Low Potential Electrochemical Synthesis of Polyfuran and Characterization of the Obtained Free-Standing Film

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A free-standing polyfuran (PFu) film has been successfully synthesized by electrochemical polymerization of furan at low potential (1.2 V vs Ag/AgCl) in a binary solvent system consisting of boron trifluoride−ethyl ether (BFEE) and additional ethyl ether (EE). The obtained polymer contains much less ring-opened component and shows higher conductivity than that prepared by chemical method or by electropolymerization in other solvent systems. Its electric conductivity is as high as 10^{-2} S cm^{-1} both in its electrochemically doped state and chemically doped state with I_2. Moreover, the obtained free-standing film shows good mechanical properties, which makes itself a powerful competitor to other conducting polymers. The orientation of PFu deposited on Au and stainless steel electrode was investigated by surface enhanced Raman spectra (SERS) and reflection−absorption infrared spectra (RA-IR) techniques. The furan ring in the polymer chain is inclined to be arranged parallel to the metal surface at the early stage of deposition.

Introduction

Electronically conducting polymers have attracted much attention over the past 20 years. Polypyrrole and polythiophene as the classical heteroaromatic polymers have been investigated widely.[1] However, the polymerization of furan, due to its lower aromaticity and drastic conditions needed for polymerization, is difficult to perform, and a number of saturated rings in the polymer chains are obtained. Hence, less attention has been focused on the study of the properties and potential application of PFu.

The synthesis of a PFu film was first mentioned by G. Touillon and F. Garnier,[2] and later by other groups, the reported polymer exhibited low electric conductivity, which ranged from 10^{-5} to 10^{-3} S cm^{-1}.[3,4]

Since it was hard to obtain a free-standing PFu film by conventional anodic coupling methods or by chemical oxidation of furan, other methods were proposed over the next several years. G. Zotti et al. prepared PFu by electrochemical reduction of 2,5-dibromofuran in acetonitrile using $Ni(bipy)_3^{2+}$ as catalyst.[5] However, the obtained polymer on the cathode was in its neutral insulating form and only in trace amount. S. Glenis and M. Benz et al.[6] tried to use terfuran as the starting monomer to lower the oxidation potential, and a polymer with a electric conductivity of 2×10^{-3} S cm^{-1} was obtained when doped with $CF_3SO_3^-$. Although the oxidation potential was lowered by this method, the resultant polymer contained a large amount of saturated rings as evidenced by its IR spectrum.[6]

More recently, furan was electropolymerized in acetonitrile at 2.1 ≪ 2.3 V vs SCE using $NaClO_4$ as the electrolyte.[7,8] However, the obtained film showed ill-defined cyclic voltammetry characterization compared with those obtained by S. Glenis or by G. Zotti et al. It was obvious that the polymer would undergo irreversible oxidation and contained a large amount of saturated ring and/or ring opened components under such high potentials.

We tried to lower the oxidation potential of furan by using boron trifluoride−ethyl ether (BFEE) complex as the solvent. However, the resonance energy of furan is so low that it acts more like a conjugated diene than heteroaromatic molecules, which makes it very sensitive to acids. When furan was directly added to BFEE, which is a strong Lewis acid, addition polymerization occurred immediately and nonconjugated polymer was precipitated. More ethyl ether was added to adjust the acidity of BFEE and the addition polymerization was suppressed. The anodic coupling reaction proceeded smoothly at the potential of ~1.2 V vs Ag/AgCl (0.1 M KCl), which is much lower than that in the conventional solvent

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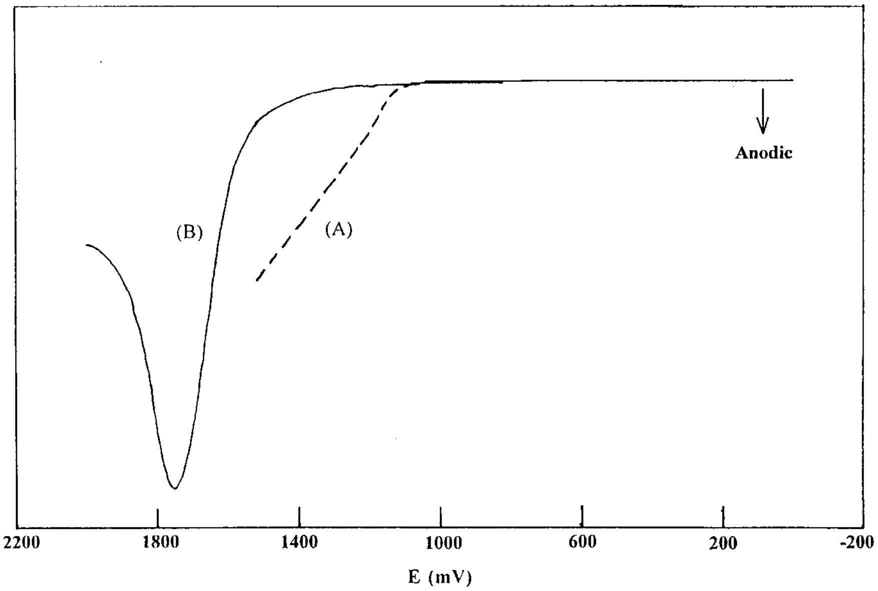

Figure 1. The current−voltage curve of furan monomer in (A) BFEE/EE (molar ratio 1:1) and (B) acetonitrile solutions. *E* vs Ag/AgCl (0.1 M KCl). Scan rate: 20 mV/s. Electrolyte: $TBABF_4$ (0.05 M).

system. In this paper, we report the synthesis and characterization of polyfuran which was synthesized in this special solvent system.

Experimental Section

Chemicals. Furan was distilled under N_2 atmosphere twice before use. Ethyl ether was dried and distilled in the presence of sodium. Boron trifluoride−ethyl ether (BFEE) was freshly distilled before use. Tetrabutylammonium tetrafluoroborate ($TBABF_4$) was dried under vacuum. Acetonitrile was purified by reflux in the presence of $KMnO_4$ for 24 h and then dried with anhydrous Na_2CO_3 before distillation.

Electrochemical Experiments. Electrochemical studies 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. All the PFu films were prepared from BFEE/EE solution with $TBABF_4$ as the electrolyte. To obtain a free-standing film, stainless steel sheets (1.5 × 7 cm^2) were employed as working electrodes and counter electrodes, which were polished with abrasive paper (1200 mesh) and diamond paste (1.5 μm), and 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 passed during film growth. (The thickness of the film prepared at a current density of 1 mA cm^{-2} for 1 h is about 10 μm.) Electrochemical measurements were carried out with a platinum disk (diameter 0.5 mm), polished and cleaned as mentioned above before each experiment. Ag/AgCl (0.1 M KCl) was used as the reference electrode, and $TBABF_4$ was used as electrolyte in organic solvents in all cases. Each solution containing furan was degassed by bubbling dry argon before the experiment, and a slight argon overpressure was maintained during the experiment.

Solutions of different molar ratio of BFEE/EE (ranging from 1:4 to 2:1) were used to examine the influence of solvent compositions on the properties of the obtained films. Cyclic voltammetry (CV) experiments in aqueous solution with sodium tetrafluoroborate and in acetonitrile with $TBABF_4$ were recorded, respectively.

Spectroscopy. UV−visible spectra were recorded with a UV-3100 spectrophotometer (Shimadzu, Japan). A film deposited onto an ITO electrode at 1 mA cm^{-2} for 200 s was used for the measurement of UV spectrum. All the Raman spectra were measured by a RFS-100 spectrometer (Bruker, Germany) with 1064-nm excitation. The film used in the conventional Raman test was about 2−3 μm thick. An electrochemically roughened Au disk (diameter 3 mm) was used as the substrate in the surface enhanced Raman scattering (SERS) experiment. The PFu film for the SERS study was deposited onto the Au disk at a current density of 1 mA cm^{-2} for 2 s. Fourier transform infrared spectra were recorded on a IFS-66V spectrometer (Bruker, Germany) under vacuum. The doped PFu film used for the IR study was about 2−3 μm thick, which was washed with acetone and dried under vacuum at room temperature before the test. Undoped PFu was prepared either by electrochemical reduction or by chemical reduction of doped PFu film with ammonia and then washed and dried as above before it was tested. PFu used in the reflection−absorption infrared spectra experiment was deposited onto a stainless steel electrode at 1 mA cm^{-2} for 3 min.

Measurement of Electrical and Mechanical Properties. After being well washed by acetone, the polymer films were stripped from the electrodes and dried under vacuum at ambient temperature; the conventional four-electrode method was utilized to measure electrical conductivity of the polyfuran film. The tensile strength of the free-standing polyfuran film was measured at a stretching rate of 5 cm min^{-1}.

Result and Discussion

Electrochemical Polymerization. Figure 1 shows the oxidation curves of furan in a solvent which contains BFEE and EE in a molar ratio of 1:1 and in acetonitrile solution (labled with A and B, respectively). It is of interest that the onset of the oxidation potential is about 1.1 V vs Ag/AgCl (0.1 M KCl) in BFEE/EE solution which is much lower than that in acetonitrile. Figure 2 shows the first and fifth current−voltage curves between 0 and 1.2 V vs Ag/AgCl (0.1 M KCl) during the synthesis of PFu on a Pt electrode in BFEE/EE solution. In the first scan, as the potential is swept from 0 to 1.0 V, the current remains low. At the electrode potential > 1.1 V, the anodic current increases sharply and a dark blue film forms on the surface of the Pt electrode. In the fifth scan, the onset of the oxidation potential is slightly reduced, partly due to the oxidation of the obtained polymer on the electrode, whose oxidation potential is lower than that of the monomer, and partly due to catalysis of the formed PFu on the nucleation of

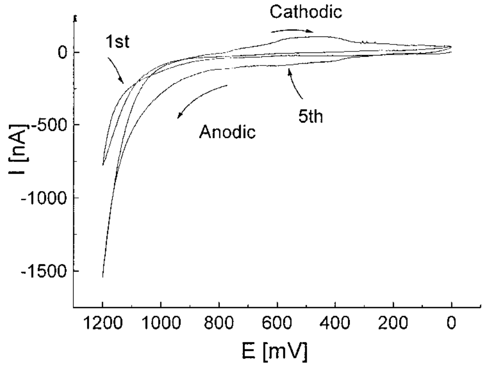

Figure 2. The repetitive scans of furan in BFEE/EE (molar ratio 1:1) solution: the first and the fifth scan. Scan rate: 20 mV/s. *E* vs Ag/AgCl (0.1 M KCl).

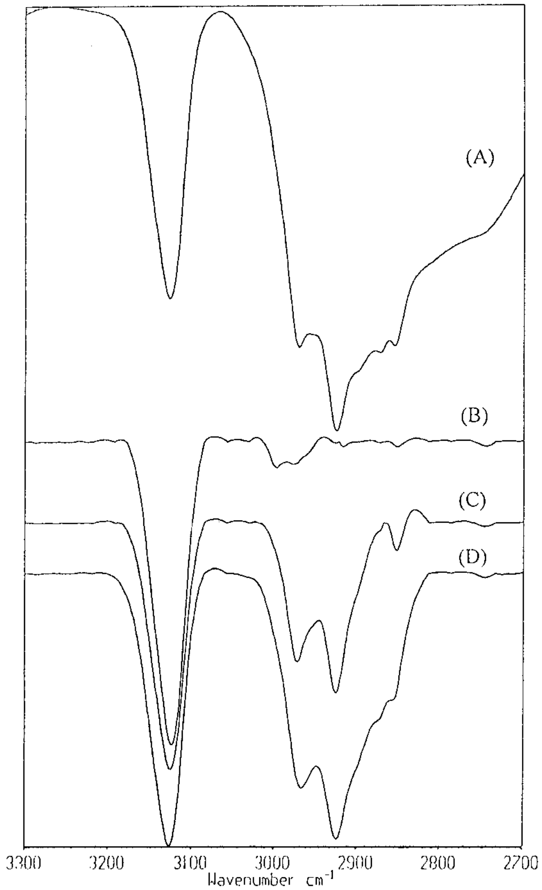

Figure 3. The IR spectra (C−H stretching region) of Pfu film (pristine state) prepared in BFEE/E solutions with different molar ratio: (A) 2:1, (B) 1:1, (C) 1:2, and (D) 1:4.

the new layer.[9] Moreover, the fifth scan shows a couple of redox peaks at ~0.5V, whose intensity increases with the increasing scan number, indicating that the film formed on the electrode is electroactive.

The influence of the molar ratio of BFEE/EE on the polymer structure as a result of the electropolymerization condition was examined. Figure 3 shows the IR spectra in the C−H stretching region of undoped PFu films obtained in solutions with different molar ratios of BFEE and EE. It is noteworthly that the peaks of the aliphatic C−H stretching vibration mode at 2975, 2926, and 2856 cm^{-1} are largely suppressed when the applied solvent mixture was in the molar ratio of 1:1. We have found that ring-opening reaction occurs when furan is added directly to the BFEE solution, which results in a nonconjugated polymer. It is not surprising that when the molar ratio of the BFEE to EE is increased from 1:1 to 2:1, the relative amount of aliphatic C−H in the polymer is also increased. We propose that the BFEE molecule undergoes an acid−base reaction with diethyl ether, thereby reducing its acidity, while the remaining BFEE molecules will react with the furan monomer directly resulting in a ring-opening product. However, when the molar ratio is reduced from 1:1 to 1:4, the relative amount of aliphatic C−H in the polymer is also increased. It may be that the existence of excess diethyl ether is also harmful to the polymerization of furan because of its basicity.

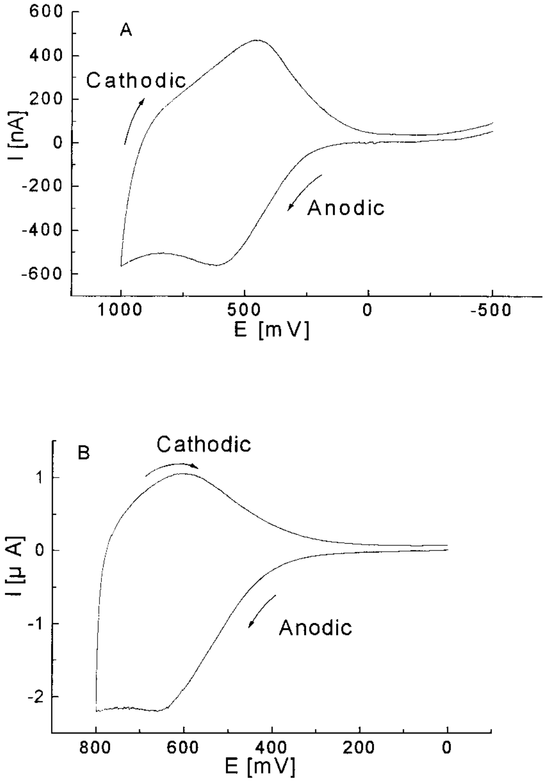

Figure 4. CV scan of PFu film in (A) BFEE/EE (molar ratio 1:1) solution and (B) acetonitrile solution. Scan rate: 20 mV/s. *E* vs Ag/AgCl (0.1 M KCl). Electrolyte: TBABF$_4$ (0.05 M). PFu was deposited onto Pt electrode from a BFEE/EE (molar ratio: 1:1) solution containing 0.1 M furan at a current density of 1 mA/cm^2 for (A) 60 s and (B) 300 s, respectively.

Cyclic Voltammetry. The electrochemical properties of PFu have not been well-characterized compared with that of polythiophene and polypyrrole, since PFu prepared directly from the electrochemical oxidation of furan showed poorly defined properties.[5−8] We have successfully prepared PFu directly from the furan monomer in BFEE/EE solution, and it was possible for us to investigate its electrochemical properties systematically.

Figure 4 A shows the first CV cycle of PFu in BFEE/EE (molar ratio 1:1). The oxidation of PFu is accompanied by a change of color from orange to dark blue which is completely reversed upon reduction to the undoped state. The redox process is found to be reversible. The onset potential for the oxidation is about 0.2

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V vs Ag/AgCl (0.1 M KCl), and this corresponds with the highest occupied states in the valence band.[6] There is a broad anodic peak at ~0.6 V vs Ag/AgCl (0.1 M KCl) due to the polymer oxidation and a broad cathodic peak at ~0.5 V due to polymer reduction. The redox process of PFu is close to a reversible reaction, although the peak separation always exceeds the expected 59 mV. This difference is commonly observed in the electrochemistry of conducting polymers due to a number of factors including the diffusion of the dopant ions in and out of the film and the change of the conformation of the polymer chain in the redox process.[10] The redox process of PFu in acetonitrile shows similar characteristics to that in BFEE/EE solution, as shown in Figure 4B. We notice that the redox potential of PFu in acetonitrile is slightly different from that in BFEE/EE solution, which may be due to the influence of the solvent.

The long-term stability of the redox activity of the PFu film was also investigated in BFEE/EE and in acetonitrile, respectively. PFu shows better long-term stability of redox activity in BFEE/EE solution ($TBABF_4$ as the electrolyte), in which 85% of electrochemical activity is maintained after 100 cycles, as shown in Figure 5A. In contract, PFu in acetonitrile solution shows a lower stability in which 40% of electrochemical activity is maintained after 100 cycles, as shown in Figure 5B.

However, The first current−voltage curve of PFu in aqueous solution shows an irreversible anodic peak, which is located at ~0.7 V vs Ag/AgCl (0.1 M KCl), and the electroactivity decreases greatly in the subsequent scans and almost disappears after 10 scans, as shown in Figure 5C. It seems that PFu is very susceptible to oxidation decomposition in aqueous solution. The decomposition process will not be slowed when the aqueous solution is adjusted to either a basic or an acidic solution. We propose that during oxidation, water molecules will incorporate into the film in the form of solvating molecules of the counteranions and react with the electroactive sites of the polymer chain at a certain potential. As a consequence, the conjugated structure in PFu is destroyed and the electroactivity is lost. We notice that similar properties were reported by Svein Sunde et al. for polythiophene and its derivatives.[11,12] They proposed that the film degradation occurs simultaneously with oxidative doping, leading to a loss in electroactive sites.

Spectroscopy. *UV−Visible Spectroscopy.* The optical properties of conjugated polymers are generally characterized by a wide absorption band due to intrinsic energetic disorder in these polymers. A broader absorption means a wider distribution of the conjugation length in the polymer.[5] The UV−visible absorption spectrum of an undoped PFu film is shown in Figure 6. The neutral polymer exhibits a much broader absorption plateau from ~500 nm to 400 nm, compared with that reported in the literature.[6] This broad absorption band, which corresponds to the $\pi-\pi^*$ interband transition, inferred the coexistence of both long and short effective conjugated lengths in the PFu film. The band gap, e.g., for a direct interband transition, which can be estimated from the absorption edge (~600 nm) of the spectrum, is about 2.07 eV, a little smaller than that reported in the

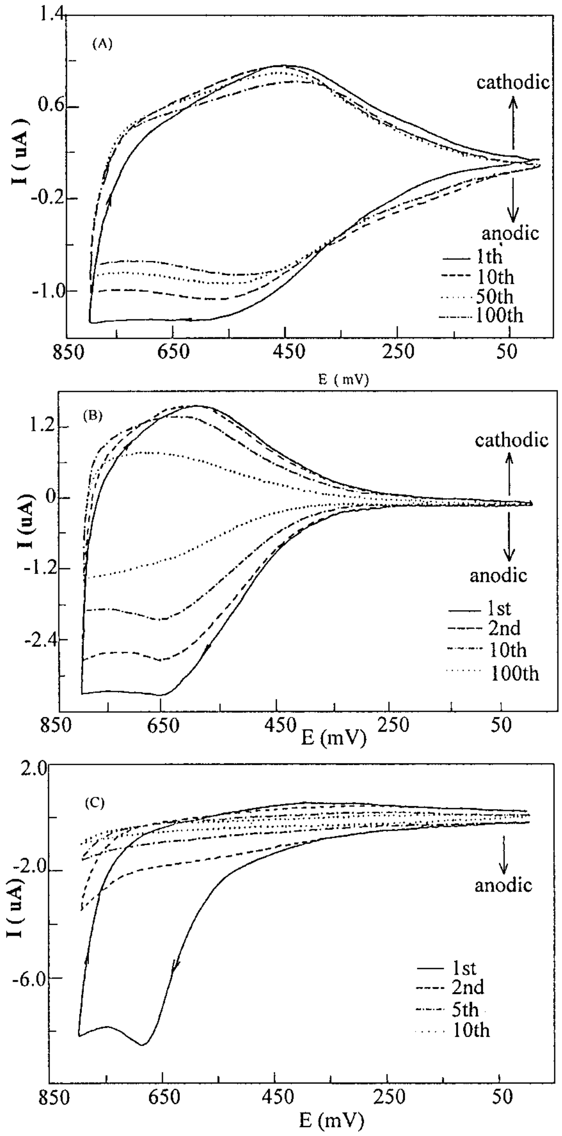

Figure 5. The long-term electrochemical activity stability of PFu film prepared in BFEE/EE (1:1) solution at a current density of 1 mA/cm^2 for 300 s in different solutions. (A) in BFEE/EE (1:1) solution, electrolyte $TBABF_4$ (0.05 M); (B) in acetonitrile solution, electrolyte $TBABF_4$ (0.05 M); and (C) in aqueous solution, electrolyte $NaBF_4$ (0.05 M). Scan rate 20 mV/s. *E* vs Ag/AgCl (0.1 M KCl)

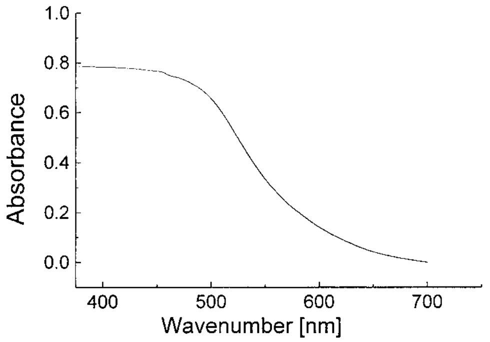

Figure 6. The UV spectra of undoped PFu film deposited on ITO electrode at a current density of 1 mA/cm^2 for 200 s from BFEE/EE (mole ratio 1:1) solution.

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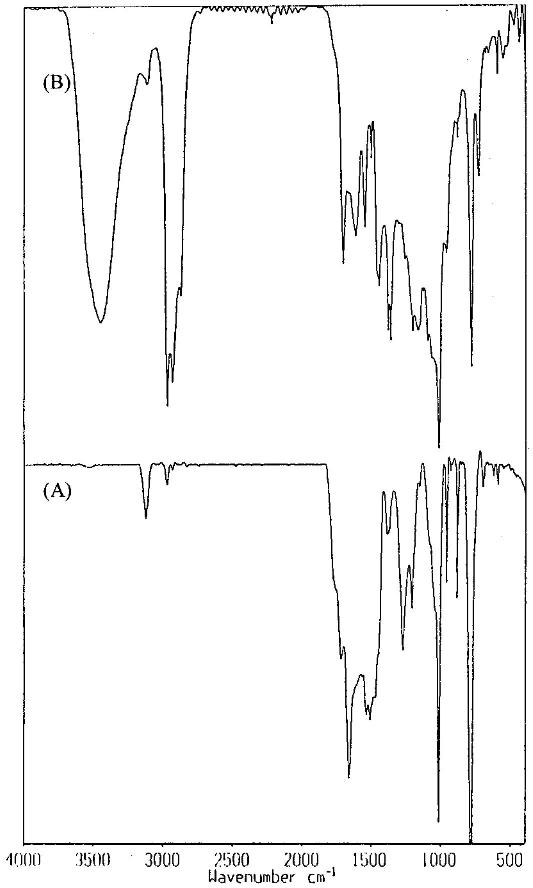

Figure 7. The IR spectra of (A) electrochemically prepared PFu (undoped) and (B) the addition polymerization product when furan was directly added into BFEE.

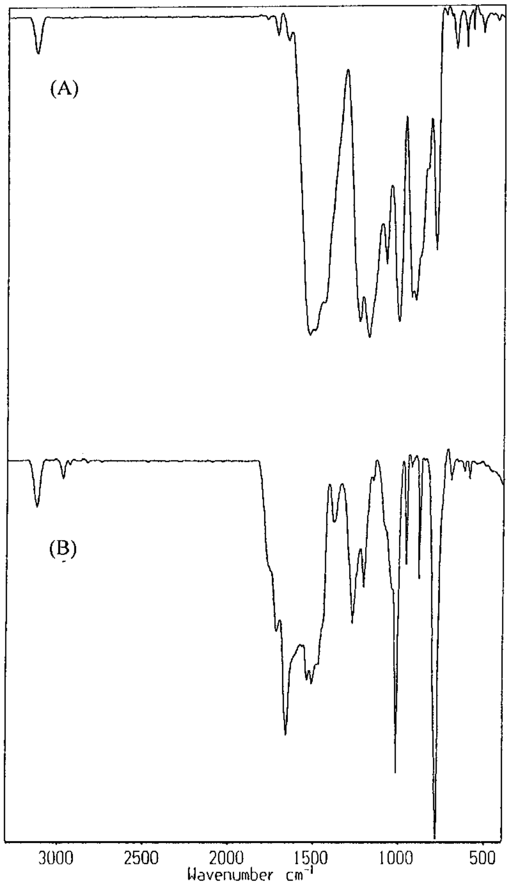

Figure 8. The IR spectra of PFu film in (A) its doped state and (B) undoped state.

literature.[6] This value, which is still in accord with the literature, is very close to that reported for polythiophene(2.0 eV) and smaller than that of polypyrrole (3.2 eV).[13,14] It should be noted that the calculated band gap value of PFu is about 6.5 eV,[15] which is much larger than the experimental one.

Infrared Spectroscopy. The IR spectra of PFu were first reported by G. Zotti et al.,[5] measured from an electroreduction polymerized PFu as the sample. However, the spectra of PFu directly synthesized from furan have always been poorly defined due to saturated-ring moieties in the polymer chains. Although S. Glenis lowered the oxidation potential using terfuran as the starting monomer to avoid the overoxidation of the obtained polymer, the recorded IR spectra still showed strong bands due to the aliphatic C−H vibration mode even when doped with $CF_3SO_3^-$.[6]

Infrared spectra provide evidence for the existence of the conjugated structure of the PFu chain, as shown in Figure 7. The IR spectra of electrochemically prepared PFu (Figure 7A) is compared with that of the addition polymerization product (Figure 7B) when furan is added to a BFEE solution directly. Figure 7B shows a very strong absorption in the aliphatic C−H stretching vibration region and a broad and strong absorption in the O−H stretching vibration region, which suggests the ring-opening reaction and the resultant aliphatic structure. In Figure 7A, the virtual disappearance of these two bands and the appearance of characteristic absorptions due to the aromatic ring stretching mode located at 1536, 1510, and 1469 cm^{-1}, indicate that most of the furan rings in the polymer chains remain intact.[6]

Figure 8 shows the infrared spectra of PFu in its doped and undoped states (labeled A and B, respectively). Several characteristics can be seen. (1) The spectrum of the film in its undoped state (Figure 8B) suggests that a small amount of nonconjugated component still exists in the undoped PFu. Bands located at 2970 and 2930 cm^{-1} indicate the existence of aliphatic C−H bonds, while bands located at 1718 and 1661 cm^{-1} indicate the existence of C=O bonds and isolated C=C bonds. The intensity of these absorptions is largely reduced and even disappears in the spectrum of the doped state (Figure 8A), the reason for which will be discussed later. (2) The spectrum of the doped state shows several largely enhanced bands which seem reminiscent of the spectrum of the undoped material. The three most enhanced absorption peaks located at 1532, 1501, and 1446 cm^{-1} in the spectrum of doped state seem in accord with the absorptions located at 1536, 1510, and 1470 cm^{-1} in that of undoped state, although a small bathochromic shift can be seen, while the enhanced absorption peaks located at 1240 and 1184 cm^{-1} in the spectrum of doped state show a much larger bathochromic shift with respect to the absorption located at 1274 and 1209 cm^{-1} in the undoped state. (3) The absorption at 784 cm^{-1} in the spectrum of undoped

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state and 791 cm^{-1} in the spectrum of doped state are the characteristic of the $\alpha\alpha'$-coupling of the carbon backbone, which indicates the main component in PFu is polyconjugated.[6]

Recently, effective conjugated coordination (ECC) theory has been widely used to interpret the IR and Raman spectra of conjugated polymers.[16-24] The ECC theory basically states that among the $3N - 6$ normal modes of a polyconjugated finite molecule, there exists a particular totally symmetric mode, which mostly involves the collective stretching and shrinking of the skeletal C=C and C—C inter-ring and intra-ring bonds, thus collectively involving the delocalization of the π-electrons. This mode describes the geometrical trajectory π-electrons have to follow when they undergo a transition from the electronic ground state (aromatic) to the first excited electronic state (quinoid structure). The difference between the spectrum of the undoped state and that of the doped state can be interpreted by using this theory. Upon doping, charges are displaced within the polymer chain and domains with a quinoid structure are introduced into the aromatic structure, then the lattice becomes highly polarized, and vibrational dipole strength is gained thus giving very strong IR activity to originally silent IR modes in the undoped material.[21]

It has been pointed out that the infrared spectrum of doped PFu originated from three parts:[21] selectively enhanced totally symmetric modes, IR active modes from the undoped part, and IR active modes from doped part. Upon doping, bands in the region from 1600 to 1100 cm^{-1}, which mostly consist of C=C and C—C stretching and shrinking modes, i.e., totally symmetric modes, were selectively enhanced, and this verified that the main component in PFu has the characteristics of typical conjugated polymers. On the contrary, because of their nonconjugated character, the aliphatic C—H stretching mode and the C=O and/or isolated C=C stretch modes, would not be enhanced; hence the relative intensity of these absorptions decreases and even the peak disappears, because they exist in such a small amount. Another possible reason for the presence of the aliphatic C—H and C=O stretching modes in the spectrum of the undoped PFu is related to the preparation of the undoped PFu. Since the doped PFu is susceptible to the acid/base effect,[6] a ring-opening reaction may occur when treated with ammonia.

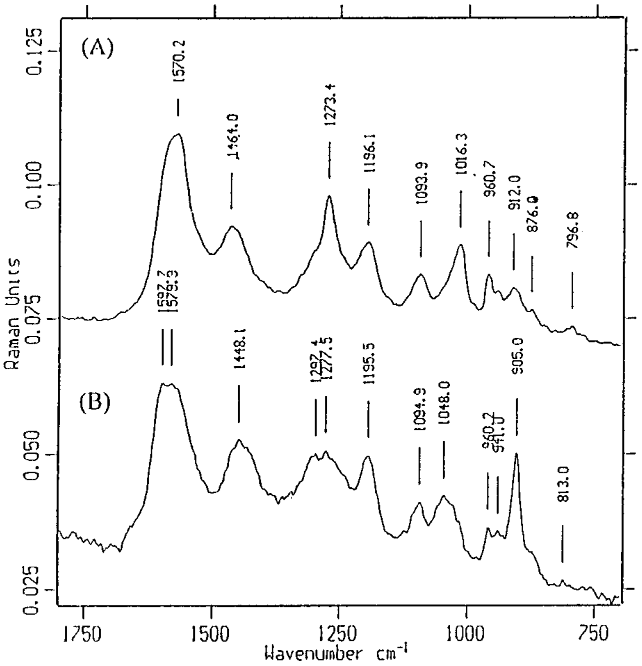

Figure 9. (A) The Raman spectrum of bulk PFu film (B) The SERS spectrum of PFu deposited onto the Au electrode at a current density of 1 mA/cm^2 for 2 s.

Table 1. Raman Active Vibrational Assignment of PFu

species	ν_{cal}[a]	Raman ν_{exp}	SERS ν_{exp}	assignment[a]
A_g	3158	–	–	$100\nu(CH)$
A_g	1597	1571	1597–1569	$53\nu(C{=}C)_{ring} + 51\nu C{-}C^*)$
A_g	1268	1273	1300, 1279	$46\nu(C{-}C)_{ring} + 41\nu(C{-}O)_{ring}$
A_g	1057	1015	1015	$83\delta(CH)$
A_g	1030	961	961	$36\delta(CH) + 36\nu(C{=}C)_{ring}$
A_g	395	–	–	$55\delta(C{-}C^*) + 25\delta_{ring}$
B_{1g}	1357	–	–	
B_{1g}	941	942	942	$61\nu(C{-}O)_{ring} + 18\delta_{ring}$
B_{2g}	895	–	905	$72\gamma(CH) + 38\gamma(C{-}C^*)$
B_{3g}	814	–	813	$74\gamma(C{-}C^*) + 34\gamma(CH)$
		1462	1447, 1462	–
		1197	1196	–

[a] From ref 21.

Raman Spectroscopy. Figure 9A. shows the Raman spectra of the bulk PFu recorded with $\lambda_{max} = 1064$ nm, which is almost the same that reported by V. Hernandez.[22,23] According to the lattice dynamics analysis, the simplest structure of the PFu chain can be taken as a one-dimensional lattice of furan units, all coplanar and in the anti conformation. If this assumption is true, PFu belongs to the piont group D_{2h} and its $k = 0$ active modes are classified into 26 optical in-plane modes and 12 optical out-of plane modes, among which 7 A_g mode, 7 B_{1g} modes (which are in-plane modes), 3 B_{2g} modes, and 3 B_{3g} modes (which are out-of-plane modes) are assumed to be Raman active.[22] The Raman spectra recorded with $\lambda_{max} = 514.5$ nm shows six resonance-enhanced lines assigned as A_g modes,[23] while the Raman spectra recorded with $\lambda_{max} = 1064$ nm give much more information, as is shown in Figure 9A. Bands which are not assigned to the A_g mode but to other Raman active modes appeared when recorded with $\lambda_{max} = 1064$ nm, and the assignment of these bands are listed in Table 2. Bands at 1462 and 1197 cm^{-1} which were not assigned in the lattice dynamic calculation may be interpreted in terms of the existence of a second component (with longer conjugation length) with at least a bimodal distribution of conjugation length.[22]

Orientation of the PFu on the Electrode Surface. Surface Enhanced Raman Scattering (SERS) and surface reflection–absorption infrared spectral tech-

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Table 2. Assignment of SERS Enhanced and Reduced Bands

Raman ν_{exp} (cm^{-1})	SERS $\nu_{exp}{}^{a}$ (cm^{-1})	assignment^{b}
1273	1279, 1300 (red.)	A_g 46ν(C−C)$_{ring}$ +ν(C−O)$_{ring}$
1015	1015, 1048 (red.)	A_g 83δ(CH)
961	961 (red.)	A_g 36δ(CH) +36ν(C=C)$_{ring}$
914	905 (enh)	B_{2g} 72γ (CH) +38γ(C−C*)
−	813 (enh)	B_{3g} 74γ(C−C*) + 34γ(CH)

[a] Key: red. = reduced; enh = enhanced. [b] From ref 21.

niques are very powerful in the investigation of molecular orientation on the metal surface. We have successfully used SERS and IR reflection−absorption to investigate the orientation of PFu on the electrode surface.

Figure 9B shows the SERS spectra of PFu deposited on a Au electrode at a current density of 1 mA/cm^2 for 2 s. Compared with the bulk Raman spectra, the SERS spectra of PFu shows several interesting changes. The bands at 1273, 1015, and 961 cm^{-1} in the bulk Raman spectra are sharply reduced, while a strongly enhanced band at 905 cm^{-1} appears in SERS spectra of PFu, which is reminiscent of the peak at 914 cm^{-1} in the bulk Raman spectra. Another new band appears at 813 cm^{-1} in the SERS spectra. The assignment of these peaks is listed in Table 2.

A successful basis for analyzing SERS spectra with respect to orientation of adsorbates has been reported in form of “surface selection rules” by Moskovits et al.[25−28] These rules are based on the electromagnetic theory of SERS intensity, which says that via resonance interaction with 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 subjected to the greatest enhancement.

On the basis of these surface selection rules for Raman spectroscopy and the relative intensity changes in Figure 9, the molecular arrangement of PFu on the Au electrode can be deduced. Bands at 1273, 1015, and 961 cm^{-1} are assigned to the in-plane vibration modes, while bands at 905 and 813 cm^{-1} are assigned to the out-of-plane modes, as shown in Table 2. The polarizability moment change of the in-plane modes is parallel to the furan ring, while the polarizability moment change of the out-of-plane modes is perpendicular to the furan ring. Since the modes involving polarizability moment changes perpendicular to the metal surface are subject to the greatest enhancement, it can be deduced that the out-of-plane mode is perpendicular to the metal surface, while the in-plane mode is parallel to the metal surface. This result suggests that the PFu rings deposited onto the Au electrode are parallel to the surface of the Au due to the complexation of the π-electrons of the aromatic ring with the metal surface.

The FT-IR reflection−absorption spectrum of PFu on stainless steel also supports this conclusion. The transmission IR spectra of PFu and the reflection−absorption IR spectra of PFu deposited onto stainless steel at 1 mA cm^{-2} for 3 min (~0.5 um) are shown in Figure 10 (labeled A and B respectively). In spectrum A, the absorptions at 3130, 1532, 1441, 913, and 792 cm^{-1} are assigned to the ν(C−H), ν(C=C), $\gamma_{in-plane}$(C−H), and $\gamma_{out-of-plane}$(C−H), respectively.[21] The dipole moment change of the ν(C−H), ν(C=C), and $\gamma_{in-plane}$(C−H) are presumably parallel to the furan ring, while that of the $\gamma_{out-of-plane}$(C−H) is perpendicular to the furan ring. The detailed assignment of these peaks is listed in Table 3. According to the IR surface selection rule, the suppression of the first three modes parallel to the ring in spectrum B strongly suggests that the rings of PFu are parallel to the surface of the metal electrode.

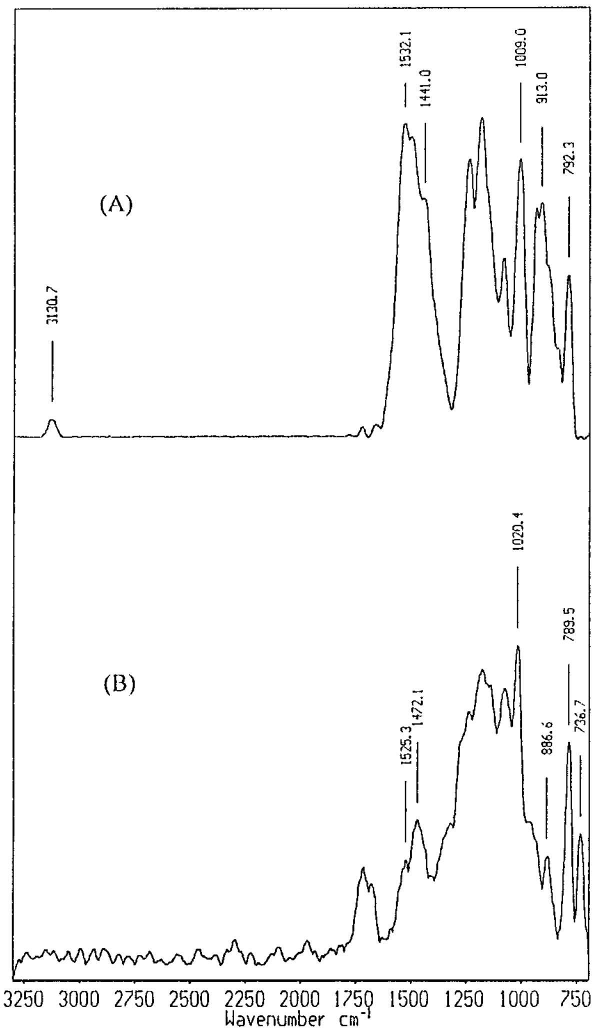

Figure 10. (A) IR spectrum of doped PFu film and (B) RA-IR spectrum of PFu deposited onto the stainless steel electrode at a current density of 1 mA/cm^2 for 3 min.

Table 3. Assignments of RA-IR Spectra of PFu

IR$_{cal}{}^{a}$ (cm^{-1})	IR$_{exp}$ (cm^{-1})	RA-IR$_{exp}$ (cm^{-1})	assignment^{a}
3157	3131	disappeared	B_{2u} 100ν(CH)
1528	1532	1525 (red)	B_{3u} 94ν(C=C)
1456	1441	1472(red)	B_{2u} 92ν(C=C) + 26δ_{ring}
926	913	disappeared	B_{2u} 38δ_{anillo} + 34δ(CH) + 24ν(C−O)$_{ring}$
782	792	790	B_{1u} 100γ_{ring}

[a] From ref 21.

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Table 4. Electric Conductivity of PFu Film Prepared in BFEE/EE Solution with Different Molar Ratios[a]

BFEE/EE molar ratio	electric conductivity (S/cm)
2:1	2.6×10^{-3}
1:1	2.4×10^{-2}
1:2	2.1×10^{-2}
1:4	9.4×10^{-3}

[a] The film was deposited onto stainless steel electrode at a current density of 1 mA/cm^2 for 1 h.

Electrical Conductivity and Mechanical Properties. The electrical conductivities of the PFu film prepared in solutions with different molar ratios of BFEE and EE were tested and are listed in Table 4. The film prepared using a BFEE/EE molar ratio of 1:1 shows the highest electrical conductivity. When the molar ratio of BFEE to EE was either increased or decreased, the conductivity of the film decreases. We ascribe this phenomenon to the increase of aliphatic C−H structure components, as evidenced by the IR spectra in Figure 3. The highest electrical conductivity of the electrochemically doped PFu (BF_4^- as counteranion) is 2.4×10^{-2} S/cm, and this value decreases when the film is exposed to air for several days due to a slow dedoping process. When chemically doped with I_2, the electrical conductivity of the PFu film is 3×10^{-2} S/cm and it is more stable in air.

The lower electrical conductivity of the PFu may be attributed to the shorter conjugation length compared with polypyrrole and polythiophene, which can be seen from its UV−visible absorption. Another reason is that the ring-opening reaction cannot be totally suppressed in this binary solvent system, and nonconjugated regions exist in the bulk polymer, although in small amounts. As a consequence, the existence of high and low electrical conductivity domains in the film restricts the charge carrier migration in the polymer.[7]

The mechanical properties of PFu has never been investigated before, due to the lack of a free-standing PFu film. With the use of a BFEE/EE binary solvent system, a flexible, free-standing PFu film can be easily peeled off from the electrode after polymerization. Since the mechanical properties are very important to the potential applications of conducting polymers, the successful synthesis of a free-standing PFu film makes this conjugated polymer a powerful competitor to polythiophene and polypyrrole. The ultimate stretching strength of PFu film was found to be 30 MPa, which is at the same level as that of normal plastics, such as polyethylene and poly(vinyl chloride) films.

Conclusions

PFu can be successfully synthesized using a BFEE/EE binary solvent system. It is very interesting that the oxidation potential of furan in the electropolymerization is lowered while the addition polymerization of furan is avoided using this method. Why BFEE/EE solution has this potential-lowering effect, however, is still not clear. We have proposed that the potential-lowering effect of BFEE on the electroplymerization of thiophene is due to the interaction of BFEE and thiophene rings, lowering the aromatic resonance energy of the thiophene rings.[29] Since the interaction of fuan with BFEE is so strong that addition polymerization of furan will occur if furan is directly added into BFEE solution, ethyl ether is used to reduce this interaction. The additional ethyl ether successfully suppressed the addition polymerization of furan. And when the molar ratio of BFEE to ethyl ether was 1:1, the best suppression effect was observed. This infers that this binary solvent system should not be simply considered as a BFEE solution diluted by ethyl ether. Further investigation is needed to clarify the polymerization mechanism of furan in this solvent system.

A free-standing PFu film with good mechanical and electric properties was obtained by using the galvanostatic method. FT-IR and Raman spectroscopy verifies that the polymer chain obtained is mainly conjugated, as is the PFu film synthesized by electrochemical reduction of 2,5-dibromofuran using $Ni(bipy)_3^{2+}$ as catalyst,[5] and much better than the PFu film electropolymerized in acetonitrile at 2.1−2.3V vs SCE using $NaClO_4$ as the electrolyte.[7,8] The obtained PFu film shows fairly good electrochemical reversibility and stability in organic solvents, while it undergoes irreversible oxidation in aqueous solution. On the other hand, the undoped state of PFu is very stable in air, similar to that of the undoped polythiophene.

The orientation of the PFu chains on the electrode in the early stages of deposition was investigated using SERS and FTRA-IR techniques. It was shown that the furan ring is almost parallel to the electrode surface, as in the case of polythiophene deposited on the electrode.[29]

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