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Effect of electrolyte solvent on the conductivity and structure of as-prepared polypyrrole films

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Eight kinds of solvents were used to study the effect of electrolyte solvents on the conductivity and structure of polypyrrole (PPy) films prepared electrochemically in the electrolyte solutions. It was found that the conductivity of PPy films strongly depended on the donor number (DN) of the electrolyte solvents used in their polymerization solutions. The conductivity increases with the decrease of the DN value of the solution solvents. High conductivity films of 10^0–10^2 S cm^{-1} were prepared only in the solutions with the solvents of low or middle DN values. For the solvents with high DN such as dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), the conductivity of the PPy films from their solutions were very low, *ca.* 10^{-6} S cm^{-1}. The addition of some alcohol or ether in the polymerization solution resulted in a serious drop of the conductivity of the as-prepared PPy film. Absorption spectra and surface morphology of the as-prepared PPy films also show the dependence on the polymerization solvents. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: solvent effect; polypyrrole; conductivity)

INTRODUCTION

Conducting polymers are regarded as potential materials for the electronics industry such as in batteries[1], molecular transistor[2], ion-gate[3], electrochromic displays[4], cable shielding[5] and in molecular electronics as the circuit elements[6]. Among them, polypyrrole (PPy) is more attractive for its ease of preparation, high electronic conductivity and good stability. Electrochemical polymerization of pyrrole is the main method in the preparation of PPy films. The polymerization parameters, such as solvent[7,8], temperature[9], potential or current density[10], concentration of monomer[11], supporting electrolyte[12] and the nature of working electrode[13], have strong effect on the polymerization processes of pyrrole.

The PPy films can be prepared from organic or aqueous solutions. One order difference of the magnitude of conductivity was observed between the PPy films prepared in aqueous solution and those formed in acetonitrile solutions[14]. Diaz and Hall investigated the effect of the addition of water or ethylene glycol (EG) into acetonitrile solution on the conductivity of PPy[15]. They found that the conductivity and the mechanical properties of PPy films greatly depended on the water or EG concentration. Produced in 99% acetonitrile and 1% water, the polypyrrole toluenesulfonate [PPy(TsO$^-$)] film showed high conductivity of 60–100 S cm^{-1} and high tensile strength of 60 MPa. Prepared in 25% water and 75% acetonitrile, the PPy films showed low conductivity of 0.5 S cm^{-1} and low tensile strength of 8 MPa. The addition of ethylene glycol and glycolene into acetoni-

trile resulted in similar decrease of the conductivity and mechanical properties. Sutton and Vaughan reported that the addition of methanol into water also led to a drop in the conductivity of PPy films[16]. A variation of three orders of magnitude in conductivity was observed for the PPy (TsO$^-$) films formed in water and in methanol solutions. Fukuyama *et al.* found that the addition of substituted phenol in the solution can improve the conductivity, thermal stability and tensile strength of the as-prepared PPy[17]. Recently, we obtained the PPy(NO$_3^-$) film with high tensile strength of 79 MPa from PC solution at 15°C. This is much stronger than that of 2.6 MPa from aqueous solution[18].

These findings mentioned above indicate that the solvents have a strong effect on the electropolymerization of pyrrole. But the origin of the effect is still ambiguous. To clarify the mechanism of the solvent effect, we studied systematically the effect of solvent on the conductivity and structure of PPy prepared from the solutions with eight kinds of solvents.

EXPERIMENTAL

PPy films were electrochemically prepared in various solutions containing 0.1 mol l^{-1} supporting electrolyte and 0.1 mol l^{-1} pyrrole. The supporting electrolytes used were Et$_4$NClO$_4$, Et$_4$NBF$_4$, LiClO$_4$, Cu(NO$_3$)$_2$ · 3H$_2$O and *p*-toluene sulfonic acid (TsOH). The solvents employed were selected from CH$_3$NO$_2$ (NM), CH$_3$CH$_2$OH (EtOH), 1,2-propanediol carbonate (PC), H$_2$O, ethylene glycol dimethyl ether (DME), trimethyl phosphate (TMP), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO). The polymerization was

performed under a constant current of $0.1\,mA\,cm^{-2}$ for DMF and DMSO as solvents and $0.5\,mA\,cm^{-2}$ for the other solvents. A stainless steel plate or an indium tin oxide (ITO) coated glass plate was used as working electrode and a stainless steel plate was used as counter electrode. Thick films of $10-30\,\mu m$ formed on the stainless steel plate electrode were used for the conductivity measurement, elemental analysis and surface morphology analysis. Thin films of *ca.* $0.3\,\mu m$ $(60\,mC\,cm^{-2})$ deposited on ITO electrode were used for absorption spectra measurement.

Vis-n.i.r. absorption spectra were recorded with a Nanometrics Nanospec/10 (Vis) and a Nanospec/10 NIR (n.i.r.) microspectrophotometer. *FT* i.r. spectra of PPy were taken on a Bruker model IFS 113V *FT* i.r. spectrophotometer. Scanning electron micrographs (SEMs) were taken using a Hitachi S-530 scanning electron microscope at an acceleration rate of $25\,kV$. The conductivity of the PPy films was measured by a four-probe technique for the films with high conductivity or by a two-probe technique for those with low conductivity.

RESULTS AND DISCUSSION

Effect of solvent donor number on the conductivity of as-prepared PPy films

The conductivity of the PPy films prepared in $0.1\,mol\,l^{-1}$ pyrrole and $0.1\,mol\,l^{-1}$ Et_4NBF_4 solutions with various solvents were measured, as shown in *Table 1*. For the convenience of discussion, the PPy films prepared in the solutions with the anion A^- and the solvent S will be represented as $PPy(A^-, S)$ in the following. The strong dependence of the conductivity on the donor number (DN) of the solvents was observed, where DN represents an empirical semiquantitative measure of the nucleophilic properties of the solvent[19], the larger the DN value, the stronger the Lewis basicity of the solvent. With the solvent of high DN value such as DMF or DMSO, the as-prepared PPy films show semiconductivity below $10^{-4}\,S\,cm^{-1}$. With the solvent of middle DN value such as TMP or H_2O, the as-prepared PPy films show middle conductivity of $10^0\,S\,cm^{-1}$. With

the low DN solvent such as PC or CH_3NO_2 the PPy films obtained show obvious metallic conductivity of $60-70\,S\,cm^{-1}$: when $LiClO_4$, $Cu(NO_3)_2 \cdot 3H_2O$ or TsOH was used as supporting electrolyte, similar dependence of the PPy conductivity on the DN of the solvents was observed (see *Table 1*). Most obviously, with only 16% increase of the DN value from TMP to DMF, four orders of magnitude of the conductivity decreased for the PPy film prepared from DMF solution as compared with that prepared from TMP solution.

It is understandable that the conductivity of the PPy films depends on the doping counteranions because they were incorporated into the polymer to compensate the positive charge on the carbon backbone[20,21]. But the effect of the solvents on the conductivity is not so easily understood since elemental analysis shows that no solvent remains in the polymer. It should come from the influence of the solvents on the electropolymerization processes of pyrrole. It has been proposed that the polymerization of pyrrole proceeds through the radical cation intermediate[22,23]. The radical cation could be attacked by the solvent molecule in the solution. The larger the DN value of the solvent, i.e. the stronger the basicity of the solvent, the shorter the life span of the radical cation will be [24]. In the solvent of high DN, such as DMF and DMSO, the life span of the radical cation is probably so short that only polymer chains with short polymerization degree can be obtained, which results in the low conductivity. Moreover, Myers found that the conductivity of the PPy films prepared by the chemical oxidation also strongly depended on the solvents[25]: with THF as solvents, the PPy films showed low conductivity below $10^{-6}\,S\,cm^{-1}$ which is much lower than that of the PPy films prepared in the solution with water as solvent[25]. The results disagree with Imanishi *et al.* who investigated the effect of several solvents and claimed that the conductivity of PPy films increased with increasing DN value of the solvents in their polymerization solutions[7]. Their conclusion may be related to their polymerization conditions at a constant voltage of $4\,V$ between working electrode and counter electrode. Anyhow, their interpretation that 'the radical cation may be stabilized more with increasing DN of the solvent' could not be accepted.

Table 1 Effect of solution solvents and anions on the conductivity of the PPy films prepared in the solutions

| Solvents | DN | Conductivity of the PPy films ($S\,cm^{-1}$) | | | |
		$PPy(BF_4^-)^a$	$PPy(ClO_4^-)^b$	$PPy(NO_3^-)^c$	$PPy(TsO^-)^d$
DMSO	29.8	7×10^{-6}		1×10^{-6}	
DMF	26.6	1×10^{-4}	5×10^{-4}	3×10^{-6}	8×10^{-3}
TBP	23.7		1		
TMP	23.0	1.0	20		0.9
THF	20.0		31		
H_2O	18.0	8.4	34	2	79
PC	15.1	67	55	3	80
CH_3NO_2	2.7	69	56^e		

^{a} Prepared in $0.1\,mol\,l^{-1}$ pyrrole, $0.1\,mol\,l^{-1}$ Et_4NBF_4 solutions
^{b} Prepared in $0.1\,mol\,l^{-1}$ pyrrole, $0.1\,mol\,l^{-1}$ $LiClO_4$ solutions
^{c} Prepared in $0.1\,mol\,l^{-1}$ pyrrole, $0.1\,mol\,l^{-1}$ $Cu(NO_3)_2 \cdot 3H_2O$ solutions
^{d} Prepared in $0.1\,mol\,l^{-1}$ pyrrole, $0.1\,mol\,l^{-1}$ TsOH solutions
^{e} Prepared in $0.1\,mol\,l^{-1}$ pyrrole, $0.1\,mol\,l^{-1}$ Et_4NClO_4 solutions

Effect of alcohol and ether on the conductivity of as-prepared PPy films

The PPy films produced in alcohol solution show lower conductivity than those prepared in aqueous solution (see *Table 2*) though alcohol has similar DN value to water and the solubility of pyrrole in alcohol is better than that in water. For Et_4NBF_4, $LiClO_4$ or TsOH as supporting electrolyte, the conductivity of the as-prepared films from alcohol solutions is 10^{-1} to $10^0 \, S \, cm^{-1}$, one or two orders of magnitude lower than that of the PPy films prepared in aqueous solution. For $Cu(NO_3)_2 \cdot 3H_2O$ as supporting electrolyte, the conductivity of the as-prepared PPy films is as low as $8 \times 10^{-4} \, S \, cm^{-1}$, four orders lower than that of the PPy films prepared from aqueous solutions. Similar preparation of the PPy films was performed in iso-propanol solution of $0.1 \, M \, Cu(NO_3)_2 \cdot 3H_2O$, and the films also show the conductivity of $1 \times 10^{-4} \, S \, cm^{-1}$.

PC is a good solvent for the preparation of smooth and highly conductive PPy films. But low ionic conductivity of PC solution due to its high viscosity makes the reaction rate of the electropolymerization very low. To improve the ionic conductivity of the solution, DME of low viscosity is often added in the PC solution. So, the electropolymerization of pyrrole in the PC solutions with the addition of DME was performed. It was found, however, that the addition of DME is harmful to the polymerization. With the incremental addition of DME in the PC solution, the conductivity of PPy films decreased sharply, as shown in *Table 3*. The conductivity of the PPy films prepared in 90% PC + 10% DME solution is $0.08 \, S \, cm^{-1}$, two orders lower than that prepared in PC solution. When DME reaches 50% in volume, the as-prepared PPy films have very low conductivity of $10^{-7} \, S \, cm^{-1}$. Moreover, the conductivity of the PPy films prepared in BF_3 ethyl ether solution is $0.05 \, S \, cm^{-1}$, two orders of magnitude lower than that produced in TMP solution, though ethyl ether (DN = 19.2) has lower DN value than TMP. Obviously, the big difference of the conductivity between them is not caused by the nucleophilicity of the solvent. It is well known that alcohol and ether can be used as termination agent in cation polymerization[26]. So, we think that they play a similar role in the radical-cation polymerization of pyrrole. In fact, methanol has been used to terminate the polymerization of pyrrole[27].

Doping degree of PPy

The conductivity of the PPy films is usually related to the doping degree of the counteranions in the films. To investigate the origin of the solvent effect on the conductivity, the doping degree of the counteranions in the PPy films produced in the solutions with different solvents was analysed by elemental analysis. The results are tabulated in *Table 4*. Surprisingly, $PPy(ClO_4^-, H_2O)$ has similar chemical composition to $PPy(ClO_4^-, NM)$ although several times difference in conductivity has been observed. Moreover, no obvious difference of NO_3^- doping degree is observed between $PPy(NO_3^-, EtOH)$ and $PPy(NO_3^-, H_2O)$ though the former shows the conductivity four orders of magnitude lower than the latter. Furthermore, no solvent is combined in the PPy films prepared in the solvent solution. Diaz and Hall also found that there is no obvious difference in chemical composition between PPy prepared in 1% water + 99% acetonitrile and that produced in 12.5% ethyl glycol + 12.5% water + 75% acetronitrile though a variation of four orders in conductivity has been observed between them[15]. Fukuyama *et al.* observed that the addition of inert additives in the polymerization solution can improve the conductivity and the mechanical properties of the as-prepared PPy films, and there are no additives combined in the films[17].

These results imply that the doping degree of the counteranions in PPy is not affected by the solvents in the

Table 2 The conductivity of the PPy films prepared from alcohol or aqueous solutions of $0.1 \, mol \, l^{-1}$ pyrrole and $0.1 \, mol \, l^{-1}$ various supporting electrolytes

	Conductivity of PPy films $(S \, cm^{-1})$	
Electrolytes	Prepared in alcohol solution	Prepared in aqueous solution
TsOH	3	79
$LiClO_4$	0.9	34
Et_4NBF_4	0.3	8.4
$Cu(NO_3)_2 \cdot 3H_2O$	8×10^{-4}	2

Table 3 The effect of the addition of DME in PC solutions on the conductivity of the PPy films prepared in $0.1 \, mol \, l^{-1}$ pyrrole and $0.1 \, mol \, l^{-1}$ $Cu(NO_3)_2 \cdot 3H_2O$ solutions

Solvent	Film conductivity $(S \, cm^{-1})$
100% PC	3
90% PC + 10% DME	0.08
80% PC + 20% DME	1×10^{-3}
50% PC + 50% DME	10^{-7}

Table 4 Composition of the as-prepared PPy from various preparation solutions of $0.1 \, mol \, l^{-1}$ pyrrole and $0.1 \, mol \, l^{-1}$ supporting electrolyte

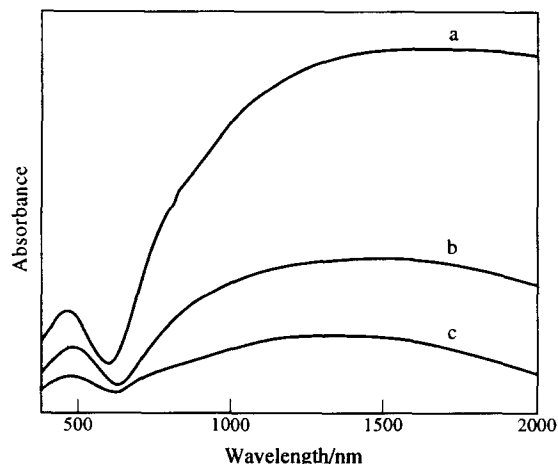|	Ratio of elements					
Polymerization solutions	C	H	N	ClO_4	NO_3	O^a
Et_4NClO_4/CH_3NO_2	4.0	4.0	0.99	0.38	—	0.35
$LiClO_4/H_2O$	4.0	3.6	1.0	0.38	—	0.65
$Cu(NO_3)_2 \cdot 3H_2O/H_2O$	4.0	3.2	1.0^b	—	0.22	0.84
$Cu(NO_3)_2 \cdot 3H_2O/PC$	4.0	2.9	1.0^b	—	0.22	1.40
$Cu(NO_3)_2 \cdot 3H_2O/CH_3CH_2OH$	4.0	3.6	1.0^b	—	0.26	1.48

[a] From balance
[b] Assumed

Figure 1 Vis-n.i.r. absorption spectra of (a) PPy(TsO⁻, H_2O) film; (b) PPy(TsO⁻, EtOH) film and (c) PPy(TsO⁻, DMF) film
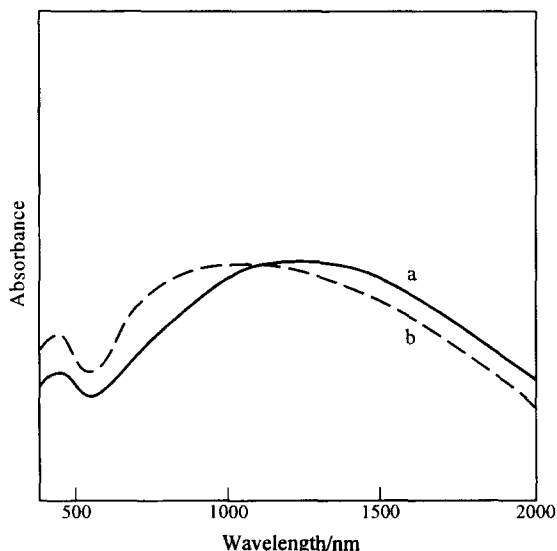

Figure 2 Vis-n.i.r. absorption spectra of (a) PPy(NO$_3^-$, PC) film and (b) PPy(NO$_3^-$, PC + DME) film

polymerization solutions. The obvious effect of the solvents on the conductivity of the PPy films may come from different conjugation length and chain structure of PPy prepared from the solutions with different solvents.

Vis-n.i.r. spectra of PPy

Figure 1 shows the vis-n.i.r. absorption spectra of the PPy(TsO⁻, H_2O), PPy(TsO⁻, EtOH) and PPy(TsO⁻, DMF) films. Two absorption bands are observed, that is, vis absorption band and n.i.r. absorption band, which are similar to those reported in the literature[21,28–30]. It has been found that the ratio of the n.i.r. peak absorbance ($A_{n.i.r.}$) to the vis peak absorbance (A_{vis}) is related to the conductivity of PPy films. The larger the ratio of $A_{n.i.r.}/A_{vis}$, the higher the conductivity of the PPy film. From *Figure 1*, it can be seen that the ratio of the three films decreased with the order: PPy(TsO⁻, H_2O) > PPy(TsO⁻, EtOH) > PPy(TsO⁻, DMF). This order agrees well with the order of their conductivities.

Effect of the addition of DME into PC solution of 0.1 M $Cu(NO_3)_2 \cdot 3H_2O$ on vis-n.i.r. absorption spectra

was studied too (see *Figure 2*). Two absorption bands can also be observed for the films prepared in PC solution [PPy(NO$_3^-$, PC)] or in 90% PC + 10% DME [PPy (NO$_3^-$, PC + DME)]. $A_{n.i.r.}/A_{vis}$ of PPy(NO$_3^-$, PC) is higher than that of PPy(NO$_3^-$, PC + DME), which agrees with the value of their conductivity. In addition, their absorption maxima in n.i.r. range appears in a different position. It appears at *ca.* 1300 nm for PPy(NO$_3^-$, PC) and shifts to *ca.* 1000 nm for PPy(NO$_3^-$, PC + DME). The absorption in n.i.r. range has referred to the bipolaron in PPy[29]. So, these results indicate that the bipolaron concentration may drop and the conjugation length of PPy may decrease with the addition of DME in the polymerization solution.

FTi.r. spectra of PPy

To study the effect of solution solvent on the structure of the as-prepared PPy, *FT*i.r. spectra of the PPy films produced from different solution solvents were measured. *Figure 3* shows the *FT*i.r. of the PPy(ClO$_4^-$) films prepared in CH_3NO_2 and in DMF. The selection of PPy(ClO$_4^-$, NM) and PPy (ClO$_4^-$, DMF) is from the consideration of their big difference in conductivity. The absorption band at 1700 cm⁻¹ appeared in PPy(ClO$_4^-$, DMF), indicating that the polymer contains an appreciable amount of C=O group probably due to over-oxidation. The over-oxidation in PPy results in the disruption of conjugated structure and the loss of conductivity. Such over-oxidation has been observed for PPy prepared in aqueous buffer solution of pH 4–5[23]. The lower conductivity of PPy(ClO$_4^-$, DMF) (see *Table 1*) may be due to its over-oxidation structure.

Surface morphology of the as-prepared PPy films

The surface morphology of the as-prepared PPy films was studied by SEM photograph, as shown in *Figure 4*. The morphology of the growth surface of PPy(NO$_3^-$, H_2O) films shows nodular structure. The growth surface of PPy(NO$_3^-$, PC) film is smooth and another structure like 'crocodile-skin' was observed among the nodular structure. Moreover, nodular structure was observed on the growth surface of the PPy(ClO$_4^-$, H_2O) and PPy(ClO$_4^-$, PC) films. But the latter
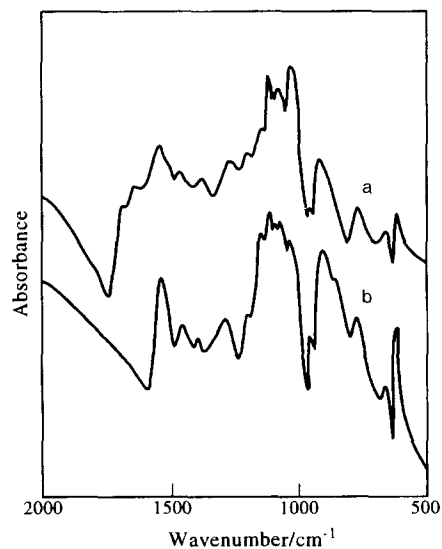

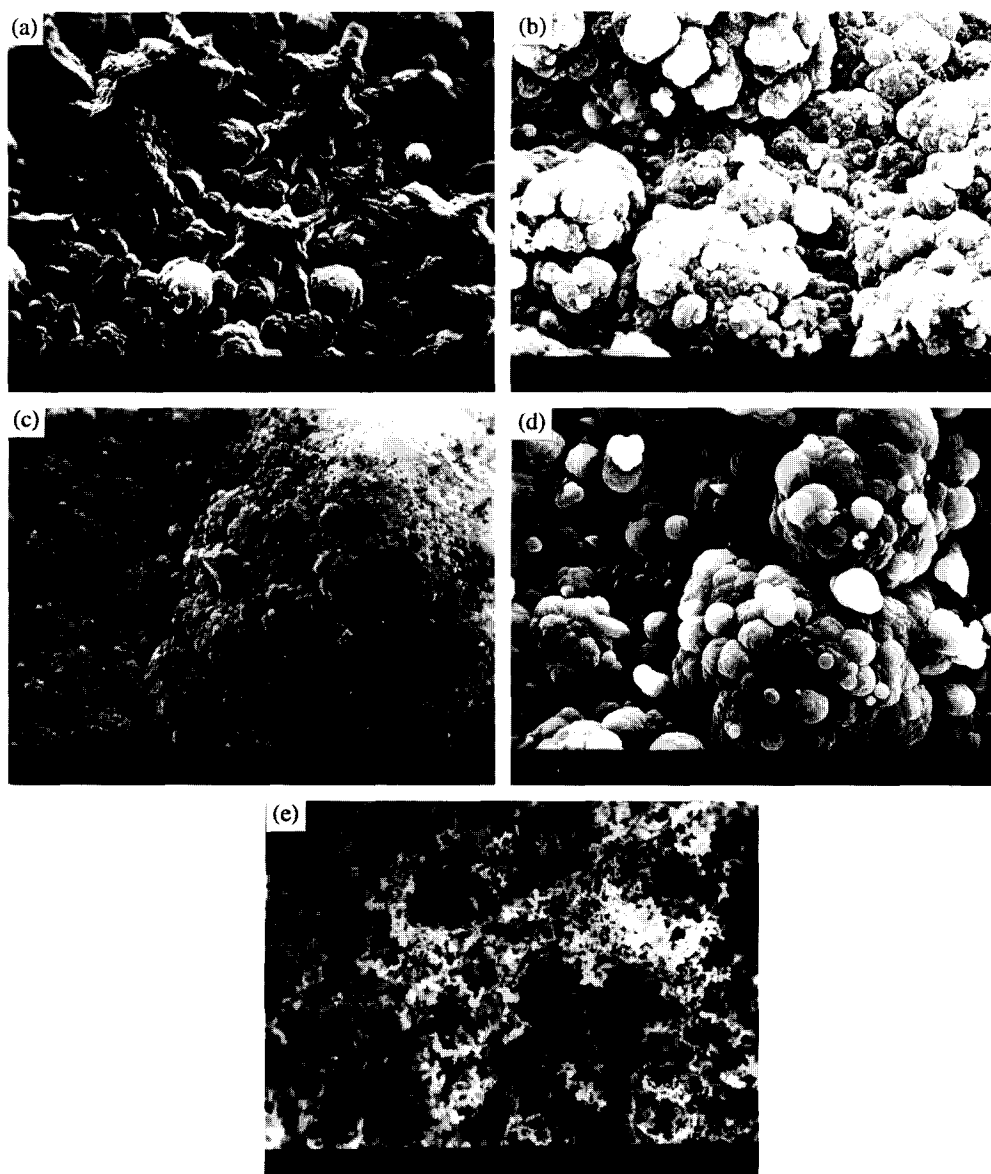**Figure 3** *FT*i.r. spectra of (a) PPy(ClO$_4^-$, DMF) and (b) PPy(ClO$_4^-$, NM)

Figure 4 SEM photographs of the growth side of (a) PPy(NO$_3^-$, PC) film; (b) PPy(NO$_3^-$, H$_2$O) film; (c) PPy(ClO$_4^-$, PC) film; (d) PPy(ClO$_4^-$, H$_2$O) film; (e) PPy(ClO$_4^-$, NM) film

is smoother and more compact. The PPy (ClO$_4^-$, NM) film shows very small granular structure. Obviously, the solvents play an important role on the morphology of PPy films prepared from the solutions.

The surface morphology of PPy films has been studied intensively to investigate the effect of various polymerization conditions, especially for the effect of solution anions[31]. But the relationship between the morphology and the properties of PPy is very complicated. Diaz and Hall observed that the surface morphology of the PPy(TsO$^-$) films prepared in 12.5% ethylene glycol + 12.5% water + 75% acetonitrile solutions resembles that of the films produced in acetonitrile solutions, even though the former are a hundred times less conductive[15]. But Sutton and Vaughan found that the growth surface of the PPy films prepared in water–methanol co-solvent changes systematically as the percentage of methanol in the solvent was increased[16]. The compact nodular surface texture from an aqueous solution changed to a more undulating wrinkled appearance. The difference of the surface morphology

between the films from water and acetonitrile solutions was also observed, which was assumed to be the result of greater hydrophobicity of PPy[32].

Anyhow, the surface morphology of the as-prepared PPy films should be related to the growth process. So, the effect of the solvents on the morphology indicates that the solvent greatly influences the growing form of PPy.

CONCLUSION

The conductivity and structure of the PPy films prepared by the electrochemical method strongly depended on DN value of the solvents in the polymerization solutions. The higher the DN value, the stronger the basicity of the solvent, the lower the conductivity of the PPy films prepared from the solvent solutions. The low conductivity of the PPy films prepared from high DN solvent solution may result from the shorter conjugation length of PPy due to the attack of the nucleophilic solvent molecule with high DN on the radical-cations during the polymerization of pyrrole. Alcohol and ether are

harmful to the preparation of highly conductive PPy films. The doping degree of the counteranions in PPy is little affected by the solvent used in the polymerization and no solvent combined in PPy. So, the effect should come from the influence of the solvent on the polymerization process of pyrrole. The surface morphology of PPy is also dependent on the solvents used in its polymerization.

ACKNOWLEDGEMENTS

REFERENCES

1   Vovak, P. and Vielstich, W. *J. Electrochem. Soc.* 1990, **137**, 1681
2   Li, Y., Ouyang, J., Yang, J., Liu, Y. and Wan, M. *Chem. J. Chinese University* 1995, **16**, 279
3   Pei, Q. and Qian, R. 'Polymers and Biomaterials' (Eds H. Feng *et al.*), Elsevier, New York, 1991, p. 195
4   Miller, L. L., Zinger, B. and Zhou, Q.-K. *J. Am. Chem. Soc.* 1987, **109**, 2267
5   Ouyang, J. and Li, Y. *J. Appl. Polym. Sci.* 1996, **59**, 1827
6   Davidson, K. *Edu. Chem.* 1991, **28**, 155
7   Imanishi, K., Satoh, M., Yasuda, Y., Tsushima, R. and Aoki, S. *J. Electroanal. Chem.* 1989, **260**, 469
8   Cervini, R., Fleming, R. J., Kennedy, B. J. and Murray, K. S. *J. Mater. Chem.* 1994, **41**, 87
9   Liang, W., Lei, J. and Martin, C. R. *Synth. Met.* 1992, **52**, 227
10   Maddison, D. S. and Unsworth, J. *Synth. Met.* 1989, **30**, 47
11   Ogamasawara, M., Funahashi, K., Demyra, T., Hagiwara, T. and Iwata, K. *Synth. Met.* 1986, **14**, 61
12   Qian, R. and Qiu, J. *Polym. J.* 1987, **19**, 157
13   Sun, B. and Schweinsberg, D. P. *Synth. Met.* 1994, **68**, 49
14   Warren, L. F. and Anderson, D. P. *J. Electrochem. Soc.* 1987, **134**, 101
15   Diaz, A. F. and Hall, B. *IBM J. Res. Develop.* 1983, **27**, 342
16   Sutton, S. J. and Vaughan, A. S. *Synth. Met.* 1993, **58**, 391
17   Fukuyama, M., Nanai, N., Kjima, T., Kudoh, Y. and Yoshimura, S. *Synth. Met.* 1993, **58**, 391
18   Ouyang, J. and Li, Y. *Synth. Met.* 1996, **79**, 121
19   Reichardt, C. 'Solvents and Solvent Effects in Organic Chemistry', second, revised and enlarged edition, VCH, Weinheim, 1988, p. 19
20   Qian, R., Qui, J. and Shen, D. *Synth. Met.* 1987, **18**, 13
21   Li, Y., Ouyang, J. and Yang, J. *Synth. Met.* 1995, **74**, 49
22   Genies, E. M., Bidan, G. and Diaz, A. F. *J. Electroanal. Chem.* 1983, **149**, 101
23   Qian, R., Pei, Q. and Huang, Z. *Makromol. Chem.* 1991, **192**, 1263
24   Sawyer, D. T. and Roberts, J. L. 'Experimental Electrochemistry for Chemists', Wiley, New York, 1974, p. 174
25   Myers, R. E. *J. Electron. Mater* 1986, **15**, 61
26   Hiemenz, P. C. 'Polymer Chemistry', Marcel Dekker, New York, 1984, p. 414
27   Lee, J. Y., Kim, D. Y. and Kim, C. Y. *Synth. Met.* 1995, **74**, 103
28   Li, Y. and Qian, R. *Synth. Met.* 1989, **28**, C127
29   Yakushi, K., Lauchlan, L. J., Clarke, T. C. and Street, G. B. *J. Chem. Phys.* 1983, **79**, 4774
30   Ouyang, J. and Li, Y. *Synth. Met.* 1995, **75**, 1
31   Qian, R., Qui, J. and Yan, B. *Synth. Met.* 1986, **14**, 81
32   Ko, J. M., Rhee, H. W., Park, S.-M. and Kim, C. Y. *J. Electrochem. Soc.* 1990, **137**, 905