02*M*) at 50 mVs⁻¹.

to different polymerization kinetics at higher current densities have been indicated as being responsible for this behavior. If the reaction temperature was varied from 05 to 40°C, some change both in the yield and conductivity of the polymer was observed (Table II). The decrease in conductivity of the polymer with the increase of temperature is attributed to a smaller conjugation length of polymer chains. The polymer yield also decreased with an increase of temperature, possibly due to the increase in the termination process with the rise of reaction temperature; consequently, more oligomers might have been formed, which did not deposit as an insoluble polymer on the anode surface.

Electrochemical Properties

Cyclic Voltammetry of Poly(3-methylthiophene) in Presence of 3-MeT

Electrochemical behavior for the polymerization of 3-methylthiophene was examined by cyclic voltammetry in 1,2-dichloroethane solution containing different electrolytes, such as tetra-*n*-butylammonium perchlorate (0.1*M*), tetra-*n*-bu-
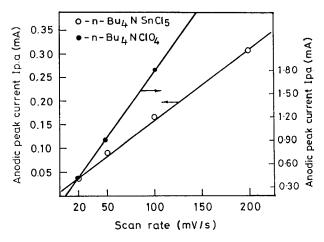
Figure 7   Plot of the anodic peak current against the scan rate.

tylammonium pentachlorostannate (0.02M), and tetra-n-butylammonium hexachloroantimonate (0.005M) in the range of −1.0 to 1.7 volt versus SCE using a platinum microelectrode (0.16 cm^2) as a working electrode and platinum foil as an auxiliary electrode. The anodic peak for the oxidation of 3-methylthiophene in the above electrolytic media appears at 850, 600, and 1150 mV, respectively, under a nitrogen atmosphere (Fig. 1). The cyclic voltammogram of 3-methylthiophene in the presence of n-Bu$_4$NClO$_4$ and Bu$_4$NSbCl$_6$ shows an asymmetrical redox peak, while in n-Bu$_4$NSnCl$_5$ as the electrolyte, a symmetrical redox peak is observed. The cyclic voltammogram of 3-methylthiophene reveals that the redox peak current increases with the increase in the scan rate and peak separation also increases (Figs. 2 and 3). The peaks are also broad, which are probably due to the presence of mixed valence species, such as the cation, radical, and dication of polymer anion salts. From Figures 2 and 3, it is

clear that the polymerization process is reversible with n-Bu$_4$NSnCl$_5$ and irreversible with n-Bu$_4$NSbCl$_6$. The cyclic voltammetric data of these voltammograms are tabulated in Table III.

Cyclic Voltammetry of Poly(3-methylthiophene) in the Absence of 3-MeT

The cyclic voltammetry of poly(3-methylthiophene) film was investigated in 1,2-dichloroethane containing tetra-n-butylammonium perchlorate (0.05M), n-Bu$_4$NSnCl$_5$ (0.02M), and n-Bu$_4$NSbCl$_6$ (0.005M) in the potential range of 1.0 to 1.6 V versus SCE on a platinum microelectrode (0.16 cm^2) without a monomer (Figs. 4 and 5). The polymer film was found to be fairly stable without any severe film degradation because there is little change in anodic and cathodic peak, current at the multiple sweep cycle. The behavior of poly(3-methylthiophene) ClO$_4^-$ film at different scan rates (Fig. 6) suggests that the redox peak current increases with the increase of scan rate. The plot of anodic peak currents (data from the voltammetric curve in Figs. 2 and 6) is linear with the scan rate (Fig. 7), suggesting that the redox reaction is reversible. The same conclusion is drawn for poly(3-methylthiophene) ClO$_4^-$ film, where the reversibility is confirmed by the fact that the peak current ratio was found to be unity. The results of cyclic voltammogram of poly(3-methylthiophene) ClO$_4^-$ film are also given in Table III.

Effect of Dopant Concentration and Morphology

The polymerization reaction of 3-methylthiophene was also carried out electrochemically at different dopant concentrations of Bu$_4$NSnCl$_5$ (Table IV). The yield of polymer increases in a

Table IV   Yield and Conductivity of Poly(3-methylthiophene) Doped with SnCl$_5^-$ Formed with Different Concentration of Doping Agent n-Bu$_4$NSnCl$_5$ and in Different Solvents 3-Methylthiophene (0.1M) at Pt (6.25 cm^2) Electrode

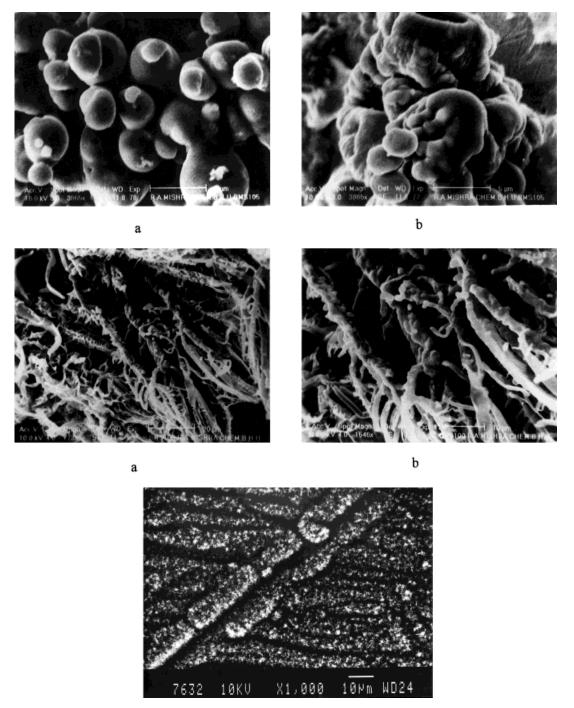| Sl. No.	Concentration of n-Bu$_4$NSnCl$_5$ (mol L^{-1})	Solvent	Yield (mg)	Conductivity (S cm^{-1})
1	0.01	1,2-Dichloroethane	240	3.32×10^{-4}
2	0.02	1,2-Dichloroethane	243	4.35×10^{-4}
3	0.03	1,2-Dichloroethane	270	4.96×10^{-4}
4	0.01	Dichloromethane	232	2.85×10^{-4}
5	0.01	Acetonitrile	160	1.13×10^{-4}
6	0.01	Nitrobenzene	226	0.86×10^{-5}

Figure 8   (A) SEM picture of (a) $SnCl_5^-$-doped poly(3-methylthiophene) and (b) single globule magnification $\times 3865$; (B) SEM picture of ClO_4^--doped poly(3-methylthiophene) magnification (a) $\times 773$ and (b) $\times 1546$; (C) SEM picture of $SbCl_6^-$-doped poly(3-methylthiophene) magnification $\times 1000$.

small proportion with the increase of dopant concentration, as expected. Similarly, conductivity also increases with the increase of dopant concentration, which leads to a decrease in the band gap between conduction and the valence band, thereby causing an increase in the conductivity of the polymer. The morphology of the P3-MeT film with different counterions was studied using scanning electron microscopy (SEM). The different morphologies obtained for P3-MeT polymer
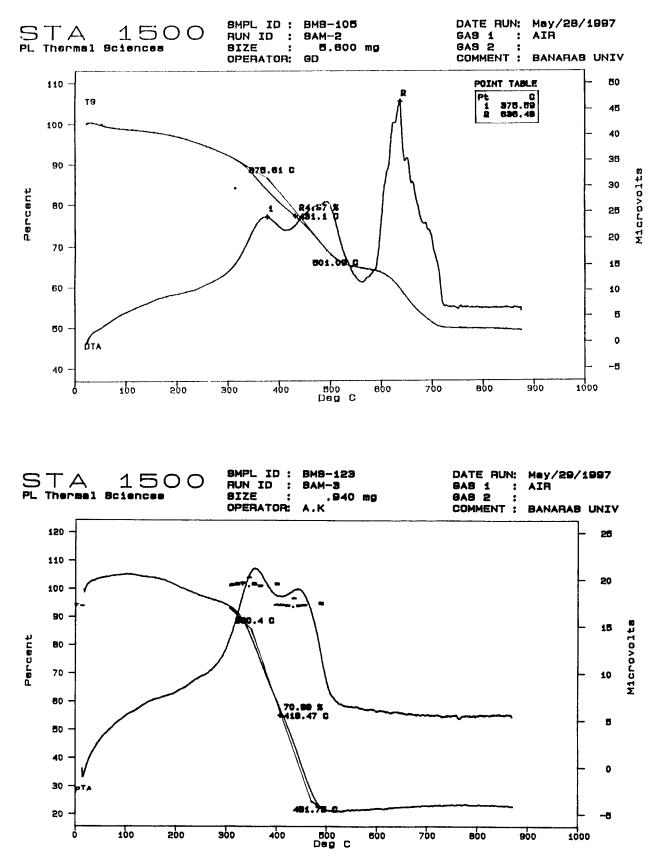
Figure 9   TGA and DTA curve of (a) $SnCl_5^-$-doped poly(3-methylthiophene) and (b) $SbCl_6^-$-doped poly(3-methylthiophene) with a heating rate of 10°C min^{-1}.

oxidized with different counterions are presented in Figure 8. The surface morphology of the polymer film containing $SnCl_5^-$ [Fig. 8(A)] counterion shows a distinct globular structure, while with the ClO_4^- anion [Fig. 8(B)] dopant, the surface is found to be branched and fibrous. The polymer film reveals a compact, spongy, fibrous surface when the counterion was $SbCl_6^-$ [Fig. 8(C)].

Thermal Properties

Thermogravimetric analysis (TGA) of poly(3-methylthiophene) $SnCl_5^-$ shows three stages of weight loss [Fig. 9(a)]. The one around 150°C may be due to the loss of water, and the weight loss around 300–500°C may possibly be due to the loss of a low-molecular-weight compound like pentachlorostannate anion. The third stage of weight loss around 500–700°C represents the decomposition of the polymer sample, which is followed by the breakdown of polymer chain. The thermal analysis of $SbCl_6^-$-doped [Fig. 9(b)] poly(3-methylthiophene) shows that the weight loss from 250–481°C is possibly due to the loss of the $SbCl_6^-$ anion and decomposition of the polymer matrix dynamic thermal analysis (DTA) of poly(3-methylthiophene) doped with $SnCl_5^-$ [Fig. 10(a)] and $SbCl_6^-$ [Fig. 9(b)] shows the exothermic peak at 375, 635 and 375, 450°C, respectively. The exothermic decomposition possibly corresponds to the branching or crosslinking of the polymer chain (Table V). The maximum decomposition of the polymer chain doped with $SnCl_5^-$ [Fig. 10(a)] and $SbCl_6^-$ [Fig. 10(b)] occurs at 700 and 500°C, respectively.

The thermal stability of the P3-MeT with the $SnCl_5^-$ and $SbCl_6^-$ counterion was studied using TGA. From Table V, it is clear that the percentage of degradation for P3-MeT $SnCl_5$ and P3-MeT
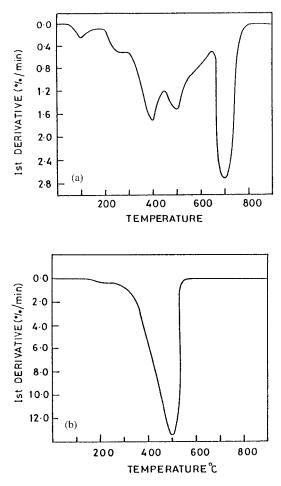

Figure 10   Derivative thermogravimetry (DTG) curve of (a) $SnCl_5^-$-doped poly(3-methylthiophene) and (b) $SbCl_6^-$-doped poly(3-methylthiophene) with a heating rate of 10°C min^{-1}.

$SbCl_6$ was nearly the same at 300°C. Thermograms obtained for P3-MeT $SnCl_5$ suggest that the degradation takes place at the following dif-

Table V   Thermogravimetric Analysis of Poly(3-Methylthiophene)

| Sl. No. | Polymerization | | | Polymer TGA | | | |
	Monomer	Solvent	Electrolyte	Percentage Loss at 300°C	Percentage Loss at 400°C	Residue Percentage[a]	DTG[b] (T in °C)
1	3-Methylthiophene	1,2-Dichloroethane	TBAPCS	4.90	18.30	49.0	700
2	3-Methylthiophene	1,2-Dichloroethane	TBAHCA	5.00	40.00	23.2	500

Measurement performed at 10°C min^{-1} under air.
[a] Weight percentage of residue at 900°C.
[b] High rate of decomposition of polymers.

Table VI   Analytical Data of Poly(3-methylthiophene) with Different Anion

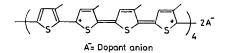| Sl. No.	Polymer	Found (calc, %)		
		C	H	S
1	Poly(3-methylthiophene) perchlorate	40.56 (41.16)	2.87 (2.74)	22.53 (21.95)
2	Poly(3-methylthiophene) tetrafluoroborate	43.87 (43.01)	3.13 (2.86)	23.48 (22.93)
3	Poly(3-methylthiophene) pentachlorostannate	24.93 (24.98)	1.56 (1.63)	13.73 (13.10)
4	Poly(3-methylthiophene) hexachloroantimonate	23.35 (22.78)	1.74 (1.51)	13.24 (12.15)
5	Poly(3-methylthiophene) hexafluorophosphate	34.91 (35.61)	2.97 (2.37)	9.36 (8.99)

ferent stages: 150, 300–500, and 500–700°C; whereas in case of P3-MeT, $SbCl_6$ degradation occurs at 250 and 300–500°C. The rate of degradation was high in the case of P3-MeT $SbCl_6$ compared to P3-MeT $SnCl_5$ at the temperature range between 300–400°C. The percentage of degradation for P3-MeT $SnCl_5$ and P3-MeT $SbCl_6$ at 500°C was 30 and 76.8%, respectively. Around 900°C, only 23.2% of the residue remained in the case of P3-MeT $SbCl_6$, whereas about 49% of the residue was present in the case of P3-MeT $SnCl_5$. These TGA studies show that the thermal stability of P3-MeT $SbCl_6$ is less compared to P3-MeT $SnCl_5$.
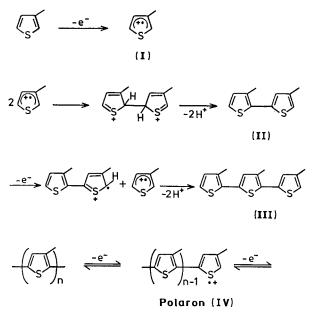
Structural Study

The IR spectra data of ClO_4^--doped poly(3-methyl thiophene) shows absorption bands at 1478 and 1438 cm^{-1}, which can be assigned to the stretching vibration mode of thiophene ring present in polymer chain. The peak at 1110 cm^{-1} shows the presence of ClO_4^- anion in the polymer matrix. Disubstitution in the poly(3-methylthiophene) confirmed by the absorption band at 780 cm^{-1} reveals that the coupling of 3-methylthiophene rings occurs preferentially at the 2,5-positions. The absorption band at 780 cm^{-1} may be attributed to the C—H out-of-plane vibration. An average result of elemental analysis of electrochemically synthesized poly(3-methylthiophene) is presented in Table VI. According to the result, the empirical formula was defined, and $[C_5H_4S]_4$ $2A^-$ indicates that the presence of two anions for every four aromatic ring unit. The above studies and elemental analysis are indicative that the poly(3-

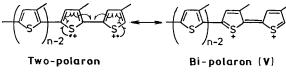methylthiophene) has the following possible structural frame work (Scheme 1).

Mechanism

The postulation of the mechanism of polymerization is based on the cyclic voltammetry (CV) study and on the commonly accepted cation radical coupling mechanism. The oxidation of the 3-MeT monomer at the anode surface produces charged species precursors, which require the transfer of 2 electrons per molecule. Scheme 2 represents the mechanism proposed for the electropolymerization of 3-MeT, by analogy to the already known coupling reactions of aromatic compounds.[31,32] Since the electron transfer reaction leading to radical cation is much faster than the diffusion of the monomer from the bulk solution, it follows that a high concentration of radicals is continuously maintained near the electrode surface. In the subsequent step, the coupling of two radical cations produces a dihydrodimer cation, which leads to a dimer after the loss of two protons and rearomatization. This rearomatization constitutes the driving force of the chemical reaction. Due to applied current, the dimer, which is more easily oxidized than the monomer (3-MeT), occurs in its radical form and undergoes a further coupling with a monomeric radical. Electropolymerization pro-

A$^-$= Dopant anion

Scheme 1

Scheme 2

ceeds then through successive electrochemical and chemical steps according to Scheme 2.

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