

Review

LOW POTENTIAL ELECTROPOLYMERIZATION OF ANISOTROPIC CONDUCTIVE POLYTHIOPHENE FILMS AND FABRICATION OF ELECTRICAL DEVICES

Xiao-bo Wan, Yun Lu, Xiao-rong Liu,
Liang Zhou, Shi Jin and Gi Xue *

*Department of Polymer Science and Engineering, the State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093, China*

Abstract The complexation of thiophene with a Lewis acid with moderate acidity as a solvent, such as BF_3 -ethyl ether (BFEE) remarkably lowered the electrochemical polymerization potential. The positively charged metal surface of electrode in the process of electrochemical deposition enhanced the coordination interaction between π -electrons of thiophene unit and the metal, which makes thiophene rings lie parallel to the surface of electrode, resulting in a highly ordered polymeric structure. Because of the large intra-chain transfer integrals, the transport of charge is believed to be principally along the conjugated chains, which is much greater than the inter-chain hopping. The specific electrical resistance across the polythiophene film thickness is more than 10^4 times than that along the surface plane of the film. In this paper we review the recent development of polymerization technique by low potential electrochemical method performed in our lab and several electrical devices in which the compact polythiophene films, such as anionic and cationic sieves, and laminate film junction of undoped polythiophene derivatives were used.

Keywords Conductive polymer, Polythiophene, Anisotropy, Electric device, Film junction

INTRODUCTION

During the last decade conducting polymers have received considerable attention due to their potential applications^[1-4]. Among a number of conducting polymers, polythiophene (PT) has attracted much interest as it is stable to both oxygen and moisture^[5]. Most conductive PT films were prepared by the electrochemical polymerization of thiophene in an organic solvent such as acetonitrile, nitromethane, nitrobenzene or propylene carbonate^[6-8]. However, electrooxidation of thiophene in these media requires potentials above 1.6 V versus SCE. The high potentials (above 1.5 V^[9,10]) would irreversibly damage the conjugated system, due to overoxidation. Although thiophene oligomers can be polymerized at lower potentials, yet it must be emphasized that the resulting polymers show a lower average conjugation length when oligomers are used as starting molecules^[11-13].

In moderately concentrated HClO_4 (5 mol/L) the polymerization of thiophene can take place at a very low potential (0.9 V versus SCE). However, the electrical conductivity of the resulting PT film is rather low (0.10 S cm^{-1}) as compared with that polymerized in organic media due to the decreased average length of its conjugated segments evidenced by the hypochromic shift of the absorption maximum of the resulting polymer^[14].

*Corresponding author: Qi Xue (薛 奇), E-mail: xuegi@nju.edu.cn

Received October 19, 1997

Electrooxidation of benzene can be achieved at a lower potential (1.6 V) in strong acidic media such as AlCl_3 /nitrobenzene solution than in liquid sulphur dioxide (2.1 V versus Ag/AgCl)^[15-17]. The significant decrease in the oxidation potential of benzene in strong acidic media can be rationalized in two ways: Firstly, benzene forms a complex with the strong acid, thereby reducing the resonance stabilization of the aromatic ring, and shifting the oxidation potential to less anodic potential^[18]. Secondly, the increased acidity of the solvent imparts greater stability to the cation-radical, which can promote the electrooxidative polymerization.

Nevertheless, thiophene is quite unstable in this strong acidic solvent and an acid initiated additive polymerization can take place^[19, 20], resulting in a nonconjugated polymer. This factor prevents the preparation of films with high conductivity in strong acidic solvents by electrochemical polymerization of thiophene.

Recently, we found that the oxidation potentials of thiophene in solvated Lewis acids were related to the aromaticity of the thiophene rings, by studying the FT-Raman spectra. Low potential polymerization of thiophene in BF_3 -ethyl ether (BFEE) could be successfully performed using the solvated strong Lewis acids BF_3 -ethyl ether (BFEE) and $\text{AlCl}_3/\text{CH}_3\text{CN}$. The polymer obtained from BFEE was characterized as a conducting film with long effective conjugated length and with mechanical properties better than an aluminium metal sheet. Of particular interest is that the conductivity of the film in the direction of the film plane is more than 10^4 times higher than that in the perpendicular direction. This anisotropic conductivity is related to the molecular orientation. Fourier transform surface enhanced Raman scattering (SERS) and infrared reflection-absorption spectroscopy were used to characterize the molecular arrangement of PT chains on metal.

EXPERIMENTAL

Chemicals

Thiophene and BFEE were purified by distillation before use. Acetonitrile was successively refluxed with potassium permanganate and phosphoric anhydride, then distilled in the presence of anhydrous potassium carbonate. Nitromethane was distilled after reflux with concentrated sulfuric acid. Anhydrous aluminum chloride was used as received. $\text{AlCl}_3/\text{CH}_3\text{CN}$ solutions were used at a concentration of 3 mol L^{-1} .

Electrochemical Experiments

Electrochemical examinations and polymerization were performed in a one-compartment three-electrode cell with the use of a PARC M273 potentiostat under the control of a computer. To obtain a free-standing film, stainless steel sheets ($1.5 \times 7 \text{ cm}^2$) were employed as working electrodes, and counter electrodes respectively, which were polished with abrasive paper (1200 mesh) and diamond paste ($1.5 \mu\text{m}$), and were then cleaned in an ultrasonic acetone bath before use. The galvanostatic method was used for electrochemical polymerization at a current density of 1 mA cm^{-2} and the thickness of the deposited films was controlled by the electric charge applied during film growth. Electrochemical measurements were carried out on a platinum disc (diameter 0.5 mm), which was polished and cleaned as mentioned above before each experiment. All potentials were measured versus an Ag/AgCl (3.5 mol/L KCl) reference. Each solution containing 0.1 mol L^{-1} thiophene was purged by bubbling dry argon before the experiment and maintaining a slightly positive argon pressure during the experiment.

Measurement of Electrical and Mechanical Properties

After a good wash with acetone, the polymer films were stripped from the electrodes and dried under vacuum at ambient temperatures and the conventional four-electrode was utilized to measure the electrical conductivity of the PT film. The tensile strength of the free standing PT film

was measured at a stretching rate of 5 cm min^{-1} . The anisotropy in conductivities was measured by the method reported in the literature^[21].

Spectroscopic Experiments

FT-Raman studies of thiophene solutions were carried out at a concentration of 1 mol L^{-1} . All of the normal FT-Raman and surface enhanced Raman scattering (SERS) measurements were performed with a Bruker Model RFS 100 Fourier transform Raman spectrometer with an air-cooled diode-pumped Nd:YAG laser and a Ge detector cooled to liquid nitrogen temperature. The incident laser excitation was 1064 nm. The outputs were 30 and 50 mW for surface enhanced and normal FT-Raman measurements, respectively. Spectra were obtained with a resolution of 4.0 cm^{-1} and 100 scans. The scattering light was collected at an angle of 180° . The UV-visible spectrum was recorded with a Shimadzu UV-3100 spectrophotometer. A UV-visible spectrum was obtained from a PT film deposited on to an ITO (Indium Tin Oxide coated optical glass) at a deposited charge of 100 mC cm^{-2} under a current density of 1 mA cm^{-2} . An electrochemically roughened Au disk (diameter 3mm) was employed as the substrate in the SERS experiment. In each experiment, the PT layer was deposited onto the electrode at a current density of 1 mA cm^{-2} for 20 s. For IR measurements, the PT films deposited onto stainless steel electrodes had been dedoped with 20% ammonia, washed with distilled water and acetone, and dried under vacuum at 80°C for 24 h before spectroscopic characterization. IR spectra were recorded with a Bruker IFS-66V spectrometer under vacuum.

RESULTS AND DISCUSSION

Low Potential Polymerization and FT-Raman Studies of Thiophene in Solvated Lewis Acid

The donor number is a property indicating the strength of the interaction between the solvent and the acceptor, i.e. the Lewis acid, and is of particular significance in evaluating the coordination-chemical reactions in solution. The interaction between the solvent and the Lewis acid increases with increasing donor number of the solvent. Due to the relatively weak interaction between Lewis acid and solvent, solvated AlCl_3 (or BF_3) in nitromethane (donor number = 2.7)^[22] can initiate the additive polymerization of thiophene, resulting in nonconjugated chains. When we selected CH_3CN (donor number = 14.1) and $(\text{C}_2\text{H}_5)_2\text{O}$ (donor number = 19.2)^[22] as the solvent, the interaction between the solvent and the Lewis acid is somewhat increased. As a result, the acidity of these solvated Lewis acids becomes too weak to initiate the additive polymerization of thiophene. Additive polymerization is not expected in an electrochemical reaction since it would result in a nonconjugated chain. These solvated Lewis acids seem to be suitable for electrochemical polymerization because thiophene is quite stable in these media.

Due to its sensitiveness toward the carbon skeleton, FT-Raman spectroscopy is an effective technique for studying the interaction between the acceptor and donor. A spectrum subtraction technique was employed to study the interaction between thiophene and the solvated Lewis acid. The absorbance of solvent was subtracted from that of each electrolyte solution and the resulting spectrum reveals the interaction between thiophene and solvent. The difference spectra are shown in Fig. 1B, C, and D. Figure 1A is the Raman spectrum of pure thiophene, which shows ring C—H stretching bands at 3109.3 and 3083.6 cm^{-1} , C=C and C—C stretching bands at 1407.0 cm^{-1} and 1359.6 cm^{-1} , and C—H in-plane deformation at 1079.9 and 1033.5 cm^{-1} , respectively. The absorption bands at 833.6 and 605.8 cm^{-1} are attributed to the deformation vibration of ring and C—S—C, respectively^[23]. In an aromatic ring, the difference in bond length between the C=C and C—C is reduced due to conjugation. Furthermore, the force constant of a bond relates to its bond strength. Therefore the frequency difference indicating the difference of the bond force constant between the $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}-\text{C}}$ can be employed to evaluate the aromaticity of a thiophene ring. The

decrease in aromaticity of thiophene in the solvated Lewis acids was evident from the frequency changes in Fig.1B, C, and D, and was expected to reduce the oxidation potentials. This point was verified by us experimentally.

Figure 2 shows the anodic polarization curves of thiophene in various electrolyte solutions. The virgin oxidation of thiophene is initiated at 1.4 V in the presence AlCl_3 (B), which has a lower anodic potential compared with that in the absence of the Lewis acid (A) (with a threshold potential of 1.7 V). Furthermore, the threshold potential of thiophene in BFEE solution (C) has a higher cathodic potential (1.3 V) than that in $\text{AlCl}_3/\text{CH}_3\text{CN}$ solution.

The frequency differences between $\text{C}=\text{C}$ and $\text{C}-\text{C}$ stretching lines in Fig.1 and the corresponding oxidation potential of thiophene in three solutions are listed in Table 1.

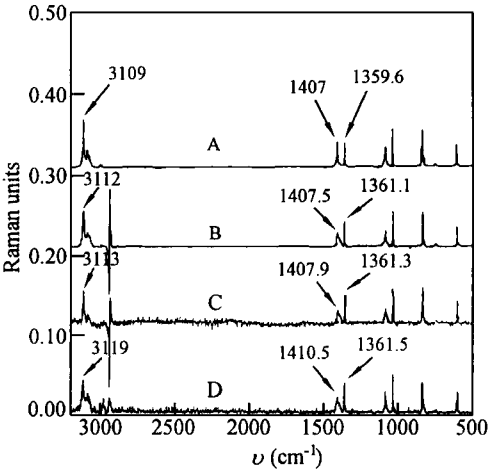


Fig. 1 FT-Raman spectra of thiophene and thiophene in various solutions (A) Raman spectrum of pure thiophene; (B)-(D) are the difference spectra by subtracting corresponding solvents from the solutions; (B) Thiophene in CH_3CN ; (C) Thiophene in $\text{AlCl}_3/\text{CH}_3\text{CN}$; (D) Thiophene in BFEE.

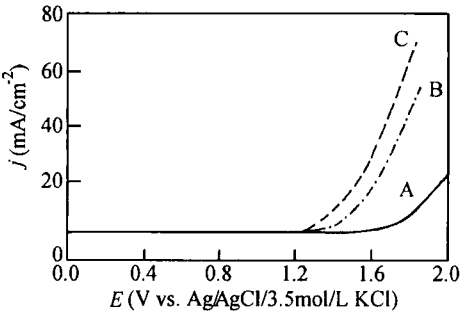


Fig. 2 Anodic polarization curves of $0.1\text{ mol L}^{-1} \text{N(Et)}_4\text{ClO}_4/\text{CH}_3\text{CN}$ (A) $3\text{ mol L}^{-1} \text{AlCl}_3/\text{CH}_3\text{CN}$ (B), BFEE(C) at a scan rate of 10 mV S^{-1} All solutions contain 0.1 mol L^{-1} thiophene.

Table 1. Difference of frequency between $\nu_{\text{C}=\text{C}}$ and $\nu_{\text{C}-\text{C}}$ and oxidation potential of thiophene in corresponding solution

Solution	Frequency difference ($\nu_{\text{C}=\text{C}} - \nu_{\text{C}-\text{C}}$) (cm^{-1})	Oxidation potential (V)
CH_3CN	46.4	1.7
$\text{AlCl}_3/\text{CH}_3\text{CN}$	46.6	1.4
BFEE*	49.0	1.3

* BFEE: BF_3 -ethyl ether

It can be seen clearly that the aromaticity of a thiophene ring is reduced in the presence of Lewis acid. The strength of interaction between thiophene and the solution increases in the order of CH_3CN , $\text{AlCl}_3/\text{CH}_3\text{CN}$ and BFEE, which accords with their acidity order. With the increased interaction strength and decreased aromaticity, the oxidation potentials of thiophene in solvated Lewis acid are markedly lowered. The oxidation potentials of thiophene in $\text{AlCl}_3/\text{CH}_3\text{CN}$ and BFEE are 1.4 V and 1.3 V, respectively, instead of 1.7 V in CH_3CN . It must be emphasized that these potentials are lower than the overoxidation potential of PT (1.45 ~ 1.55 V). In other words, high quality PT film may be electrosynthesized in our systems. With this aim in mind, we prepared

high quality PT films with high conductivity (200 S cm^{-1}), excellent tensile strength (140 MPa), and high anisotropy by electrooxidative polymerization of thiophene in BFEE.

Compared with the films polymerized in HClO_4 at low potential, the average effective mean conjugation length of our polymers are rather high. The UV-visible spectrum of a dedoped PT film polymerized in 0.1 mol/L thiophene/BFEE solution is shown in Fig. 3. The absorption maximum appears at 500 nm instead of 460 nm of that prepared in HClO_4 ^[14], indicating higher conjugation in films prepared from the thiophene/BFEE system. Table 2 shows the electrical and mechanical properties of PT films obtained in various systems.

The conductivity data of the doped film agrees with the result of UV-visible analysis. A PT film prepared from the BFEE exhibits conductivity as high as 100 S cm^{-1} , while that obtained from the HClO_4 system has a lower conductivity in the range of $0.1 \sim 1 \text{ S cm}^{-1}$ ^[14]. With the repression of overoxidation of deposited PT by the lower polymerization potentials, PT can be deposited onto the electrode more regularly and compactly, which results in high anisotropy and compact morphology. Additionally, the repression of overoxidative degradation supports a high degree of polymerization.

Table 2. Electrical and mechanical properties of PT films electropolymerized in various systems.

Solvent	Conductivity (S cm^{-1})	Tensile strength (MPa)	Anisotropy* ($\sigma_{\parallel}/\sigma_{\perp}$)
CH_3CN	10	brittle	—
BFEE	100	140	$>10^4$
HClO_4	0.1-1	—	—

* The electrical conductivities for anisotropy calculation were measured using two-electrode technique.

The transmission IR spectrum of a dedoped PT film shows a degree of polymerization of about 80 in contrast with about 40 in common media^[24]. Furukawa et al. proposed the relationship^[24, 25]:

$$DP = 2(R_0 / R + 2)$$

where R is the ratio of the integrated intensities of the two IR bands attributed to out-of-plane vibrations for monosubstituted (692 cm^{-1}) and 2, 5-disubstituted (788 cm^{-1}) thiophenes. R_0 is the value of R estimated for the α, α' sexithiophene. The free-standing polymer film prepared from thiophene/BFEE solution is flexible and has good mechanical properties. Its tensile strength (140 MPa) is higher than any conductive polymers reported in the literature^[26], and is also higher than that of metal aluminum sheets (100 to 110 MPa). The extremely high tensile strength is a result of the high degree of polymerization and regular structure with compact morphology.

The obtained PT films were characterized as two-dimensional conducting polymer films by their high anisotropy. This property is associated with the orientation of PT deposited onto the surface of the electrode. FT-Raman SERS and IR reflection-absorption spectroscopy are useful for studying the orientation of molecules on the surface of the metal. Figure 4A shows the FT-Raman SERS spectrum of a PT film deposited onto gold from thiophene/BFEE solution after the polymerization had proceeded for 20 s. The corresponding SERS spectrum obtained from thiophene/nitromethane solution was illustrated in Fig. 4B for comparison. The normal FT-Raman spectra recorded from a PT film with a thickness of $2 \mu\text{m}$ deposited on a ITO electrode are also illustrated in Fig. 4C.

The FT-Raman spectra depicted in Fig. 4A are not characterized as resonance Raman spectra because they were recorded by laser excitation at $1.064 \mu\text{m}$ and there is no absorption in this region for UV-visible spectra of PT. As can be seen from Fig. 4A, the interaction with the surface will cause a change in the spectrum. These changes include the marked bathochromic shift of $\text{C}=\text{C}$

skeleton vibration (frequency shifted about 30 cm^{-1}), the appearance of new Raman lines, and changes in relative intensities of some Raman lines, as compared with the normal Raman spectra of PT. These spectral changes along with the high signal-to-noise ratio in Fig. 4A are characteristics of a typical SERS spectrum. In Fig. 4A, the bands at 1417 , 1220 cm^{-1} are attributed to the ring C=C stretching and inter-ring C—C stretching vibration^[27–29], respectively. C—H in-plane bending vibration is found at 1049 cm^{-1} . Ring-deformation vibrations appear at 734 cm^{-1} and 692 cm^{-1} . The most interesting feature of the SERS of PT is the appearance of two new bands at 1155 cm^{-1} and 794 cm^{-1} , arising from inter-ring C—C stretching vibrations of the distorted parts^[28] and out-of-plane bending vibrations of $\beta_{\text{C-H}}$ ^[29], respectively. The appearance of these bands in large enhancement in the SERS spectrum is shown in Fig. 4A.

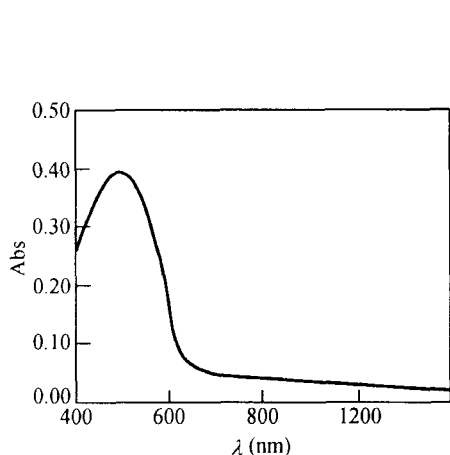


Fig. 3 UV-vis spectrum of a dedoped PT film deposited onto ITO electrode at a deposited charge of 100 mC cm^{-2}

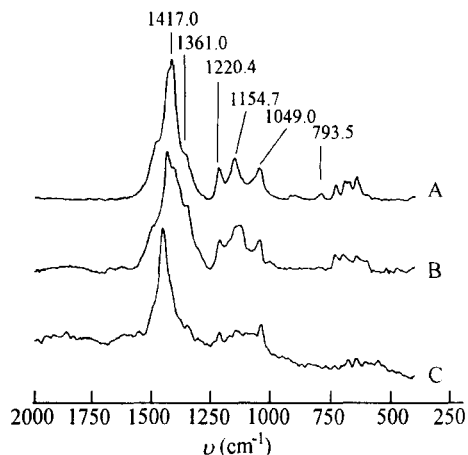


Fig. 4 FT-Raman spectra of undoped polythiophene

(A) Surface enhanced Raman spectrum of a thin layer PT film deposited onto gold disk from 0.1 mol/L thiophene/BFEE after the polymerization has proceeded for 20 s ; (B) FT-Raman spectrum of a PT film deposited onto gold disk from 0.1 mol/L thiophene/nitromethane solution; (C) FT-Raman spectrum of a PT film deposited onto ITO at a thickness of about $2\mu\text{m}$.

A successful basis for analyzing SERS spectra with respect to orientation of adsorbates has been reported in the form of "surface selection rules" by Moskovits et al.^[30–33]. These rules are based on the electromagnetic theory of SERS intensity, which says that, *via* resonance interaction with the surface plasmons of the metal, incident light increases in the electromagnetic fields which are most normal to the surface; normal modes of the adsorbed molecule involving changes in molecular polarizability with a component perpendicular to the surface are subject to the greatest enhancement. Based on these "surface selection rules" for Raman spectroscopy and the relative intensity changes in Fig. 4, the molecular arrangement of PT on stainless steel could be deduced. The polarizability moment change of $\beta_{\text{C-H}}$ is perpendicular to the thiophene ring. This Raman inactive band becoming active in SERS implies a higher degree of ordering with thiophene ring parallel to the metal surface for facilitating the polymerization. Likewise, the polarisability moment change of distorted $\nu_{\text{C-C}}$ (inter-ring) is not parallel, but lie at an angle with the thiophene ring. The large enhancement of these two bands compared with normal Raman implies a higher degree of ordering with the thiophene ring parallel to the metal surface for polymerization. The relatively strong band at 1155 cm^{-1} in Fig. 4B, which associates with the stretching mode of C—C bond of

distorted parts of the polymer implies that there are more distorted thiophene rings in PT prepared from thiophene/nitromethane solution, which results in less coplanarity. Additionally, very weak out-of-plane bending band at 794 cm^{-1} and strongly enhanced stretching vibration of inter-ring C—C bond at 1361 cm^{-1} and much lower signal/noise ratio of Fig. 4B than that of Fig. 4A also suggest that PT films polymerized from thiophene/BFEE solution have a much more orderly structure than that from thiophene/nitromethane solution.

The IR reflection-absorption spectrum of PT on stainless steel supports the same conclusion. IR spectra of PT deposited onto stainless steel at a thickness of 300 nm (B) and 600 nm (C) are shown in Fig. 5. A transmission IR spectrum of PT film (Fig. 5A) is given for comparison. In spectrum A, absorptions at 3064 , 1491 , 1440 and 788 cm^{-1} are attributed to the $\nu_{\alpha\text{C-H}}$, $\nu_{\text{asC=C}}$, $\nu_{\text{sC=C}}$ and $\beta_{\text{C-H}}$ ^[25, 27], respectively. The dipole moment change of $\nu_{\alpha\text{C-H}}$, $\nu_{\text{asC=C}}$ and $\nu_{\text{sC=C}}$ are parallel to the thiophene ring, while that of $\beta_{\text{C-H}}$ is perpendicular to the thiophene ring. According to the IR surface selection rule, the suppression of these modes parallel to the ring in spectra B and C strongly suggests that the rings of PT are parallel to the surface of the metallic electrode. A highly regular arrangement of PT chains can be observed at a thickness of 600 nm on stainless steel surface.

The results of SERS and IR reflection-absorption spectra suggest that an orientation of PT deposited onto the surface of stainless steel by electrochemical polymerization can be described as follows: At the beginning of polymerization, the adsorbed thiophene rings lay parallel to the surface of the stainless steel due to the interaction between π -electrons of the aromatic ring and the metal surface. The metal surface was coated with a layer of polymer in which the thiophene rings were parallel to the metal surface. The polymer was then oxidized to a positively charged form which will interact with π -electrons of successive monomer layers. When depositing layer by layer, very few defects formed in the polymer chains that acted as the distorted parts not coplanar to the conjugated segments. The high anisotropy in conductivity of the PT film is due to the regular molecular arrangement.

Cation-Sieving and Anion-Sieving Effects of Polythiophene Films

A conducting polymer, such as polypyrrole, is electrochemically oxidized to be doped with anions and is neutralized to dedope these anions^[34, 35]. These charging and discharging processes involve simultaneous transport of charges and ions in the polymer matrix. The transport of anions is affected by their sizes. The larger anions may be prevented from doping the polymer film because of their sizes. This was called the “ion-sieving” effect, which is found for polypyrrole^[36, 37] and poly(3-methylthiophene)^[38]. No anion-sieving effect on polythiophene has been mentioned due to its fibrous structure, which is less compact than polypyrrole and poly(3-methylthiophene). Furthermore, no cation-sieving effect has been reported for any conductive polymer.

The development of low potential electrochemical polymerization technique allows us to electrochemically deposit thiophene in freshly distilled BF_3 -diethyl ether (BFEE). Under optimized conditions, a conductive polythiophene film with very compact structure was obtained. This makes possible selective permeability for ions diffusing into this polymer. In this communication, we report that the electrosynthesized polythiophene in BFEE is the first example of a conducting polymer which shows both cation- and anion-sieving effects.

A thin polythiophene film was synthesized on a working electrode by galvanostatic polymerization at 1 mA/cm^2 and the deposition charge was controlled at 150 mC/cm^2 . The polythiophene coated electrode had been kept at 0 V for at least 20 min to remove the doped anions, then the film was washed well with distilled water and acetonitrile before electrochemical measurements for anion-doping or cation-doping. Aqueous solutions containing 0.2 mol/L NaBF_4 , Na_2SO_4 , and CH_3COONa were used for anion-doping, and acetonitrile solutions containing 0.2 mol/L LiClO_4 , $\text{N}(\text{Et})_4\text{ClO}_4$ and $\text{N}(\text{Bu})_4\text{ClO}_4$ were used for cation-doping experiments, respectively.

Different pulse voltammetries were used to evaluate the rate of electrochemical doping. Figure 6 shows the differential pulse voltammograms of a polythiophene film in three aqueous solutions.

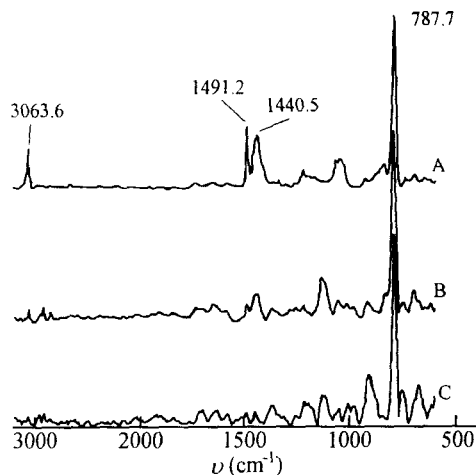


Fig. 5 FT-IR spectra of PT

(A) Transmission IR of undoped PT films with a thickness of 10 μm ; (B) Infrared reflection-absorption spectrum of a PT film deposited onto stainless steel at a thickness of 600 nm; (C) Infrared reflection-absorption spectrum of a PT film deposited onto stainless steel at a thickness of 300 nm

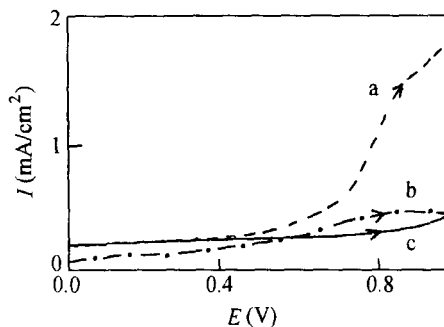
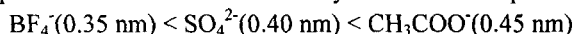


Fig. 6 The differential pulse voltammograms of polythiophene film in aqueous solutions containing (a) NaBF_4 , (b) Na_2SO_4 and (c) CH_3COONa

The film used in the experiment as shown in Fig. 6 was first set a potential of 0 V and then scanned from 0 to 1 V at a scan rate of 5 mV/S in various solutions. The anodic current is attributed to the oxidation of polythiophene, which is accompanied by anion-incorporation into the polymer matrix. The sequence of the diameter of these hydrated ions in aqueous solution is:



It is noted that the anodic current decreased dramatically with an increase in anion size. The cut-off radius of an ion which can pass through the film is about 0.40 nm. Clearly, the polythiophene film synthesized in BFEE solution has an anion-sieving effect.

Figure 7 illustrates the differential pulse voltammograms of polythiophene film in acetonitrile solutions containing 0.2 mol/L LiClO_4 , $\text{N}(\text{Et})_4\text{ClO}_4$ and $\text{N}(\text{Bu})_4\text{ClO}_4$, respectively.

The potential in Fig. 7 was first at -1 V and then scanned to -2 V at a rate of 5 mV/S in various electrolyte solutions. The polythiophene film was electrochemically reduced to give cathodic current, which was followed by cation-incorporation into the film. The cation-doping current of $\text{N}(\text{Et})_4^+$ and $\text{N}(\text{Bu})_4^+$ are comparable. In sharp contrast, the suddenly decreased current of cation-doping for Li^+ was observed. It is well known that the size of non-solvated Li^+ is small. However, the radius of the solvated Li^+ in acetonitrile is much larger than $\text{N}(\text{Bu})_4^+$ and $\text{N}(\text{Et})_4^+$ due to its strong solvability. Obviously, the polythiophene film shows a noticeable cation-sieving effect.

Electrochemical Fabrication of All Organic Heterojunction from Polythiophene and its Derivatives

A new kind of all-organic heterojunction consisting of polythiophene and its derivatives can be prepared by the electrochemical method in the presence of boron trifluoride diethyl ether as

supporting electrolyte on indium-tin oxide glass electrode. It was observed that sequential-different oxidation potential for layer and layer of polythiophenes is a prerequisite for the heterojunction showing rectification effect. The carrier-flow of three semiconductors for PBrT/PT/PMT heterojunction was also interpreted in detail. The rectification ratio, the barrier height, and the ideality factor were $392 (\pm 2 \text{ V})$, 0.89 eV , and 8.1 respectively for PBrT/PT/PMT heterojunction.

Conducting polymers have attracted much attention and were considered for potential use in polymer batteries, displays, sensing devices, organic electrode, and recording devices. Among the various applications of conducting polymers to functional devices, a fabrication of rectifying junctions with metals or semiconductors has been studied intensively, since it provides the basic properties of the conducting polymer to act as electronic devices^[39, 40]. Several types of junctions such as (A) homojunction with *n*- and *p*-type conducting polymers^[41], (B) heterojunction between conducting polymers and inorganic semiconductors^[42], and (C) Schottky barrier between metal and semiconductive conducting polymers have been examined^[43]. Unfortunately, traditional conducting polymers are relatively brittle and show low mechanical strength and poor environmental stability because of high oxidation potentials of the monomers during the electropolymerization. Therefore, the applications of these materials are limited. We previously reported a method for improving tensile strength and stable environmental conductivity of polythiophene and its derivatives by electropolymerization of monomers on the stainless steel electrode from freshly distilled BF₃-diethyl ether (BFEE)^[44-46]. So these high quality materials are very promising in view of their use in microelectronic industries^[47, 48].

The band parameters of energy gap (E_g), work function (Φ), and electron affinity (χ) are different for conducting polymers, due to the backbone structure of the polymers, although valence band (VB) and conduction band (CB) are derived primarily from the bond alternation in conjugated π electron system. For electrochemical doping, the starting potentials of *p*-type and *n*-type doping against a given reference electrode depend on the types of the conducting polymers, indicating the energy levels at the top of VB and the bottom of CB, respectively, with respect to the reference electrode. Therefore, layer and layer films with different conducting polymers are expected to form another type of heterojunction which consists of all-organic materials.

In this paper, the characteristics of the heterojunction diodes consisting of layer and layer films of undoped polythiophenes prepared by electrochemical method is described. The oxidation potentials of polythiophene (PT), poly-3-methylthiophene (PMT), poly-3-butylthiophene (PBT), and poly-3-bromothiophene (PBrT) are 0.75 V , 0.48 V , 0.81 V and 1.05 V , respectively. To our knowledge, no reports about the heterojunction of double and/or three layers prepared by organic compounds have been found so far.

Heterojunction layers were prepared on the ITO (indium-tin oxide) glass electrode by electrochemical polymerization of the monomers. The layer and layer films of PT, PMT, PBrT, and PBT were deposited galvanostatically (current density, 1 mA/cm^2) using a three-electrode-type cell at room temperature. A counter-electrode was a Pt plate and the ITO electrode acted as an anode, and the distance between the counter and anode electrodes was 0.5 cm . A reference electrode was Ag/AgCl (3.5 mol/L KCl). BFEE was used as a supporting electrolyte. The area of an ITO anode exposed to the electrolytic solution was 2.7 cm^2 . The thickness of the polymer films was controlled by controlling the amount of charge consumed during electrochemical polymerization, and for PBrT/PT/PMT junction the thickness is $1.5 \text{ }\mu\text{m} / 3 \text{ }\mu\text{m} / 3 \text{ }\mu\text{m}$. The cathodic treatment of all junction films was as follows: after the deposition of layer and layer films, the potential of the working ITO substrate was maintained at 0 V versus a counter Pt plate for 10 min , and then cathodic reduction of the junction was performed by applying a negative potential at -0.3 V . The cathodic treatment was conducted in the same electrolyte solution where the heterojunction was formed, so that no contamination was induced.

The heterojunctions obtained were washed repeatedly with acetone to remove residual solvent and monomers. An ITO electrode ($S = 2.7 \text{ cm}^2$) was placed with pressure on the top of the polymer film before the current (I)-potential (V) curve was characterized for the junctions. I-V curves indicating the rectification effect of various devices were measured with EG&G Model 273 at room temperature.

PBrT, PT, PMT, and PBT films are poor semiconductors in their undoped states and a linear correlation could be observed between current and applied voltage, indicating the Ohmic contact between the ITO substrate and the conducting polymer. For the I-V curves of PBrT/PT and PBrT/PMT junctions using ITO as the substrates, however, it was found that these two-layer devices exhibited better rectification effect, indicating the formation of a heterojunction similar to inorganic semiconductor. For the I-V curves of three-layer film heterojunctions consisted of PT, PBrT, and PMT, it was observed that PBrT/PT/PMT heterojunction using ITO as the electrodes shows an excellent rectification effect (shown in Fig. 8), while PBrT/PMT/PT heterojunction gives a small rectification effect, and the PT/PBrT/PMT heterojunction presented completely Ohmic property. From the I-V experiments of the fabrication of conducting polymers, it seems that sequential-different oxidation potential for layer and layer is a prerequisite for a heterojunction showing rectification effect, since the oxidation potentials for PBrT, PT, and PMT are 1.09 V, 0.75 V, and 0.48 V, respectively. A four-layer film junction of PBrT/PBT/PT/PMT exhibits less of a rectification effect than the three-layer film junction of PBrT/PT/PMT.

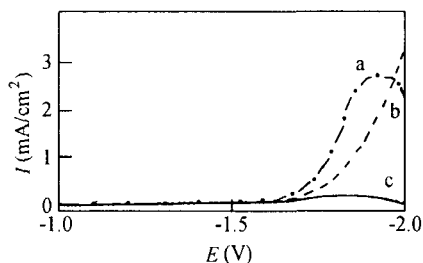


Fig. 7 The differential pulse voltammograms of polythiophene film in acetonitrile solutions containing (a) $\text{N(Bu)}_4\text{ClO}_4$, (b) $\text{N(Et)}_4\text{ClO}_4$, (c) LiClO_4

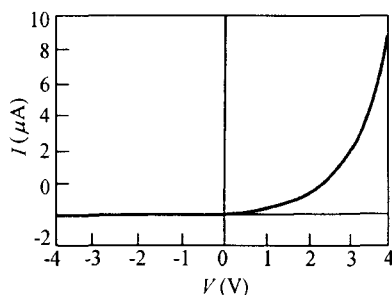


Fig. 8 Current (I)-voltage (V) characteristics of PBrT/PT/PMT heterojunction at room temperature

Considering the energy-band profile of three isolated pieces of semiconductor films, PBrT, PT, and PMT exhibit different band gaps (E_g), dielectric constants (ϵ), work function (Φ), and electron affinities (χ). First, to the contact between PBrT and PT (neglecting the effect from the contact of PT/PMT), when PBrT is making intimate contact with PT, the position of Fermi level of $E_{\text{F,PBrT}}$ is lower than that of $E_{\text{F,PT}}$. Carriers (e^-) will flow from PBrT to PT. Therefore, an increasing negative charge is built up at the PBrT surface. An equal and opposite charge (positive) must also exist in the surface of the PT. Because of the relatively low carrier concentration, charge is distributed over a barrier region near the PBrT and the PT surface (for an ideal contact), and a thermal equilibrium is established^[49, 50]. The Fermi level (E_F) between the two semiconductors must be coincident at thermal equilibrium. So the Fermi levels on both sides line up. Relative to Φ_{PBrT} , Φ_{PT} is lowered by an amount of the difference between the two work functions. And as a result, an opposite electric field is produced. Since the internal electric field in the neutral regions of the semiconductor must be zero under thermal equilibrium, the total negative charge per unit area in the PBrT side must be precisely equal to the total positive charge per unit area in the PT side, and space-charge region forms (neglecting the effect of interface)^[51]. The direction of the

internal electric field from the PT side to the PBrT side obstructs the flow of carrier (e^+) from the PBrT side to the PT side. The contact between two semiconductors of PT and PMT can be analyzed with the same method.

For PBrT/PT/PMT heterojunction, when forward bias was applied at the PBrT side, an external field formed. The direction of external field is from the PBrT side to the PMT side. This external field could reduce the strength of the internal electric field in the neutral region of PBrT/PT and PT/PMT, resulting in a decrease of the amount of space-charge. Meanwhile, the widths on either side of the interface of PBrT/PT or PT/PMT narrows. Therefore, the PBrT/PT/PMT heterojunction shows rectification effect. Because of a forward applied voltage, the current increases exponentially and little current flows under a reverse applied bias. It could be assumed that the current density (J)-voltage (V) relationship can thus be given as the standard diode equation^[52-55]:

$$J = J_0 (\exp \frac{qV}{nk_B T} - 1)$$

where

$$J_0 = A^* T^2 \exp(-\frac{qV_D}{K_B T})$$

and

$$A^* = 4\pi q m^* K_B^2 / h^3$$

Where J_0 is the saturation current density, q is the electron charge, V is the voltage, n is the ideality factor, K_B is the Boltzman constant, T is the absolute temperature, V_D is the barrier height, m^* is the effective electron mass, h is the Planck constant, and A^* is the Richardson's constant. Assuming that the value of m^* is 1, so the value of A^* is $120 \text{ A} / (\text{cm}^2 \cdot \text{K}^2)$.

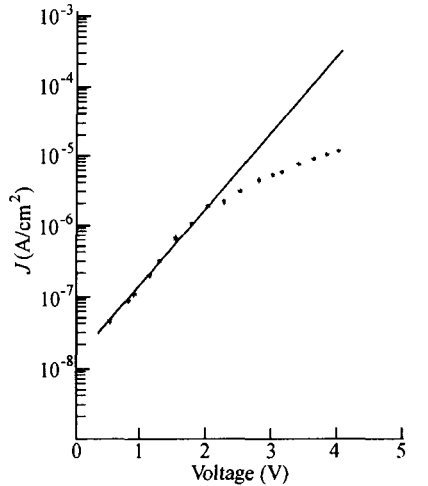


Fig.9 J - V logarithmic plot for the PBrT/PT/PMT heterojunction

Figure 9 shows a logarithmic relationship between the current density and the forward applied voltage. As can be seen from the curve, when the voltage increased, the current density deviated from the exponential trend. At large forward voltages, the horizontal displacement ΔV between the actual curve and the extrapolation of the linear region deviated from exponential. This is due to a voltage drop across the series resistance (R_s), associated with the neutral region of the semiconductor^[56]. From the intercept and the slope in Fig.7, $J_0 = 1.06 \times 10^{-8} \text{ A/cm}^2$, the barrier height $V_D = 0.89 \text{ eV}$, and the ideality factor $n = 8.1$ instead of unity for an ideal junction, were

obtained. So the PBrT/PT/PMT heterojunction appears to be a nonideal contact. This is probably due to the presence of a thick interfacial layer and/or recombination in the depletion region which will be investigated in a later study. At large forward voltages, the horizontal displacement ΔV gave the voltage drop IR_s , across the neutral region. By plotting ΔV against I (Fig.8), the value of R_s was calculated to be $1.0 \times 10^7 \Omega$ at room temperature. This resistance limits the exponential behavior of the values to ≤ 2 V. Therefore, the current density is related to the voltage by the equations:

$$J = J_0 (\exp^{\frac{qV}{nk_B T}} - 1) \quad \text{at the low voltage } (V \leq 2V)$$

$$J = J_0 \left\{ \exp \left[\frac{q(V - IR_s)}{nK_B T} \right] - 1 \right\} \quad \text{at the high voltage } (V > 2V)$$

The rectification ratio for the PBrT/PT/PMT heterojunction was 392 (at $\pm 2V$). The tensile strength of this film heterojunction was 31.4 MPa at room temperature, indicating the compact structure of the junction.

CONCLUSION

FT-Raman studies of thiophene in various solutions show that aromaticity of thiophene is somewhat reduced by the interaction with Lewis acid. Increasing the acidity of Lewis acid solution results in a decrease in the aromaticity of the thiophene ring and lowers oxidation potential of the monomer.

PT films deposited onto stainless steel in BFEE solution at low potentials are highly anisotropic, and display high electrical conductivities and excellent mechanical properties. FT-Raman SERS and IR reflection-absorption studies indicate that the thiophene rings of polymer chains lay nearly parallel to the surface of the metal^[57].

Polythiophene film electrosynthesized in thiophene/BFEE solution under optimized conditions exhibits both anion-sieving and cation-sieving effect.

A kind of all-organic heterojunction consisting of polythiophene and its derivatives has been prepared by the electrochemical method. It is found that sequential-different oxidation potential for layer and layer is a prerequisite for the formation of a heterojunction showing diode characteristic.

REFERENCES

- 1 Tourillon, G. and Garnier, F.J., *Electroanal. Chem.*, 1982, 135: 173
- 2 Yamamoto, T., Wakayama, H., Takahashi, F. and Takaki, K., *J. Phys. Chem.*, 1992, 96: 8677
- 3 Downard, A.J. and Pletcher, D., *J. Electroanal. Chem.*, 1986, 206: 147
- 4 Tourillon, G. and Garnier, F., *J. Phys. Chem.*, 1983, 87: 2289
- 5 Garnier, F., Tourillon, G., Gazard, M. and Dubois, J. C., *J. Electroanal. Chem.*, 1983, 148: 299
- 6 Diaz, A.F. and Logan, J.A., *J. Electroanal. Chem.*, 1980, 111: 111
- 7 Sato, M., Tanaka, S. and Kaerigama, K., *J. Chem. Soc., Chem. Commun.*, 1985, 713
- 8 Imanishi, K., Satoh, M., Yasuda, Y., Tsushima, R. and Aoki, S., *J. Electroanal. Chem.*, 1988, 242: 203
- 9 Krische, B. and Zagorska, M., *Synth. Met.*, 1989, 28: C263
- 10 Gratzl, M., Hsu, D-F., Riley, A.M. and Janata, J., *J. Phys. Chem.*, 1990, 94: 5973
- 11 Roncali, J., Garnier, F., Lemaire, M. and Garreau, R., *Synth. Met.*, 1986, 15: 323
- 12 Yumoto, Y. and Yoshimura, S., *Synth. Met.*, 1985, 13: 185
- 13 Haviga, E.E. and Van Horssen, L.W., *Makromol. Chem. Makromol. Symp.*, 1989, 24: 67
- 14 Bazzazoui, E.A., Aeiyaeh, S. and Lacaze, P.C., *J. Electroanal. Chem.*, 1994, 364: 63
- 15 Tsuchida, E., Yamamoto, K., Asada, T. and Nishide, H., *Chem. Lett.*, 1987, 1541
- 16 Yamamoto, K., Asada, T., Nishide, H. and Tsuchida, E., *Bull. Chem. Soc. Jpn.*, 1988, 61: 1731
- 17 Hara, S. and Toshima, N., *J. Electroanal. Chem.*, 1994, 379: 181

- 18 Andrew, L.J. and Keefer, R.M., *J. Am. Chem. Soc.*, 1949, 71: 3644
- 19 Kovac, P. and McFarland, K. N., *J. Polym. Sci., Poly. Chem. Ed.*, 1979, 17: 1963
- 20 Margosian, D. and Kovacic, P., *J. Polym. Sci., Poly. Chem. Ed.*, 1979, 17: 3695
- 21 Dutta, A.K., *Phys. Rev.*, 1953, 90: 187
- 22 Gutmann, V. and Schmied, R., *Coord. Chem. Rev.*, 1974, 12: 263
- 23 Louarn, G., Mevellec, J.Y., Buisson, J. P. and Lefrant, S., *Synth. Met.*, 1993, 55-57: 587
- 24 Furukawa, Y., Akimoto, M. and Harada, I., *Synth. Met.*, 1987, 18: 151
- 25 Sauvajol, J.L., Chenouini, D., Lère-Porte, J.P., Chorro, C., Moukala, B. and Petrisans, J., *Synth. Met.*, 1990, 38: 1
- 26 Shi, G., Jin, S., Xue, G. and Li, C., *Science*, 1995, 267: 994
- 27 Fujita, W., Teramae, N. and Haraguchi, H., *Chem. Lett.*, 1994, 3: 511
- 28 Bazzou, E.A., Levi, G., Aeyach, S., Aubard, J., Marsault, J.P. and Lacaze, P.C., *J. Phys. Chem.*, 1995, 99: 6628
- 29 Louarn, G., Buisson, J.P., Lefrant, S. and Fichou, D., *J. Phys. Chem.*, 1995, 99: 11399
- 30 Suh, J.S. and Moskovits, M., *J. Am. Chem. Soc.*, 1985, 108: 4711
- 31 Allen, C.S. and Van Duyne, R.P., *Chem. Phys. Lett.*, 1979, 63: 45
- 32 Ni, F. and Cotton, T.M., *J. Raman Spectrosc.*, 1988, 19: 429
- 33 Xue, G., Lu, Y. and J. Zhang, *Macromolecules*, 1994, 27: 809
- 34 Kanazawa, K.K., Diaz, A.F., Gill, W.D., Grant, P.M., Street, G.B., Gardini, G. P. and Kwak, J.F., *Synth. Met.*, 1979/80, 1: 329
- 35 Rasch, B. and Vielstich, W., *J. Electroanal. Chem.*, 1994, 370: 109
- 36 Burgmayer, P. and Murray, R.W., *J. Am. Chem. Soc.*, 1982, 104: 6139
- 37 Shinohara, H., Aizawa, M. and Shirakawa, H., *J. Chem. Soc., Chem. Commun.*, 1986, 87
- 38 Zhang, W., Dong, S., *J. Electroanal. Chem.*, 1990, 284: 517
- 39 Kanicki, J., *Mol. Cryst. & Liq. Cryst.*, 1984, 105: 203
- 40 Sato, M., Tanaka, S. and Kaeriyama, K., *J. Chem. Soc., Chem. Commun.*, 1987, 1725
- 41 Ozaki, M., Peebles, D., Weinberger, B.R., Heeger, A.J. and MacDiarmid, A.G., *J. Appl. Phys.* 1980, 51: 4252
- 42 Rendu, P.L., Nguyen, T.P., Gaudin, O. and Tran, V.H., *Synth. Met.* 1996, 76: 187
- 43 Zhou, L., Jin, S. and Xue, G., *Macromol. Chem. Phys.*, 1996, 197: 3309
- 44 Zhou, L. and Xue, G., *Synth. Met.*, 1997, 87: 193
- 45 Jin, S., Ji, M., and Xue, G., *Appl. Phys.*, 1996, A63: 397
- 46 Jin, S., Ji, M., Zhang, C. and Xue, G., *J. Mater. Sci. Lett.*, 1996, 15: 1305
- 47 Sze, S.M., "Physics of Semiconductor Devices", 2nd Ed., John Wiley & Sons, New York, 1981
- 48 Anderson, R.L., *Solid State Electronics*, 1962, 5: 341
- 49 Milnes, A.G. and Feucht, D. L., "Heterojunction and Metal-Semiconductor Junction", Academic Press, New York, 1972
- 50 Campos, M., Camaioni, N., Casalbore-Miceli, G., Geri, A., Giro, G. and Zini, Q., *Synth. Met.*, 1995, 75: 61
- 51 Kaneto, K., Takeda, S. and Yoshino, K., *Jpn. J. Appl. Phys.*, 1985, 24: L553
- 52 Campos, M., Casalbore-Miceli, G. and Lamaioni, N., *J. Phys. D: Appl. Phys.*, 1995, 28: 2123
- 53 Glenis, S. and Frank, A.J., *Synth. Met.*, 1989, 28: C681
- 54 Hoshino, K., Ogata, T. and Kokado, H., *Jpn. J. Appl. Phys.* 1995, 34: L1241
- 55 Chen, S.A. and Fang, Y., *Synth. Met.*, 1993, 60: 215
- 56 Fang, Y., Chen, S.A. and Chu, M. L., *Synth. Met.* 1992, 52: 261
- 57 Jin, S. and Xue, G., *Macromolecules*, in press