

**CHARGE TRANSPORT IN POLYPYRROLE FILMS CONTAINING IMIDE ANIONS****HAESIK YANG AND JUHYOUN KWAK**

Dept. of Chem., KAIST, Kusung dong, Yusung, Taejon 305-701 Korea

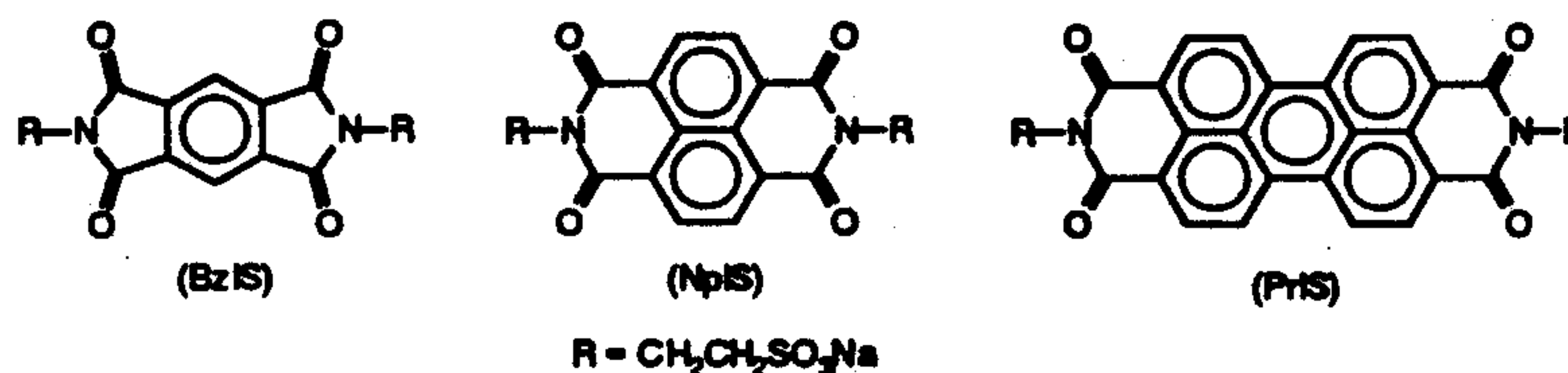
**CHANGJIN LEE AND SUH BONG RHEE**

Advanced Polymer Div., KRICT, P.O. BOX 107, Yusung, Taejon 305-600 Korea

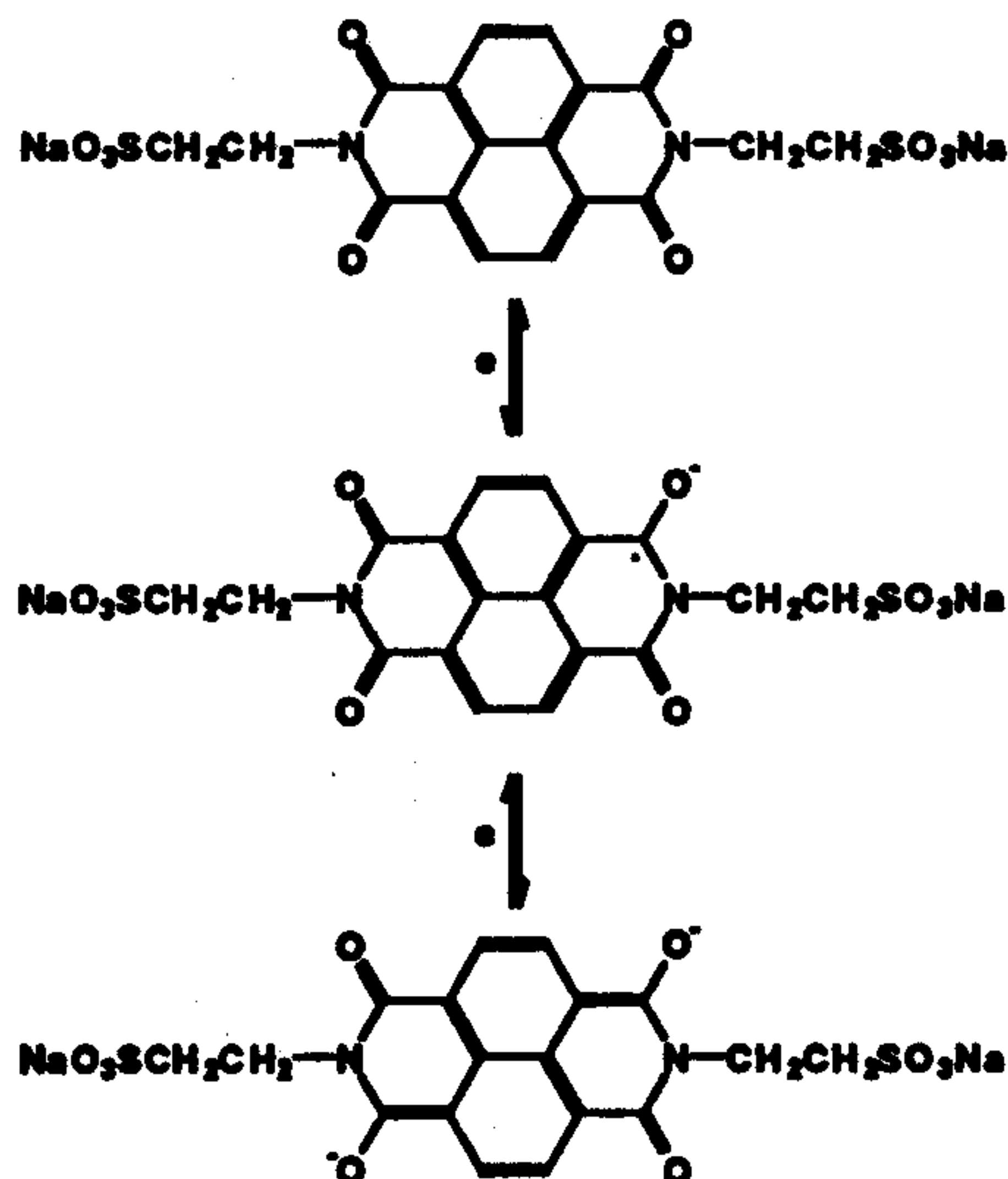
**ABSTRACT** New electroactive imide sulfonates were synthesized and their electrochemical properties characterized in aqueous solution. The charge transport and redox properties of polypyrrole films containing imide sulfonates were investigated using cyclic voltammogram and UV/VIS spectroscopy.

**INTRODUCTION**

A number of interest has been given to polypyrrole composite, utilizing various electroactive ion complexes that serve as charge-balancing dopant ion during electropolymerization.<sup>1</sup> Organic multistage redox compounds<sup>2</sup> such as imide, viologen, and quinone can be used to this purpose, which sometimes have good electron-mediating properties, definite redox color changes, or high charge capacities. Of them, imides showed good redox reversibilities and mild redox potentials.<sup>3-4</sup>



The electrostatic binding and electroactivity of electroactive dopants are affected by solvent, electrolyte, polymer morphology, and so on. To investigate these influences, we studied the redox chemistry of three water-soluble imide sulfonates in water solution and polypyrrole film.



## EXPERIMENTAL

Three imide sulfonates were prepared from tetracarboxylic dianhydride (1,2,4,5-benzenetetracarboxylic dianhydride, 1,4,5,8-naphthalenetetracarboxylic dianhydride, and 3,4,9,10-perylenetetracarboxylic dianhydride), taurine, and sodium carbonate in dimethylacetamide solution according to the reported procedure.<sup>5</sup> The products were used after recrystallization in water solution.

As the electrode, a gold electrode (0.02 cm<sup>2</sup>) was used except for spectrochemical measurements, where an indium-tin-oxide coated glasses plate was used.

Electropolymerization of pyrrole was carried out galvanostatically at 0.5 mA/cm<sup>2</sup> under N<sub>2</sub> atmosphere using an aqueous 0.1M pyrrole solution containing each imide sulfonate in 0.01M.

Cyclic voltammetry was carried out using an EG&G Princeton Applied Research (PAR) Model 273 potentiostat/galvanostat, and UV/VIS spectrum was obtained using Guied Wave Model 260.

## RESULTS AND DISCUSSION

Cyclic voltammograms of three imide sulfonates in aqueous 0.1 M NaClO<sub>4</sub> and 0.1 M HClO<sub>4</sub> is shown in Fig. 1. In neutral solution all three undergo two-stage redox

reaction (BzIS :  $E^\circ = -0.71$  and  $-0.83$  V, NpIS :  $E^\circ = -0.40$  and  $-0.65$  V, PrIS :  $E^\circ = -0.38$  and  $-0.73$  V). The more conjugated imide undergoes the easier reduction. In acidic solution, BzIS undergoes irreversible chemical reaction after reduction, reversible two electron transport process appears in NpIS case, and sharp oxidation peak related to surface process is observed in PrIS case. NpIS and PrIS undergo good reversible redox reaction in acidic solution in contrast to general organic multi-stage redox species.

Fig. 2a shows cyclic voltammogram of polypyrrole/imide sulfonate films ( $0.5 \mu\text{m}$  thick). The redox peaks appear at potentials where imide peak appears in aqueous solution. As the number of cycling increases, the peak of electroactive dopant decreases gradually. The decreasing rate is more slow in larger and more rigid imide sulfonate.

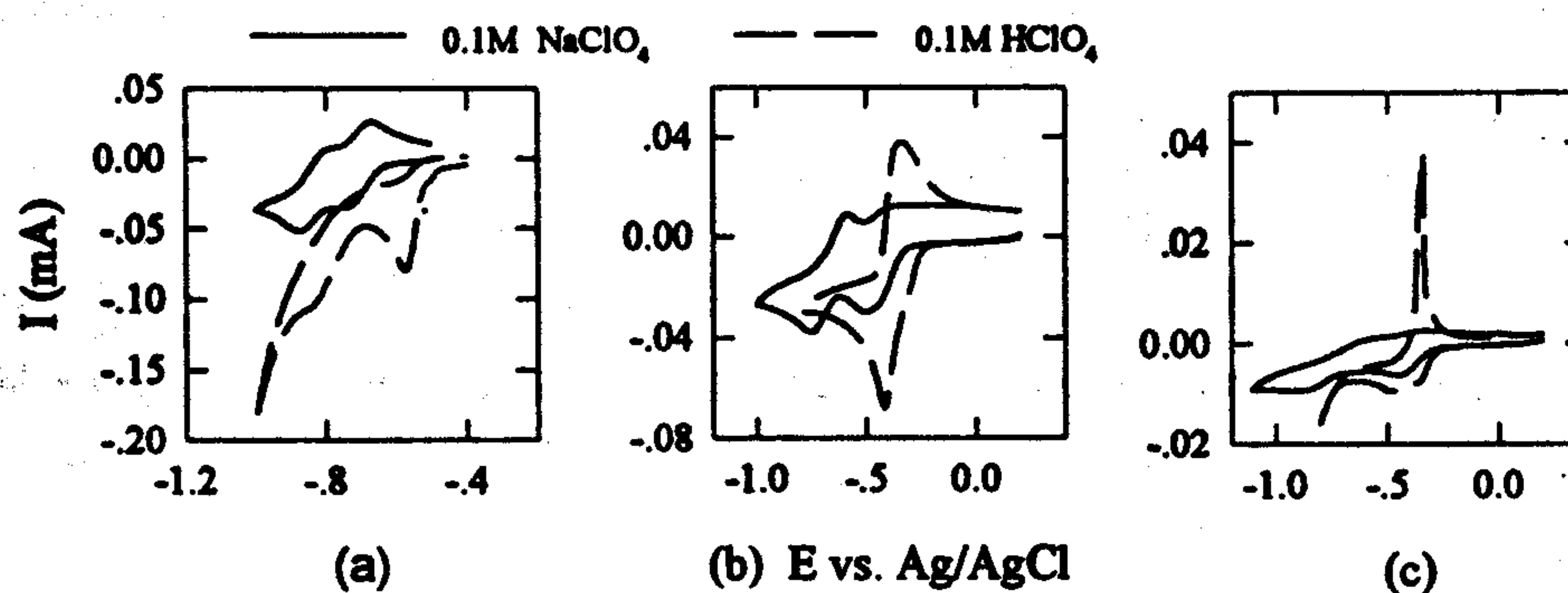


Fig. 1. Cyclic voltammograms of 4 mM (a) BzIS, (b) NpIS, and (c) PrIS in 0.1 M  $\text{NaClO}_4$  and 0.1 M  $\text{HClO}_4$  ( $v =$  (a, b) 50 and (c) 10 mV/sec).

Fig. 2b shows the cyclic voltammogram PPy/NpIS in 0.1M  $\text{TEAClO}_4/\text{Acetonitrile}$ . Compared to water solution case, the reduction peak of NpIS appears more negative potential. In contrast, in 0.1M  $\text{LiClO}_4/\text{Acetonitrile}$  solution no imide reduction peak appears and small polypyrrole peak is observed. It has been reported that Li ions make strong ion-pairing to radical anions or dianions of quinones, which make the redox reactions of them difficult in aprotic solvent. The same situation seems to be met in imide sulfonate.

Fig. 3. shows UV/VIS spectra of PPy/BzIS, PPy/NpIS, and PPy/PrIS at several different potentials. In these spectra, the 400 nm feature corresponds to the interband transition of PPy, and the long wavelength feature to the transition from  $\pi$ -band to polaron or bipolaron state.<sup>7</sup> As the oxidized polymer is reduced, the absorption maxima



of the 400 nm feature increase but those of the long wavelength feature decrease. The absorption maxima of BzIS, NpIS, and PrIS are 350, 400, and 500 nm, respectively. In each oxidized state its absorption feature appears, during reduction the absorption maximum is changed because of reduction of imide sulfonate.

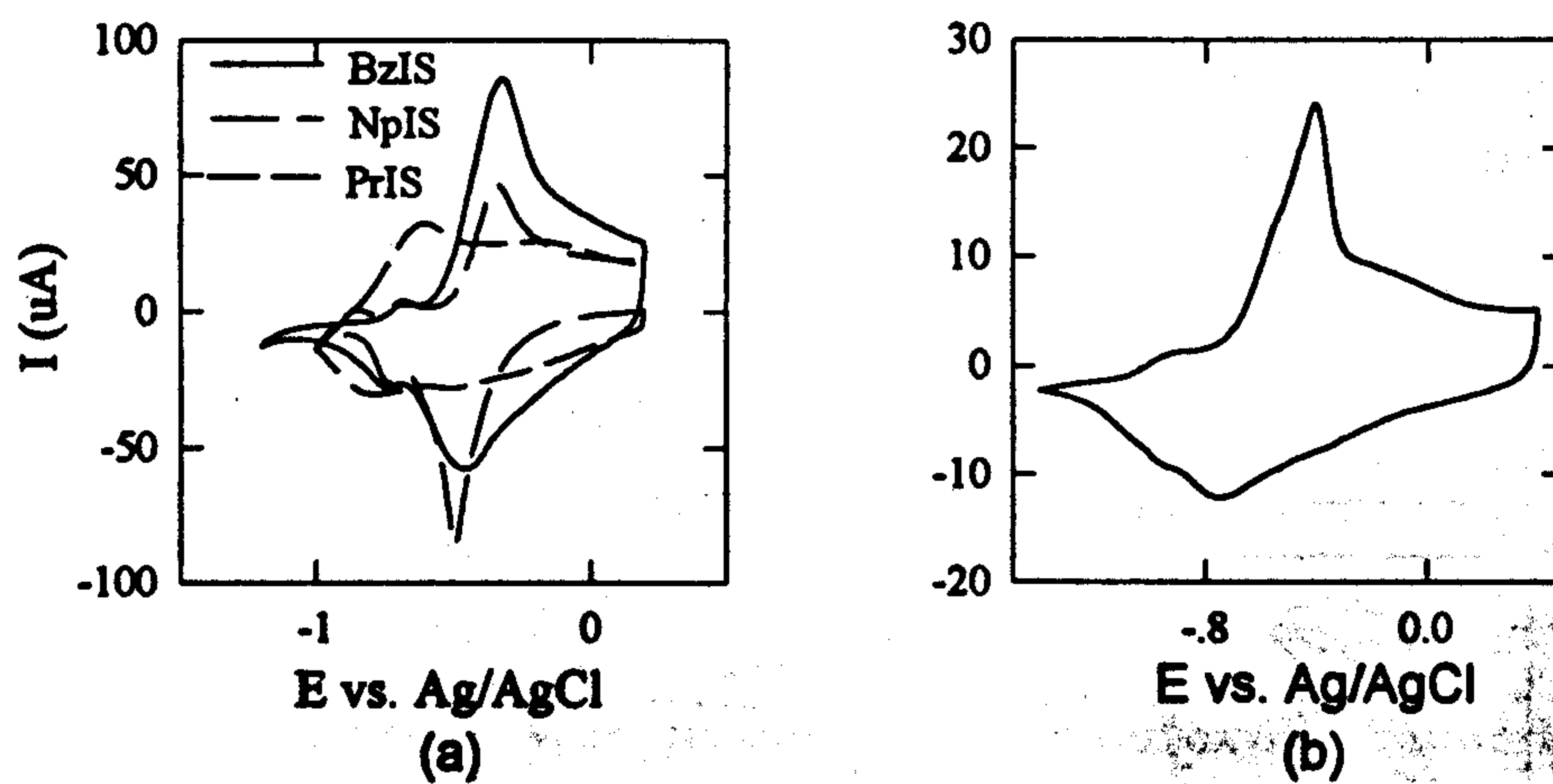


Fig. 2. Cyclic Voltammograms of (a) PPy/Imide sulfonate in 0.1 M NaClO<sub>4</sub> ( $v = 50$  mV/sec). (b) PPy/NpIS in 0.1 M TEAClO<sub>4</sub>/CH<sub>3</sub>CN ( $v = 20$  mV/sec).

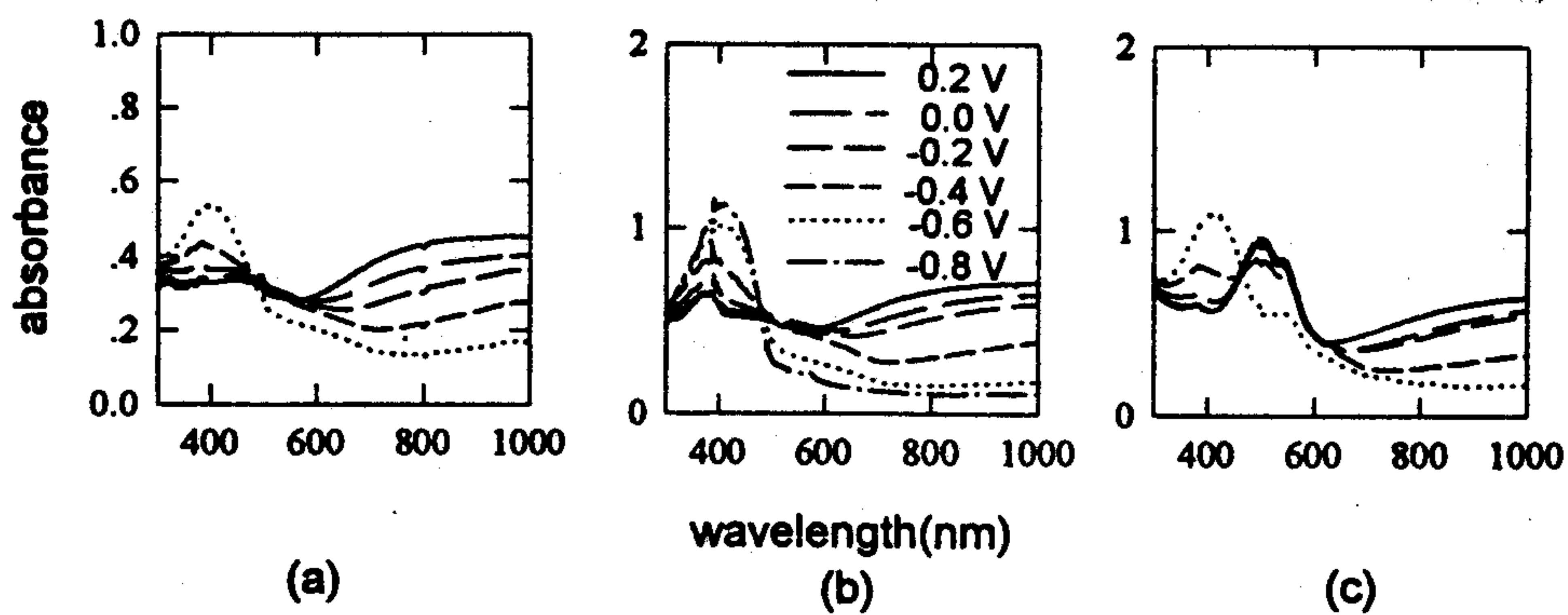


Fig. 3. UV/VIS spectra of (a) PPy/BzIS, (b) PPy/NpIS, and (c) PPy/PrIS in 0.1M LiClO<sub>4</sub> (0.5 $\mu$ m thick)

## CONCLUSION

Imide sulfonates show good redox reversibility in aqueous neutral solution. In acid solution NpIS and PrIS show redox reversibility in contrast to other organic multi-stage redox compounds. PPy/Imide sulfonate in aqueous solution show two-stage redox peaks superimposed on the redox currents of polypyrrole, during the redox reaction the imide sulfonate smear slowly out from the polypyrrole film. UV/VIS spectra indicate the incorporation of imide sulfonate into the polymer film.

The results presented here showed that a stable and reversible anion can be incorporated into a polypyrrole matrix. Further studies to evaluate the charge transport behavior of the imide anion in polypyrrole film is being conducted.

## REFERENCES

1. Bedioui, F.; Devynck, J. *Acc. Chem. Res.* **1995**, *28*, 30.
2. Deuchert, K.; Hunig, S. *Angew. Chem. Int. Ed.* **1978**, *17*, 875.
3. Zhong, C. J.; Kwan, W. S. V.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1423.
4. Viebeck, A.; Goldberg, M. J.; Kovac, C. A. *J. Electrochem. Soc.* **1990**, *137*, 1460.
5. Penneau, J.-F.; Stallman, B. J.; Kasai, P. H.; Miller, L. L. *Chem. Mater.* **1991**, *3*, 791.
6. Eggins, B. R. *J. Chem. Soc. Chem. Comm.* **1969**, 1267.
7. Son, Y.; Rajeshwar, K. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 605.