Polymer 40 (1999) 4907–4914

Synthesis of high-quality polypyrrole in a binary solvent system consisting of boron trifluoride-ethyl ether and additional ethyl ether

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Received 9 June 1998; received in revised form 14 September 1998; accepted 24 September 1998

Abstract

Polypyrrole (PPy) was electrochemically synthesized in boron trifluoride ethyl ether (BTEE) whose acidity was adjusted with additional ethyl ether (EE). A high quality PPy film can be synthesized in a wide mole ratio range of BTEE/EE and under mild conditions. The obtained film showed the highest tensile strength (90 MPa) we had ever seen and good anisotropy in electrical conductivity. The structure was investigated using surface enhanced Raman scattering (SERS). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polypyrrole; Binary solvent system; Trifluoride-ethyl ether

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1. Introduction

Polypyrrole (PPy) is one of the extensively investigated conducting polymers that have potential application prosperity in battery electrodes [1], gas sensors [2], biological sensors [3], ion-sieving [4], corrosion protection and microwave shielding [5,6]. Films can be prepared in either aqueous or nonaqueous media using a variety of electrochemical techniques. The synthesis conditions together with the solvent and the electrolyte influenced the conductivity, morphology and mechanical behavior of the deposited films [7–9]. Generally, PPy films have fairly good mechanical properties. The ultimate tensile strength of the unstretched polypyrrole films is reported to vary between 54 and 61 MPa [10,11].

Recently, we have successfully prepared polythiophene films whose ultimate tensile strength has exceeded that of aluminum in the boron trifluoride ethyl ether (BFEE) [12]. As a Lewis acid, BFEE can interact with the thiophene ring hence lowering the oxidation potential of thiophene and thus allowing high quality conducting polythiophene to be prepared. However, the acidity of BFEE is so strong that if it was used as the solvent for pyrrole, addition polymerization then occurred and only nonconjugated polymer resulted. We then chose ethyl ether (EE) as a Lewis base to adjust the acidity of BFEE to avoid the additive polymerization. PPy films were synthesized in a BFEE/EE binary solvent system and the mole ratio of BFEE to EE was varied over a wide range. The influences of current density and the mole ratio of BFEE/EE on the film formation were studied and the polymerization conditions were investigated. The obtained films have a high electrical conductivity ($>100\ \mathrm{S\ cm^{-1}}$) and a high anisotropy in conductivity, ($\sigma_{\parallel}/\sigma_{\perp} = 10^4$). The ultimate tensile strength of the films (90 Mpa) is the highest among the unstretched PPy films prepared at room temperature we have ever seen.

2. Experimental section

2.1. Chemicals

Pyrrole, BFEE and diethyl ether were purified by distillation before use. Dichloromethane was used as received and acetonitrile was dried and distilled before use.

2.2. Electrochemical experiments

Electrochemical examination 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 at room temperature. The free standing films were obtained using stainless steel plates ($1.5 \times 4\ \mathrm{cm^2}$) as the working electrode and counter electrode, which were polished with abrasive paper (1200 mesh) and diamond

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PII: S0032-3861(98)00692-2

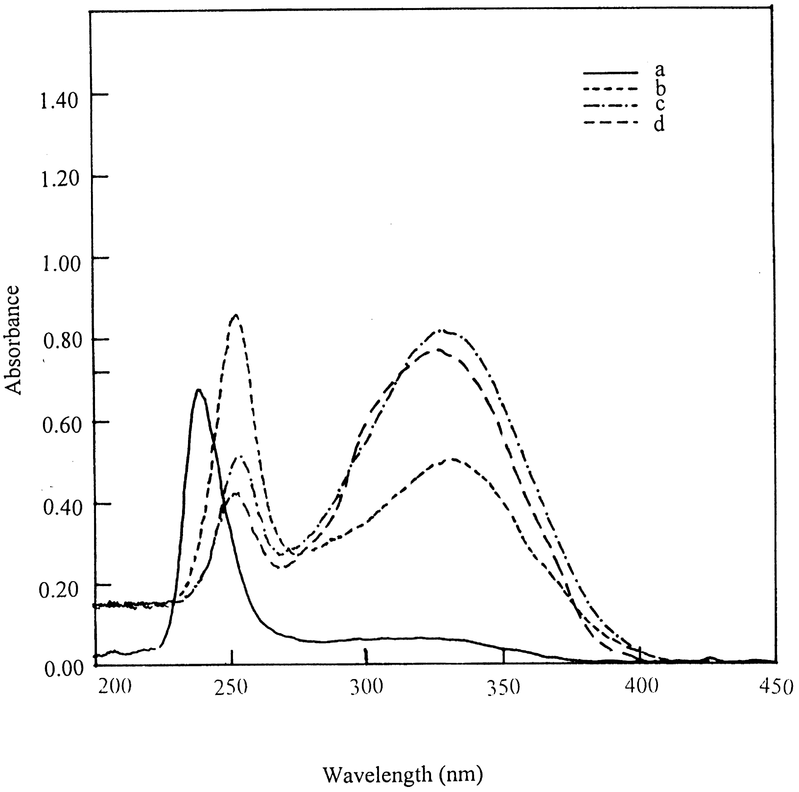

Fig. 1. The UV-spectra of pyrrole (0.1M) in BFEE/EE solutions with different BFEE/EE mole ratio: (a) 1:4, (b) 1:2, (c) 1:1, (d) 2:1.

paste (1.5 μm) and then cleaned in an ultrasonic acetone bath before use. An Ag/AgCl (0.1 M KCl) electrode was used as the reference electrode. The galvanostatic method was also used for electrochemical polymerization in a current range from 0.05 to 2 mA cm^{-2} and the thickness was controlled by the electric charge passed in the polymer growth. The electrochemical behavior of pyrrole and PPy was examined on a Pt disc electrode (1.96×10^{-3} cm^2) as the working electrode and was analyzed using the cyclic voltammetry method (CV). The mole ratio of BFEE/EE in most solutions was 1:1 except when the effects of a different mole ratio on the polymerization needed to be analyzed. The concentration of pyrrole in conventional film preparation was 0.05 mol l^{-1}.

2.3. Measurement of electrical and mechanical properties

The obtained films were first washed well with acetone before being stripped off the electrode and then dried under vacuum at ambient temperature. The conventional four-probe method was utilized to measure electrical conductivity of the PPy film. The two-probe method was used to measure the electric conductivity anisotropy of polypyrrole films. The tensile strength of the free-standing films was measured at a stretching rate of 5 cm min^{-1}.

2.4. Spectroscopy experiment

UV-visible spectra were recorded on a UV-240 spectrophotometer (Shimadzu, Japan) to investigate the change of pyrrole in the BFEE/EE solutions. Raman spectra were measured at room temperature on a RFS100 spectrometer controlled by a computer (Bruker, Germany). An electrochemically roughened Au disc (diameter 3 mm) was used as the substrate in the surface enhanced Raman scattering (SERS) experiment. The PPy film was deposited onto the Au disc at a current density of 1 mA cm^{-2} for 10 s. A roughened silver foil was used to collect the possible side-reaction products produced by the BFEE-pyrrole interaction and also examined by the SERS technique. All the Raman spectra were recorded with 1064 nm excitation.

3. Results and discussion

3.1. Mechanism of the electrochemical polymerization

The aromaticity of pyrrole is lower than thiophene, and it is more unstable to Lewis acid. When pyrrole was added into BFEE, the solution would turn red. An attempt at electrochemical polymerization of pyrrole in BFEE solution failed in our experiment. PPy can not be obtained in BFEE solution since BFEE is a well-known initiator in cation polymerization, ring-opening reactions will occur and only nonconjugated polymer will be formed. The acidity of BFEE should be reduced to avoid the occurrence of additional polymerization. We then chose diethyl ether as a

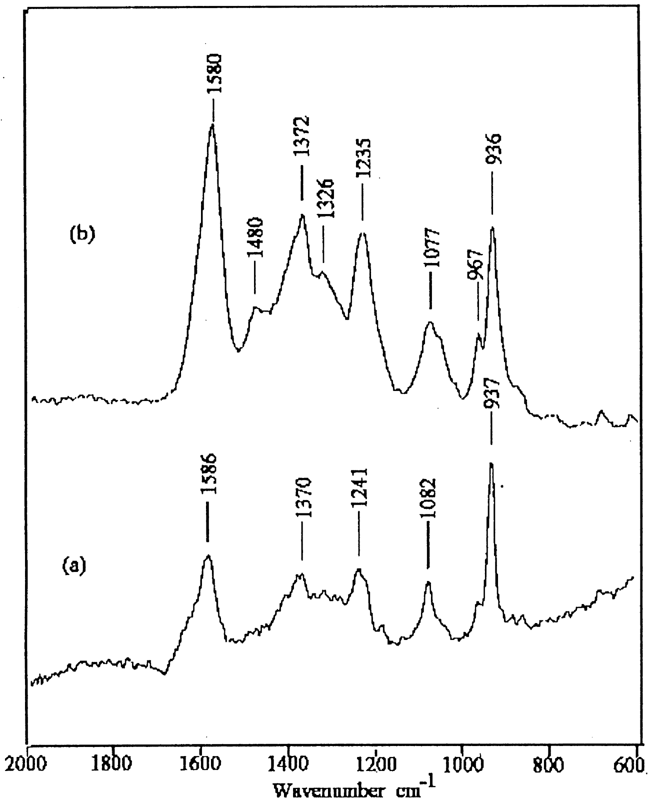

Fig. 2. The SERS spectra of pyrrole oligometers collected onto Ag from BFEE/EE (1:1) solution (a) and polypyrrole deposited on Au (b).

suitable Lewis base to adjust the acidity of BFEE solution. Other Lewis bases have also been chosen to adjust the acidity of BFEE solution. However, if the basity of the chosen Lewis base is stronger than ethyl ether, such as is the case with CH_3OH, it will react with BFEE, and it is hard to identify the composition of the resultant binary solvent system; if the basity of the chosen Lewis base is lower than ethyl ether, such as in the case of CH_3CN, it is hard to lower the acidity of BFEE and hence the ring-opening reaction of pyrrole will still occur. Because diethyl ether may interact with BFEE, the direct interaction of pyrrole and BFEE may be avoided.

However, we observed evidence that a kind of interaction between BFEE and pyrrole really happened. The characteristic UV-absorption peak of pyrrole in diethyl ether appeared at 234 nm, but when a catalytic amount of BFEE (50 mmol) was added into the solution, a bathochromic shift to 236 nm occurred. The more BFEE was added, the larger the bathochromic shift that occurred, as shown in Fig. 1. When the mole ratio of BFEE/EE increased to 1:2, this characteristic peak shifted to 253 nm, which was accompanied by a new broad absorption peak at 330 nm, as shown in Fig. 1. The new absorption may be ascribed to the appearance of oligomers, which will be discussed later. No new bathochromic shift or new absorption occurred if the mole ratio still increased. However, the intensity ratio of $\gamma_{253\ \mathrm{nm}}/\gamma_{330\ \mathrm{nm}}$ decreased when additional BFEE was added to the solution, which inferred that more pyrrole oligomers were resulting. The existence of pyrrole oligomers can also be verified by using other methods. A roughened silver plate is used to collect the oligomers in the solution, and the SERS experiment revealed that their Raman spectra are the same as that of PPy deposited on Au electrochemically, as shown in Fig. 2. It was clear that the existence of additional ethyl ether not only hindered the ring-opening reaction of pyrrole, but also produced some oligomers which may accelerate the polymerization of pyrrole.

Yen Wei and Jing Tian have discussed the influence of oligomeric additives on the polymerization of thiophene [13–15]. The presence of oligomer was claimed to result in a reduction in the activation energy and an increase in the preexponential factor. The applied potentials for the polymerization can be reduced to values lower than the oxidation potential of the monomers. The oligomers of pyrrole in the BFEE/EE solutions have a lower oxidation potential than the monomer and may function as the initiators in the polymerization. Hence the polymerization can be facilitated.

3.2. Optimization of the polymerization

Free-standing PPy films can be obtained in a wide mole-ratio range of BFEE/EE solutions from 1:4 to 3:1. Although catalytic amounts of BFEE in EE also have some influence on pyrrole, as shown in the UV-visible spectra (Fig. 1), it is hard to find a suitable electrolyte which is soluble in ethyl

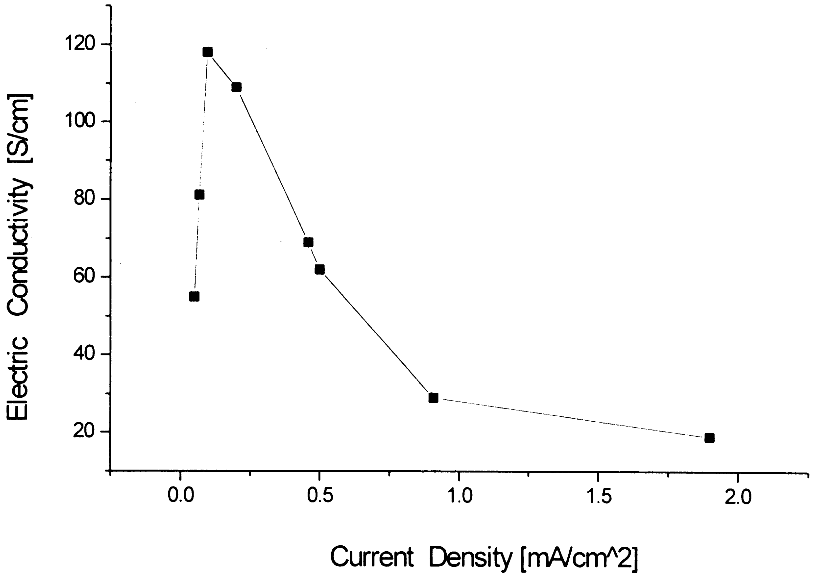

Fig. 3. The relationship between electric conductivity of the obtained polypyrrole film in BFEE/EE solution and the current density.

ether, so no attempt to polymerize pyrrole in a diethyl ether solution containing trace amounts of BFEE has been made in our experiment. Free-standing films were obtained in 1:1 solution with the highest electric conductivity of 135 S cm^{-1} and highest tensile strength of 100 MPa, which is nearly the same strength as that of an aluminium foil (100 ± 50 MPa).

The influence of current density on the polymerization of pyrrole was investigated. It was found that the optimal current density for high electric conductivity is about 0.1 mA cm^{-2} as shown in Fig. 3. If the current density was too high or too low, the electric conductivity decreased. We ascribe this phenomena to the arrangement of the polypyrrole chain and the possible chemical side reaction. The electric conductivity is determined by both the intrachain charge carrier (polaron or bipolaron) transportation and the interchain charge carrier transportation [16]. The more ordered arrangement of the chain favors the easier interchain charge carrier transportation. If the current density is too high, the deposition rate of the polypyrrole will be too fast to arrange the chain, and the interchain charge carrier transportation will be more difficult. As a consequence, the electric conductivity decreases. If the current density is too low, the chemical side reaction may compete with the electrochemical reaction. Although pyrrole was more stable in BFEE/EE solution than in BFEE solution, it is difficult to avoid the side reaction completely, and relatively more oligomers may be produced at lower current density. The more oligomer incorporated into the film, the space between the polymer chain will be larger and the interaction of the chain will be more difficult, hence the electric conductivity will decrease.

The influence of current density on the mechanical properties of the film was not accordant with that on the electric conductivity. The largest ultimate tensile strength of the film was obtained at a current density of ca. 1 mA cm^{-2}. It may be interpreted by the entanglement of the chains. As mentioned above, it may be difficult for the polypyrrole chain to be arranged in an orderly manner due to the fast deposition process at higher current density; entanglement of the chain may occur. The entanglement may increase the strength of the chain to a certain extent. Again, if the current density is too high, the too quickly generated film will be placed loosely, with poor mechanical properties.

3.3. Electrochemical properties of PPy films

Fig. 4 shows the evolution of cyclic voltammetry of PPy films which were deposited onto a Pt disc at 1 mA cm^{-2} for 1 h from BFEE/EE (1:1) and dichloromethane solutions, respectively. All the CV grams were recorded in aqueous solution containing 0.1 mol dm^{-3} $\mathrm{NaBF_4}$ as the electrolyte. In all cases there is a broad anodic peak due to polymer oxidation accompanied by a rapid current increase beyond 400 mV vs Ag/AgCl (0.1 M KCl) in the first cycle. This rapid current increase disappeared in the subsequent cycles and was replaced by a current plateau which has been ascribed to the Faradaic charging and double-layer charging. This current increase could be interpreted as the existence of some most sensitive sites in polypyrrole which were irreversibly oxidized in the oxidation cycle [17]. Furthermore, compared with those films obtained in dichloromethane solution, the film obtained in BFEE/EE (1:1) solution has less most sensitive sites which can be seen in the intensity of the reversible oxidation peak relative to the irreversible oxidation peak as shown in Fig. 4. The better CV properties of the polymer obtained in BFEE/EE solution should be connected with the speciality of this synthetic system. We noticed that the onset of the electropolymerization potential in polymerization of pyrrole in BEEE/EE

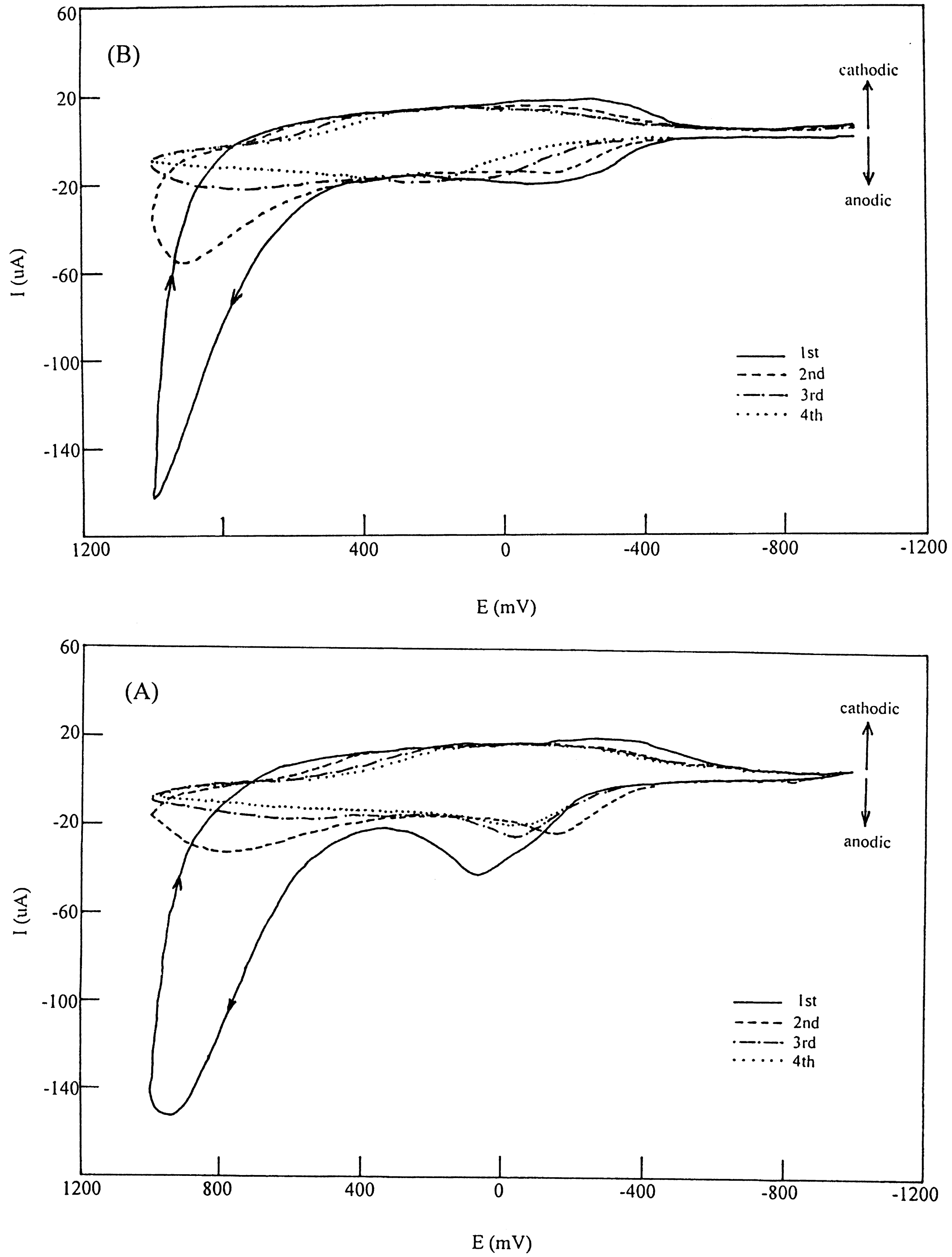

Fig. 4. The first several CV spans of PPy film in aqueous solution electrolyte: $NaBF_4$ 0.1M, scan rate: 20 mV/s E vs. Ag/AgCl (0.1M KCl) (A) PPy film prepared in BFEE/EE (1:1) solution at $1mA/cm^2$; (B) PPy film prepared in CH_2Cl_2-$NaBF_4$ (0.1M) solution at 1 mA/cm^2.

solution is ca. 100 mV lower than that in polymerization of pyrrole in acetonitrile or in chloroform, which may be attributed to the activation energy lowering effect of the trace amount of oligomers in the BFEE/EE solution, according to the theory of Yen Wei and Jing Tian [13–15]. Since the polymerization potential is reduced, the chance of the overoxidation of PPy is also decreased, and the obtained conjugated polymer has a lesser content of those most active sites and shows better reversibility.

The value of peak separation and the ratio of the peak current intensities of the anodic and cathodic peaks are characteristics of the electrochemical reversibility of the PPy films. After the initial several cycles, stable CV grams were obtained. The tenth CV cycles of PPy films

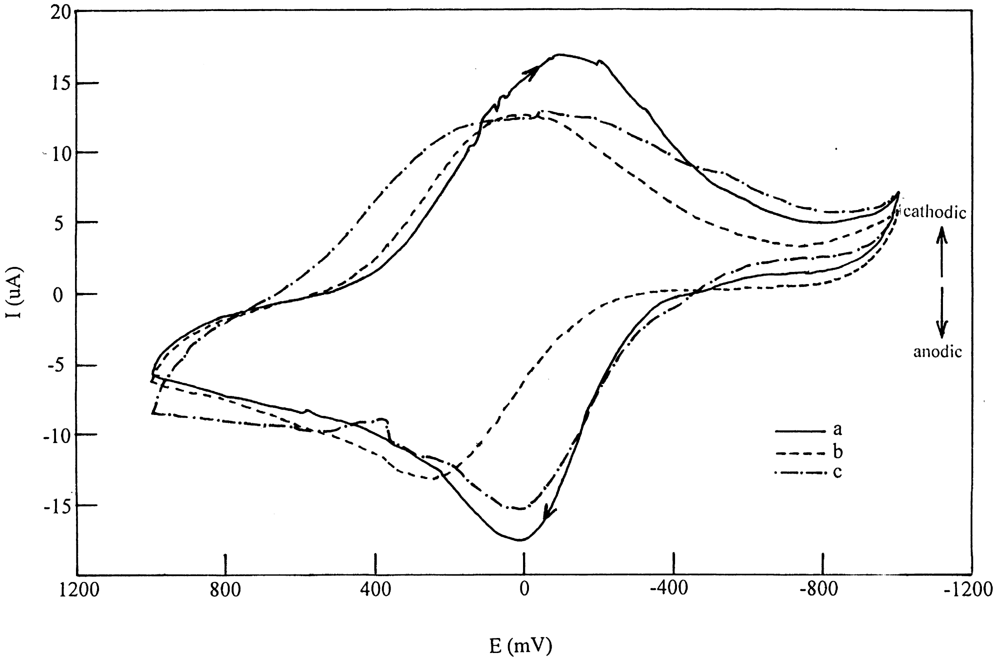

Fig. 5. The 10th scan of PPy film in aqueous solution (electrolyte: $NaBF_4$ 0.1M, scan rate: 20 mV/s, vs Ag/AgCl(0.1M KCl). (a) PPy film prepared in 1-1 BFEE/EE solution at $1mA/cm^2$; (b) PPy film prepared in CH_2Cl_2-$NaBF_4$ (0.1M) solution at $1mA/cm^2$; (c) PPy film prepared in CH_3CN-$NaBF_4$ (0.1M) solution at $1mA/cm^2$.

deposited on the electrode from different solutions are shown in Fig. 5. The values of peak potential and peak separation, together with the peak current intensity are listed in Table 1. The lowest peak separation value and the largest I_{pc}/I_{pa} ratio of the film obtained in BFEE/EE solution indicated better electrochemical reversibility than those obtained in acetonitrile and in CH_2Cl_2 solutions [18]. In all cases, the film obtained in BFEE/EE (1:1) solution shows sharper anodic and cathodic peaks, while the film obtained in CH_3CN solution exhibits a much broad cathodic peak whose potential could not be well defined. The peak separation value of film obtained in dichloromethane solution is twice that obtained in BFEE/EE (1:1) solution.

The width of the redox peak is attributed to the wide distribution of the effective conjugated length in conducting polymers [19]. The sharper redox peak of PPy obtained in BFEE/EE (1:1) solution may indicate a relatively narrow distribution of the effective conjugated length. Furthermore, the oxidation peak potential of both the film obtained in BFEE/EE (1:1) solution and in acetonitrile solution is 20 mV lower than that obtained in CH_2Cl_2 solution. Since the redox potential decreases with the increase of the effective conjugated length, this result indicates that the effective conjugated length of films obtained in BFEE/EE (1:1) solution and in acetonitrile solution is longer than that obtained in CH_2Cl_2 solution. Again, we attribute this to the activation energy lowering effect (hence the electropolymerization potential lowering effect) of the oligomers in the solution, avoiding the possible destruction of the conjugated structure of the polymer chain at high potentials.

3.4. Mechanical properties of PPy films

The mechanical properties of PPy have been widely investigated [20,21,10,11,22]. Several factors influencing the mechanical properties such as counterions, the degree of order of the films, the potential applied in the polymerization were discussed. It was found that counterions containing an aromatic ring such as *p*-toluenesulfonate favored better tensile strength since the aromatic ring led the polymer chain to a more ordered structure [20]. It was also found that lower polymerization temperature improved the mechanical properties [21]. The ultimate tensile strength of conventionally prepared PPy films doped by *p*-toluenesulfonate varied from 54 to 61 MPa [10,11]. More recently, Jianyong Ouyang and Yongfang Li synthesized flexible

Table 1
Peak potential and peak current of PPy films prepared in different solutions

Solutions	E_{pa} (mV)	E_{pc} (mV)	ΔE (mV)	I_{pa} (uA)	I_{pc} (uA)	I_{pc}/I_{pa}
BFEE/EE (1:1)	10.8	− 118.0	128.8	− 17.65	16.9	0.96
Acetonitrile	6.9	–	–	− 15.6	12.3	0.79
Dichloromethane	246.3	0.0	246.3	− 13.2	12.6	0.95

Table 2
Relationship between the mechanical properties of PPy films and the current density in preparation

Current Density	Average ultimate stretch strength
0.2 (mA cm^{-2})	74.4 (MPa)
0.5 (mA cm^{-2})	74.7 (MPa)
1.0 (mA cm^{-2})	90.0 (MPa)

polypyrrole-nitrate films in 1,2-propanediol carbonate solution using 0.1 M $Cu(NO_3)_2 3H_2O$ and 0.2 M $LiNO_3$ as electrolyte at − 20°C [22]. It was also reported that a high polymerization potential may improve the mechanical properties because of crosslinking. The PPy films obtained in BFEE/EE solution also showed excellent mechanical properties. The ultimate tensile strength of PPy films obtained at different current densities are listed in Table 2. Films synthesized on stainless steel with a current of 1 mA cm^{-2} at room temperature had an ultimate tensile strength as high as 90 MPa.

3.5. Electric conductivity anisotropy

The electric conductivities for anisotropy of PPy were measured using a two-probe technique. An Au electrode was used to form ohmic contact with PPy films. The electric resistance for the film surface and across the film thickness were recorded simultaneously. The conductivity parallel to the film surface is 10^4 times that across the film. It is the highest electric conductivity anisotropy compared with those reported in the literature [23,24]. The anisotropy in properties inferred that there should be some kind of anisotropy in the structure of polypyrrole. The orientation of the polymer chains is expected to be parallel to the surface of electrode.

SERS spectra can provide some information on the polymer chain orientation on the electrode surface. Bazzaaoui et al. investigated the SERS spectra of polythiophene on silver in its doped and undoped states [25]. SERS spectra of polythiophene on Au were also discussed by Jin' Shi and Xue'

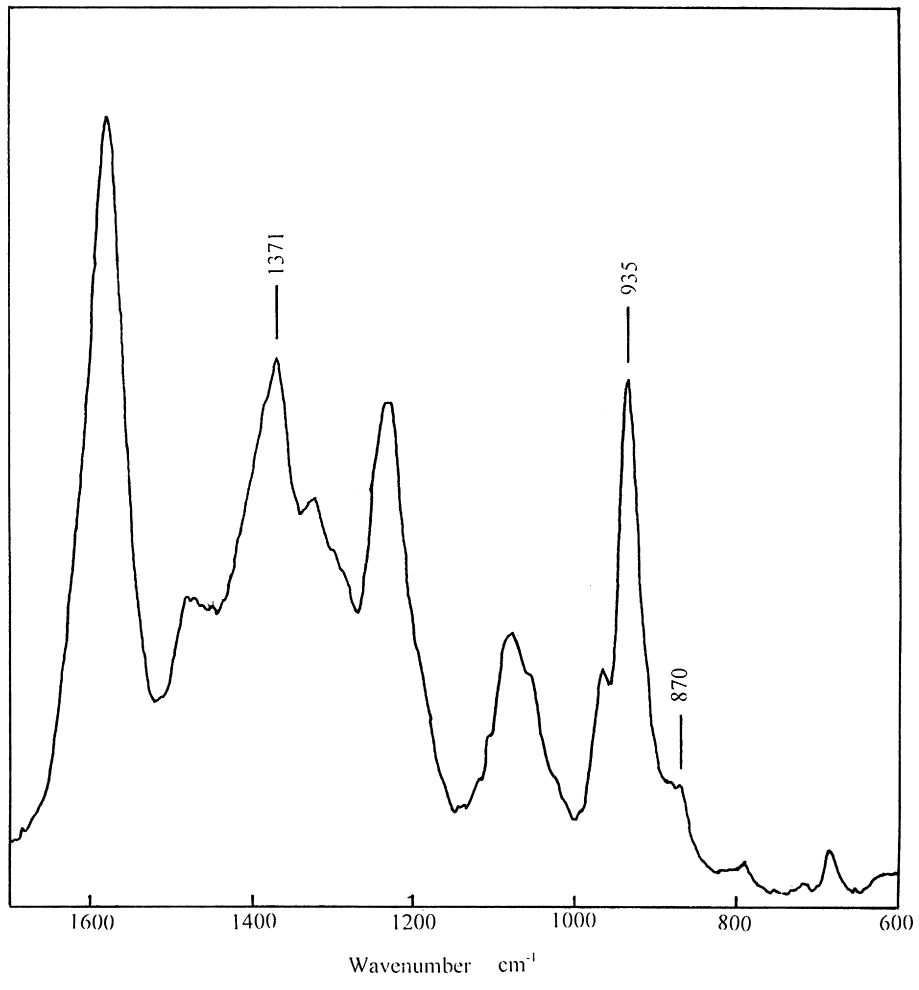

Fig. 6. The SERS spectra of PPy film deposited on Au at 1mA/cm^2 for 10s.

Gi [12]. We applied this method to investigate the orientation of PPy. SERS spectra shown in Fig. 6 were recorded using a roughened Au electrode on which polypyrrole was deposited at 1 mA cm^{-2} for 10 s. The sharp absorption at 1371.1 cm^{-1} was ascribed to the bipolaron ring stretch, which contained a mainly C–C stretch mode. There is also a sharp peak at 935 cm^{-1} which is ascribed to the C–H polaron in-plane deformation. A very weak peak at 870 cm^{-1} is due to the C–H out-of-plane deformation [26]. According to the surface selection rules [12], incident light increased in the electromagnetic fields which are most normal to the surface, normal modes of the absorbed molecule involving changes in molecular polarizability with a component perpendicular to the surface are subject to the greatest enhancement. The polarizability moment change of the C–H in-plane deformation is parallel to the pyrrole ring, while that of the C–H out-of-plane deformation is perpendicular to the pyrrole ring. The largely enhanced C–H in-plane deformation inferred that the pyrrole ring was 'standing' on the Au surface, in other words, the ring planes make a significant angle to the metal surface.

We assume that in the early stage of electropolymerization, the monomer or the oligomer is absorbed to the Au surface. There may be two ways through which the pyrrole rings are absorbed: one is the interaction between the π-electrons in the pyrrole rings and the Au atoms, and the other is the interaction between the nitrogen atoms of the pyrrole rings and the Au atoms. The former results in the parallel arrangement of the pyrrole ring to the Au surface and the latter results in the standing arrangement of the pyrrole ring to the Au surface. The SERS spectra of PPy revealed that the interaction between the nitrogen atom of the pyrrole ring and the Au atoms plays a very important role in the arrangement of the PPy chains. So, when polymerization begins, the Au surface is firstly coated with a layer of polymer in which the pyrrole rings are standing on the surface through the interaction between the nitrogen atoms of the pyrrole rings and the Au atoms, and it is this interaction that makes the polymer chains (i.e. the carbonbone of the polymer) parallel to the Au surface.

4. Conclusion

Polypyrrole was synthesized using a BFEE/EE binary solvent system. The obtained film showed good electric conductivity, large electric anisotropy, fairly good electrochemical redox switching reversibility and excellent mechanical properties. The mechanism of polymerization was discussed. SERS spectra were used to investigate the orientation of the polypyrrole chain on the metal surface. The pyrrole ring was found to be standing on the Au surface, i.e., the ring planes make a significant angle to the surface.

Acknowledgements

We are grateful for the financial support from the National Science Foundation of China and the Science Foundation of Jiangsu province.

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