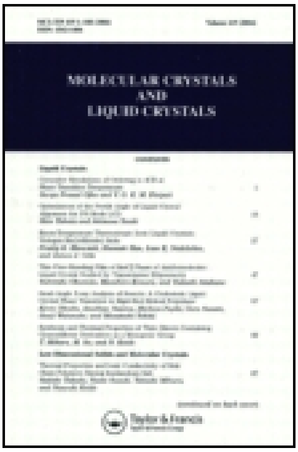

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# Effects of pH of Electrolyte Solution Systems on the Electrochemical Properties of Poly(N-substituted Pyrrole)s

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# EFFECTS OF pH OF ELECTROLYTE SOLUTION SYSTEMS ON THE ELECTROCHEMICAL PROPERTIES OF POLY(N-SUBSTITUTED PYRROLE)S

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Abstract Effects of pH of different electrolyte solution systems on the electrochemical activities and stabilities of polypyrrole(PPy), poly(N-methylpyrrole) [poly(N-M.P.)], poly(N-ethylpyrrole) [poly(N-E.P.)] , and poly(N-phenylpyrrole) [poly(N-P.P.)] films were investigated. For electrolyte solution systems, used were TBADS/ACN, $LiClO_4$/PC, $LiClO_4$/THF, $LiClO_4$/DMSO, and $LiClO_4/H_2O$. The electrolyte solution systems became more basic as the monomers were polymerized and the polymerized films were cycled. The oxidation peak potential was increased and the stability of polymer films was decreased as the pH of the electrolyte solution systems was decreased. It was found that the film surface became less dense when the cycling was done in the strong acidic electrolyte solution systems.

## INTRODUCTION

Polypyrrole (PPy) has raised great interests as a promising material in applications to rechargeable battery, electrochromic display and molecular electronics due to the convenience of its formation by electrochemical polymerization and high stability against air and heat.[1-8]

It has been reported that the electrochemical properties of PPy are strongly dependent on dopant anions,[9] growth/oxidation rates,[10] solvent systems,[11] electrode substrates and types[12] and synthesis method. In general, it has been known that limited dendrite growth has been achieved in low polarity aprotic solvents,[13] such as acetonitrile, resulting in better conductivities and electron transfer properties during electropolymerization.[11] PPy produced in aqueous solvent systems shows slightly lower conductivities than in non-aqueous solvents, although a quantitative comparison between different solvent systems is difficult due to the fact that different solvent systems require different dopant anions. The flexibility of PPy was improved by using

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dopants with long aliphatic chains. It was found that hydrophobic nature of aliphatic portion of dopants in an aqueous solution embedded the dopants tightly in PPy on polymerization. The dopants were hardly removed on reduction of the polymer.

In this study, we report the effect of pH of different electrolyte solution systems on the electrochemical properties of polypyrrole and poly(N-substituted pyrrole)s. The redox behavior and electrochemical stability of PPy films has been examined by means of cyclic voltametry in various electrolyte solution systems such as tetrabutylammonium dodecylsulfate (TBADS)/acetonitrile(ACN), lithiumperchlorate($LiClO_4$)/propylene carbonate(PC), $LiClO_4$/tetrahydrofuran(THF), $LiClO_4$/dimethylsulfoxide(DMSO), and $LiClO_4/H_2O$.

## EXPERIMENTAL

Pyrrole, N-substituted pyrroles and solvents were dried and purified as described elsewhere[11] and TBADS, used as an electrolyte, was synthesized in our laboratory.[14] PPy and poly(N-substituted pyrrole)s were formed galvanostatically on a platinum electrode (1.5 X 3 $cm^2$) in a one-compartment cell containing 0.036 M TBADS and 0.36 M monomer in ACN. The current density was maintained at 10.0 $mA/cm^2$ for 1 hour. The film on the platinum electrode was peeled off and thoroughly rinsed in ACN for a couple of hours. To investigate on the electrochemical behavior, thin PPy films were prepared on a platinum electrode(1 X 1 $cm^2$) by the similar method as described above. Cyclic voltammograms were obtained using a potentiostat (EG&G model 362). The electrolyte concentration for the electrochemical study was fixed at 0.1 M to reduce solution resistance.

The pH of electrolyte solution systems were measured by using a pH-meter(Metrohm model 632). Table I shows the pH value of various electrolyte solution

TABLE I pH values of various electrolyte solution systems used in this work.

| Electrolyte solution system | Concentration(M) | pH |
|---|---|---|
| TBADS / ACN | 0.1 | 0.52 |
| TBADS / ACN | 0.036 | 0.61 |
| $LiClO_4$ / PC | 0.1 | 3.86 |
| $LiClO_4$ / THF | 0.1 | 4.23 |
| $LiClO_4$ / $H_2O$ | 0.1 | 6.36 |
| $LiClO_4$ / DMSO | 0.1 | 8.17 |

systems used in this work, ranging from 0.52 to 8.17. Morphology of PPy and poly(N-substituted pyrrole) films were obtained by using scanning electron microscopy(SEM) (Jeol model JSM-35CF).

## RESULTS AND DISCUSSION

Table II shows the pH changes of 0.036M TBADS/ACN system before and after polymerizations of various different monomers. The pH values of the electrolyte solution systems were increased when the monomers, pyrrole and N-pyrrole derivatives, were polymerized regardless of the kinds of the monomers. The result means that the electrolyte solution system became more basic when the monomers therein were polymerized. After the polymerized films were cycled in a different electrolyte and solvent system(conc.=0.1M), the pH of systems were also became more basic, and this is shown in Table III. It is seen that the pH values of the systems largely depends on the acidity of solvents.

TABLE II Changes in the pH values of 0.036M TBADS/ACN before and after polymerizations of various monomers.

| Monomer | pH | |
|---|---|---|
| | Before polymerization | After polymerization |
| pyrrole | 2.85 | 6.57 |
| N-methylpyrrole | 4.23 | 5.84 |
| N-ethylpyrrole | 1.07 | 7.17 |
| N-phenylpyrrole | 1.82 | 5.91 |

TABLE III pH values of electrolyte solution systems after cycled.

| Electrolyte systems | PPy | Poly(N-M.P.) | Poly(N-E.P.) | Poly(N-P.P.) |
|---|---|---|---|---|
| TBADS/ACN(pH=0.52) | 4.84 | 3.52 | 5.87 | 4.21 |
| $LiClO_4$/PC (pH=3.86) | 5.32 | 4.93 | 6.05 | 5.47 |
| $LiClO_4$/THF (pH=4.23) | 6.15 | 5.17 | 7.91 | 6.03 |
| $LiClO_4/H_2O$ (pH=6.36) | 7.13 | 7.08 | 8.25 | 7.15 |
| $LiClO_4$/DMSO(pH=8.17) | 9.23 | 8.80 | 9.41 | 9.07 |

Fig.1 shows oxidation peak potentials of PPy films in different electrolyte solution systems. As the electrolyte solution systems are more acidic, the oxidation peak potentials becomes higher. This result may be due to the fact that the polymerized films are more easily to be swollen and collapsed in stronger acids, implying that the dopant anions,$DS^-$ or $ClO_4^-$, are more apt to transfer in strong acid or base than in neutral or weak acid or base electrolyte solution systems. Electrochemical stability of PPy films is shown in Fig.2. As the electrolyte solution system was more acidic, the stability of PPy film was decreased and this might be also attributed to the easiness of swelling and collapse of the PPy film in strong acids. Fig.2 also shows that the PPy films cycled in the aqueous solution system exhibited better stability than those in the nonaqueous solution systems. It should be noted, therefore, that the electrochemical stability of PPy films cycled in different electrolyte solution systems depends not only whether the solvent is aqueous or non-aqueous but also what is the pH of the electrolyte solution system. Poly(N-substituted pyrrole) films also showed the same tendency in oxidation peak potentials and electro-chemical stabilities as for PPy films. The swelling-and-collapse mechanism of polymer films cycled in strong acidic electrolyte solution systems can be seen in their SEM micrographs.

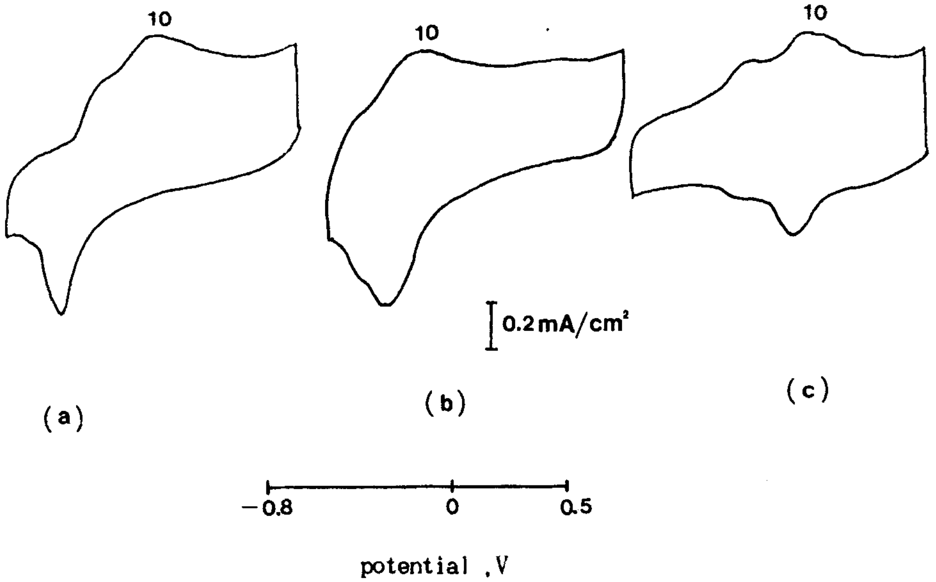

FIGURE 1 CVs of PPy films prepared in the 0.036M TBADS/ACN system and cycled in the systems of (a)$LiClO_4$/THF(b)$LiClO_4/H_2O$(c)$LiClO_4$/DMSO

As a typical example, SEM micrographs of poly(N-phenylpyrrole) in TBADS/ACN system are shown in Fig.3. The polymer films after cycling exhibited

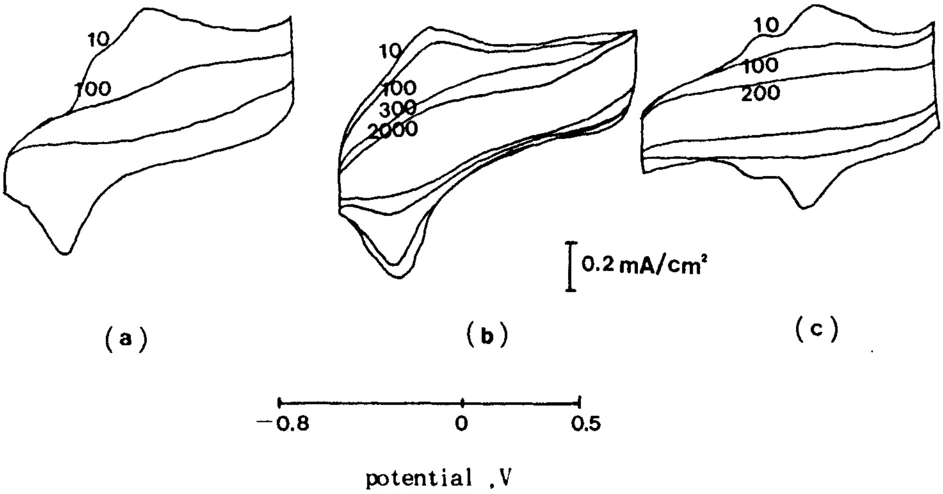

FIGURE 2 CVs for electrochemical stability of PPy films in different electrolyte solution systems (a)$LiClO_4$/THF (b)$LiClO_4$/$H_2O$ (c)$LiClO_4$/DMSO

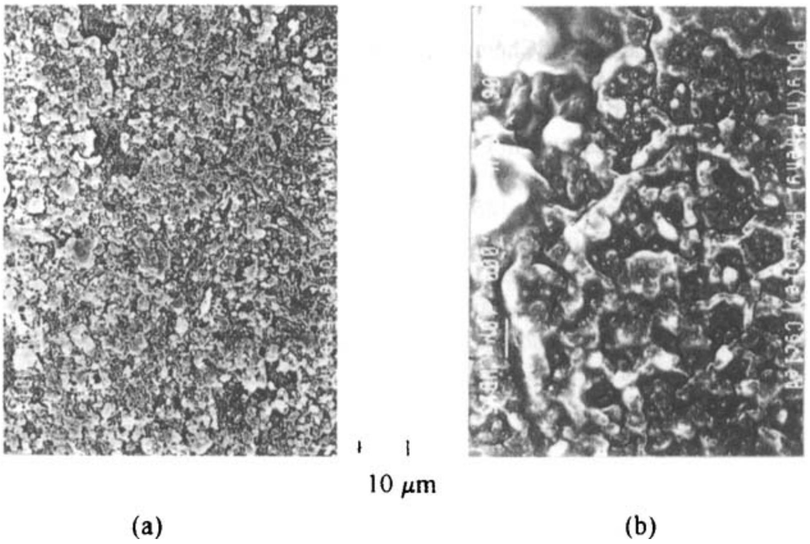

FIGURE 3 SEM micrographs of poly(N-phenylpyrrole) in 0.1 M TBADS/ACN electrolyte solution system after cycled (a)poly(N-P.P.)(fresh) (b)poly(N-P.P.)(cycled)

less dense surface structure than before cycling, since the film was collapsed during the reduction and thus the dopant anions could not easily penetrate into the film. The same morphological changes were observed for all of the other polymer films.

## CONCLUSION

The pH of an electrolyte solution system depended on the solvent used. 0.036M TBADS/ACN electrolyte system after galvanostatic polymerization showed more basic pH values than before polymerization. After cycling, the pH of electrolyte solution system was different from the original pH. In this case, it also became more basic. These phenomena were irrespective of kinds of monomers. Oxidation peak potentials of CVs were larger in strong acids or bases than in weak acids or bases, since the polymerized films were easily to swell and collapse in strong acids or bases. But, electrochemical stability was lower in strong acids or bases than in weak acid or base electrolyte systems. Charge transfer is easier in strong acids or bases and thus, surface density of films became less dense, when the polymer films were cycled in strong acidic electrolyte solution system. The surface morpological changes were identified by SEM micrographs.

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