

# ELECTROSYNTHESIS AND CHARACTERIZATION OF CONDUCTING POLYPYRROLE DOPED WITH ALKYL SULFONATE ANION

K. ANUAR, A. A. HALIM, A. R. MOHD, ZAKI, Z. ZULKARNAIN, K. DZULKEFLI, A. B. B. NITA SALINA and  
H. N. M. E. MAHMUD.

(Received 19 August 2002; Revision accepted 9 October, 2002).

## ABSTRACT

The preparation of polypyrrole conducting polymer in aqueous medium by electrochemical method containing several alkylsulfonate dopants such as methylsulfonate ( $C_1$ ), butylsulfonate ( $C_4$ ), octylsulfonate ( $C_8$ ) and dodecylsulfonate ( $C_{12}$ ) are reported. The prepared polymer films were characterized by cyclic voltammetry, infrared spectroscopy, scanning electron microscopy (SEM) and elemental analysis. The conductivity of the prepared films was found to increase with the increase of carbon number of alkylsulfonate dopant. The results of Infrared and elemental analysis show that the alkylsulfonate dopants were incorporated in the polypyrrole structure. It has been observed from cyclic voltammetry analysis that lighter dopants produced more current suggesting that the movement of the dopants in and out of the polymer surface is much more flexible than that of the cases for heavier dopants.

**Keywords.** Conducting polymer, polypyrrole, alkylsulfonate dopant, electrochemical polymerization, cyclic Voltammetry.

## INTRODUCTION

The interest in the development of conducting polymers such as polyaniline, polypyrrole, polythiophene and polyphenylene has increased tremendously during the last decade because of their versatile promising applications in the field of energy storage (Novak et al., 1997; Mermilliod and Tanguy, 1986), bioelectrochemistry (Palmisano, 1997), organic electrochemistry (MacDiarmid, 2002), electrochemical capacitors (Belanger et al., 2000), sensors (Nicolas et al., 2001; Harris et al., 1997), electronic and optical devices (Potember et al., 1987), electrochromic devices (Gazotti et al., 1999), microsystem technologies (Gardner and Bartlett, 1995), ion-exchange membrane (Wang et al., 2001) and so on. Conducting polymers can be prepared by chemical or electrochemical polymerization (Toshima and Hara, 1995). The advantage of chemical synthesis is that it offers mass production at a reasonable cost. On the other hand, electrochemical method involves the direct formation of conducting polymers with better control of polymer film thickness and morphology, which are suitable for use in electronic devices. Different electrochemical techniques for the preparation of conducting polymers include potentiostatic (constant potential), galvanostatic

(constant current) and potentiodynamic (potential scanning i.e. cyclic voltammetry) methods.

Polypyrrole is by far the most extensively studied conducting polymer since the monomer pyrrole is easily oxidized, water soluble and commercially available. Hence, pyrrole offers several advantages such as environmental stability, good redox properties, and ability to give high electrical conductivity (Rodriguez et al., 1997).

Since the properties of the resultant films depends on a number of parameters such as the type of counter-ion, the type of solvent, their concentrations, pH, synthesis temperature, electrochemical voltage and mode of synthesis (Zhou and Heinze, 1999; Kassim et al., 1992; Kuwabata et al., 1987; Pernaut et al., 1989; Mitchell et al., 1988), research on the preparation and characterization of conducting polymers is still continuing. When the polymer is produced by the anodic oxidation of monomer, the doping anions are incorporated into the polymer, the nature of which is known to influence the properties of conducting polymers. During the electrochemical redox process, the small doping inorganic anions such as  $Cl^-$ ,  $ClO_4^-$  and  $NO_3^-$  are getting out of / into the film and their electrical conductivities are too small for commercial applications (Saunders et al., 1992).

✉ K. ANUAR, Department of Chemistry, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia  
A. A. HALIM, Department of Chemistry, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia  
A. R. MOHD, Department of Chemistry, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia  
ZAKI, Z. ZULKARNAIN, Department of Chemistry, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia  
K. DZULKEFLI, Department of Chemistry, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia  
A. B. B. NITA SALINA, Department of Chemistry, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia  
H. N. M. E. MAHMUD, Department of Chemistry, Universiti Putra Malaysia, 43400, Serdang, Selangor, Malaysia

**Table 1.** Conductivity of the produced ppy-alkylsulfonate films at 25 °C

Dopant anions	Carbon number	Concentration, M	Conductivity at 25 °C, S/cm
methylsulfonate	C <sub>1</sub>	0.1	0.62
butylsulfonate	C <sub>4</sub>	0.1	0.94
octylsulfonate	C <sub>8</sub>	0.1	1.38
dodecylsulfonate	C <sub>12</sub>	0.1	1.50

**Table 2.** Elemental analysis of ppy-alkylsulfonate films using various dopants

Polymer	%C	%H	%N	%S	%O	N/S (Mole ratio)
ppy-methylsulfonate	47.92	4.78	15.35	9.29	22.66	3.77/1
ppy-butylsulfonate	49.07	5.61	13.21	11.08	21.03	2.72/1
ppy-octylsulfonate	56.83	6.76	11.60	9.48	15.33	2.79/1
ppy-dodecylsulfonate	59.48	7.70	9.42	6.58	16.82	3.36/1

N/S = Nitrogen (polypyrrole)/sulphur (sulfonate)

On the other hand, bulky doping anions such as dodecyl sulfate (Pernaut et al., 1989) and p-phenol sulfonate (Kuwabata et al., 1990) are found not to move easily out of / into the film. In order to improve the conductivity and mechanical properties, research approaches have been made on using bulky organic sulfonate dopants (Kiani and Mitchell, 1992; Wernet et al., 1984; Cheung et al., 1990; Buckley et al., 1987; Takeoka et al., 1998; Bunting et al., 1997; Warren and Anderson, 1987) or preparing composites of polypyrrole with other polymers (Yan et al., 2001; Otero and Sansinena, 1996; Niwa and Tamamura, 1984).

Wernet et al. (1984) have conducted a research on a series of conducting polymers using several n-alkylsulfate and n-alkylsulfonate dopants and demonstrated some interesting structural and electrical properties of the conducting polymers. Apart from their work (Wernet et al., 1984), bearing a different research objective, and since it is suggested that the conductivity of the polypyrrole film is affected by

the kind of dopant anions in the film (Kuwabata et al., 1987; Cheung et al., 1990; Warren and Anderson, 1987; Buckley et al., 1987), our research interest is to seek a better understanding on the role of alkylsulfonate dopants on the electrical conductivity of the polypyrrole films prepared electrochemically in aqueous medium and share our findings on the redox behaviour of the conducting polymers studied by cyclic voltammetry. We have also characterized the conducting polymer films by scanning electron microscopy (SEM), FTIR and elemental analysis.

To this end, we have chosen a series of alkylsulfonate dopants with increasing number of carbon such as methylsulfonate (C<sub>1</sub>), butylsulfonate (C<sub>4</sub>), octylsulfonate (C<sub>8</sub>) and dodecylsulfonate (C<sub>12</sub>) to incorporate into polypyrrole film in aqueous medium following electrochemical method.

### Experimental

The polypyrrole (ppy) films doped with

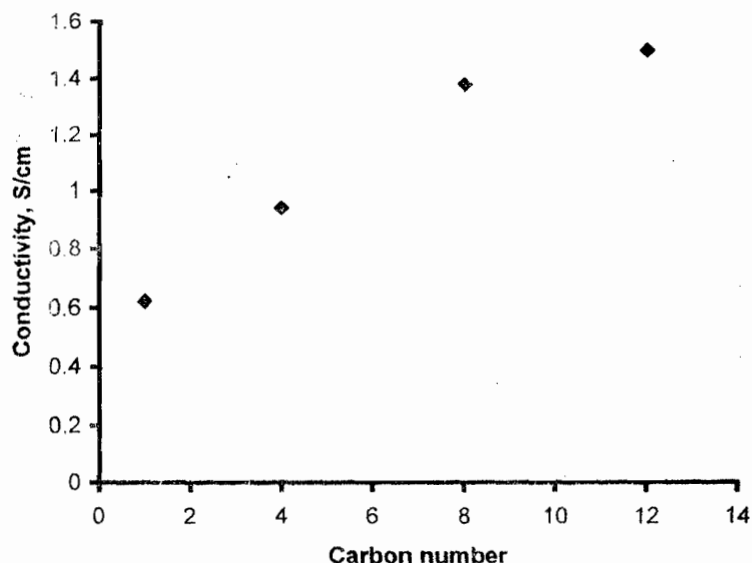
alkylsulfonate dopants used in the present investigation were electrochemically prepared by the oxidation of commercially available pyrrole (Fluka) monomer in its distilled form with various bulky aliphatic dopants. The various aliphatic sulfonated dopants used in this study were methanesulfonic acid sodium salt, 1-butanesulfonic acid sodium salt, 1-octanesulfonic acid sodium salt and 1-dodecanesulfonic acid sodium salt. All these chemicals were supplied by

Fluka. The electrochemical synthesis was carried out in a one-compartment cell using a potentiostat under computer control. An indium-tin-oxide (ITO) glass was used as the working electrode (anode) while a carbon rod was used as the counter electrode (cathode). The anodic potential of the working electrode was measured as 1.2 volt against a saturated calomel electrode

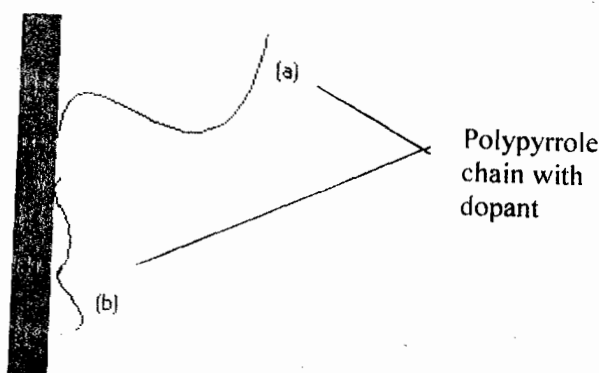
(SCE). The aqueous solution containing pyrrole of 0.2 M concentration and the dopant of 0.1 M concentration was electrochemically polymerized at 18 °C for 5 hours to form ppy-alkylsulfonate films of 0.1 mm thickness. The films thus produced on the ITO glass surface as an insoluble film were rinsed with purified water and then peeled off from the electrode.

#### Polymer characterization

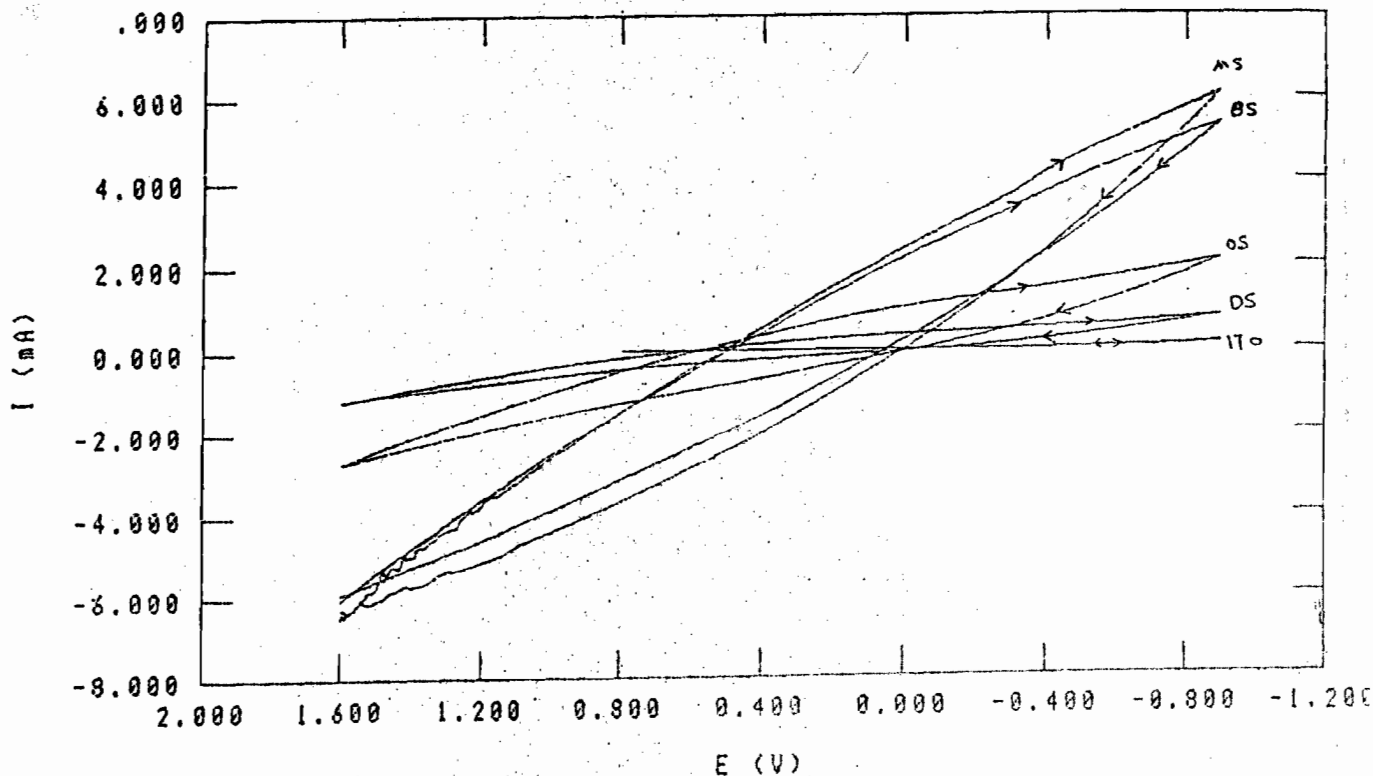
The PPy-alkylsulfonate films produced electrochemically in aqueous medium by using various alkylsulfonate dopants with varying carbon number such as methylsulfonate (C<sub>1</sub>), butylsulfonate (C<sub>4</sub>), octylsulfonate (C<sub>8</sub>) and dodecylsulfonate (C<sub>12</sub>) were characterized by cyclic voltammetry, scanning electron microscopy (SEM), FTIR spectroscopy and elemental



**Figure 1.** The correlation between the conductivity of the ppy-alkylsulfonate film and the number of carbon atoms of alkylsulfonate dopants in the film.



**Figure 2.** Schematic view of partially formed chains at the growth surface with (a) hydrophilic dopants and (b) hydrophobic dopants.



**Figure 3.** Cyclic voltammograms of polypyrrole containing various dopant anions and ITO glass (without polymer). Scans were performed in NaCl solution at a scan rate of 20 mV/s.

analysis. The conductivity of the prepared films was measured by the four-point method at 25 °C by taking the average value of five readings.

Cyclic voltammetry experiments were carried out using EG & G Princeton Applied Research (PAR) potentiostat. The working electrode was the ITO glass electrode and a Pt rod was the counter electrode and SCE was the reference electrode. Experiments were carried out in 0.1 M sodium chloride aqueous solution. The applied scanning speed was 20 mV/s and the potential range of scanning was from +1600 mV to -900 mV. The IR absorption spectra were recorded on Perkin Elmer FTIR Spectrophotometer. The elemental analysis of the polypyrrole films was done using Elementar Analysensysteme GmbH. The scanning electron microscopy (SEM) study was done by JEOL JSM-6400 microscope.

## RESULTS AND DISCUSSION

Pyrrrole monomer doped with several alkylsulfonates of 0.1 M solution in aqueous phase produced uniform ppy-alkylsulfonate films of about 0.10 mm thickness regardless of the

nature of dopants. The conductivity of the resulting polymer films with different dopant anions is presented in Table 1. The conductivity of the polymer films (at 25 °C) was found to increase with the increase of the carbon number of the dopants as shown in Figure 1. The probable explanation for this is that the alkyl group of the alkylsulfonate dopants is hydrophobic with respect to the aqueous electrolyte (Kassim et al., 1994). The sulfonate group in the alkylsulfonate dopant will be located preferentially adjacent to the pyrrole ring as it has been reported earlier for camphor sulfonate dopant (Kassim et al., 1994). Thus, the overall interaction for the polypyrrole chain and the hydrophobic part (alkyl group) of the dopant would tend to result in the continuous part of the chain 'depositing' upon the growth front (Figure 2). The shorter chain of the alkyl group present in the alkylsulfonate dopants is less hydrophobic than longer chain alkyl group. Thus, in our study, methylsulfonate dopant having shortest carbon chain provides a less hydrophobic surface to the polypyrrole chain, which in turn, allows the bulk chain growth away from the electrode surface resulting rather a thin layer of polypyrrole-

methylsulfonate film adjacent to the electrode. As a consequence, a low conductivity of polypyrrole-methylsulfonate film has been observed. The higher conductivity shown by dodecylsulfonate attributes to the dense formation of the chain growth along the electrode surface due to the more hydrophobic nature of dodecyl group (Figure 2) which favours the interaction of polypyrrole and the dodecyl group of the dopant rather than the interaction of polypyrrole and the aqueous electrolyte.

#### Cyclic voltammetry

Cyclic voltammetry is often used to characterize conducting polymer films. The oxidation and reduction can be monitored in the current-voltage diagram in cyclic voltammetry. In order to

compare the redox behaviour of the conducting polymers doped with various alkylsulfonate dopants, the cyclic voltammograms of PPy-alkylsulfonate films in 0.1 M NaCl solution, and that of ITO glass only (without polymer) in 0.1 M NaCl solution, are shown in Figure 3 by overlapping each other. The voltammograms were scanned from +1600 to -900 mV and were found varying in shape from smaller to large alkylsulfonate dopants. The broad shape of the voltammogram is associated with smaller alkylsulfonate i.e., methylsulfonate dopant while the narrow shape of the voltammogram is associated with long chain alkylsulfonate i.e., dodecylsulfonate dopant. The present observation is in good agreement with the results of other large organic sulfonate dopants (Kuwabata et al., 1990, Warren and Anderson,

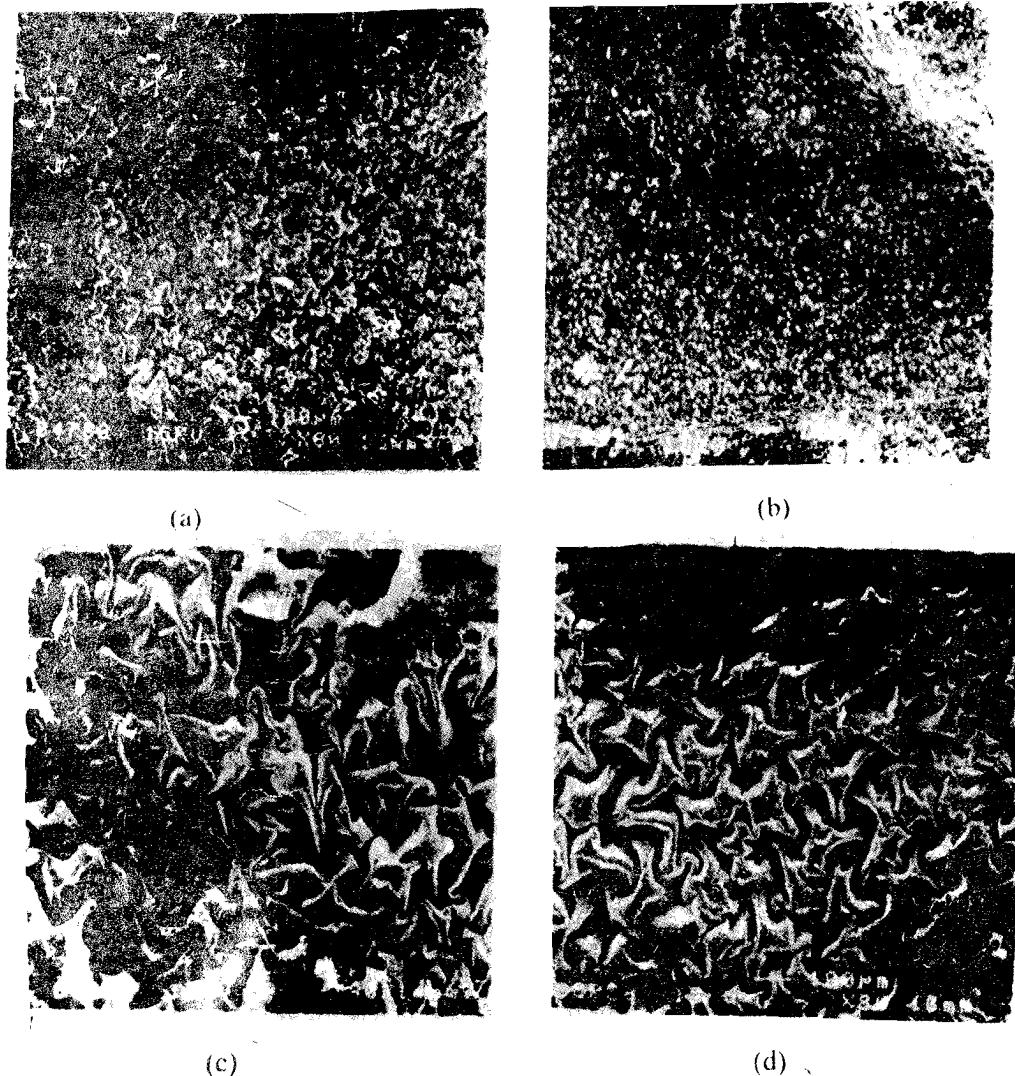
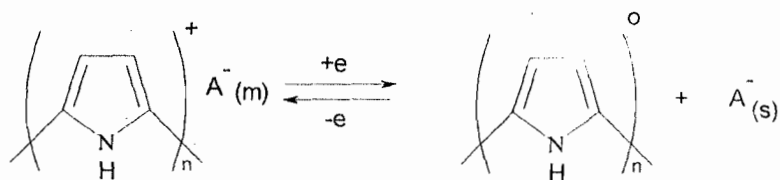


Figure 4. Scanning electron micrographs of polypyrrole incorporated in (a) methylsulfonate; (b) butylsulfonate; (c) octylsulfonate and (d) dodecylsulfonate.



.....Equation 1.

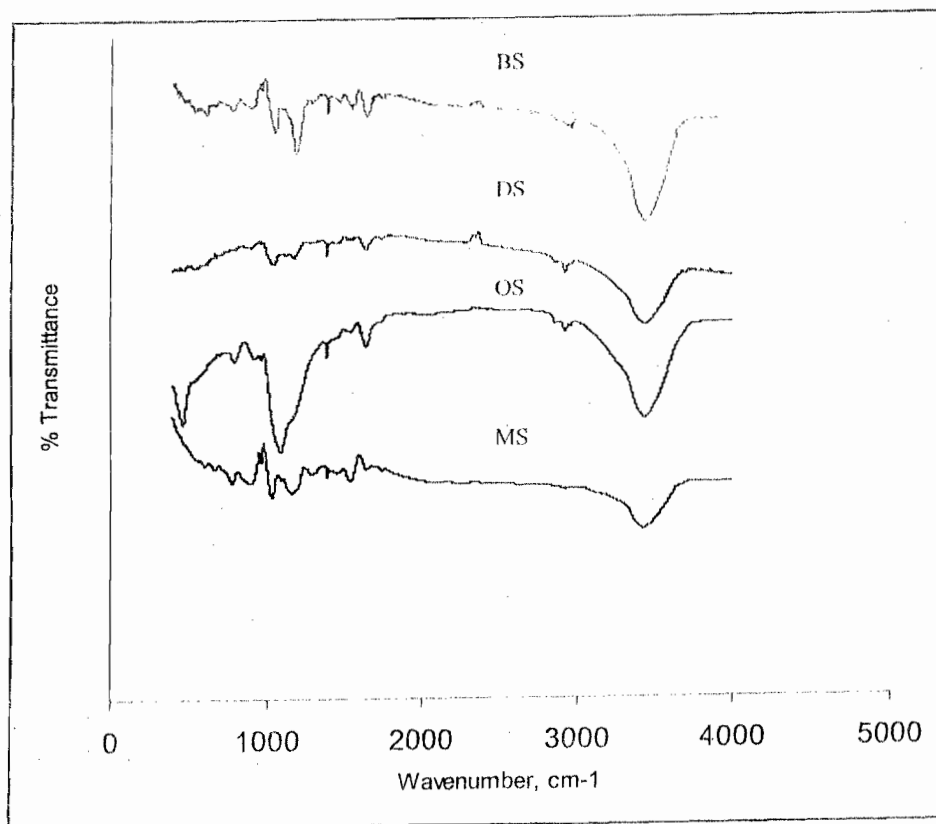
1987; Walton et al., 1992). It can be seen that at about +200 mV, there is very little current for long chain alkylsulfonate (dodecylsulfonate) dopant while there is more current associated with the curve for methylsulfonate dopant. It is clear from this observation that the transport of ions in and out of the polymer films is higher for short chain alkylsulfonate dopants while little movement of ions in and out of the films is associated with bulky long chain alkylsulfonate dopants. In the cyclic voltammogram (Figure 3), the process involves the dopant expulsion upon reduction and reincorporation upon oxidation, which is occurring according to equation 1.

In this equation,  $A^-(m)$  is the mobile dopant anion incorporated into the polymer and  $A^-(s)$  is the dopant anion expelled into the solution. In

Figure 3, the voltammogram for ITO glass only (without polymer), looks horizontal that corresponds to zero current, which suggests that the electrolyte NaCl did not interfere with the movements of dopants in the cyclic voltammograms of polypyrrole in NaCl electrolyte.

Scanning electron microscopy (SEM)

Scanning electron micrographs of all the prepared polymer films are shown in Figure 4. These micrographs indicate the difference in polymer morphology brought about by the presence of different dopant anions. The wrinkles in the micrographs can be seen getting bigger with the increase of the size from light (methylsulfonate,  $C_1$ ) to heavier dodecylsulfonate ( $C_{12}$ ) dopant.



**Figure 5.** IR-spectra of polypyrrole films using methylsulfonate (MS), butylsulfonate (BS), octylsulfonate (OS) and dodecylsulfonate (DS) dopants.

### Elemental analysis

The elemental analysis of the polypyrrole films using various alkylsulfonates as dopants has been presented in Table 2. It shows the mole ratio of pyrrole to dopant. This ratio is obtained by considering the fact that there is one nitrogen atom per pyrrole ring and one sulfur atom per sulfonated dopant.

From this elemental analysis it has been found that the mole ratio of pyrrole to dopant is 3.77/1 for ppy-methylsulfonate, 2.72/1 for ppy-butylsulfonate, 2.79/1 for ppy-octylsulfonate and 3.36/1 for ppy-dodecylsulfonate. It can be seen that for all these polypyrrole films doped by various alkylsulfonates, the mole ratios of pyrrole unit to dopant are close to 3 pyrrole/1 dopant unit which is well in agreement with the results obtained for long chain alkylsulfonate (Mitchell et al., 1988; Bunting et al., 1997).

### Infrared Absorption Spectra

The infrared absorption spectra of the polymer films using methylsulfonate, butylsulfonate, octylsulfonate and dodecylsulfonate dopants are shown in Figure 5. All the spectrum show a strong absorption band in the region 3438 - 3436  $\text{cm}^{-1}$  due to N-H stretching vibration. The C=C ring stretching vibration occurred in the region of 1636-1430  $\text{cm}^{-1}$ . Peaks near 1230, 1190, and 1130 correspond to the S-O stretching vibrations of sulfonate. Bands between 1100 and 1000  $\text{cm}^{-1}$  are all due to C-H vibrations. Bands near 2900 are due to  $-\text{CH}_2-$  group.

The IR-spectra of all these ppy-alkylsulfonate films show the characteristic polypyrrole absorption bands between 1650-1000  $\text{cm}^{-1}$  and the characteristic peak due to sulfonate near 1230-1130  $\text{cm}^{-1}$ , which confirm that the alkylsulfonates were incorporated in polypyrrole structure.

### CONCLUSIONS

In conclusion, we suggest that various alkylsulfonates with increasing carbon number can be used in aqueous solution for the preparation of polypyrrole conducting films by electrochemical polymerization of pyrrole. The hydrophobic nature of the long chain alkylsulfonate dopants with respect to aqueous electrolyte causes a more dense film formation along the electrode surface, which in turn offering a higher conductivity. The conductivity of the films thus was found to increase with the increase of carbon number of the dopants. The major peaks of all the IR-spectra of ppy-alkylsulfonate films

showed the various characteristic polypyrrole absorption bands and the bands for sulfonate, which confirm that the alkylsulfonates were incorporated in polypyrrole structure. From the elemental analysis it has been found that the mole ratios of pyrrole to alkylsulfonate are close to 3 pyrrole/1 dopant unit which also suggests that the various alkylsulfonates were successfully incorporated in the polypyrrole structure. The cyclic voltammetry analysis shows that lighter short chain dopants produced more current suggesting that the movement of the dopants in and out of the polymer surface is much more flexible than that of the cases for long chain dopants.

### ACKNOWLEDGMENT

The financial support (IRPA-fund No. 09-02-04-0109) from the Ministry of Science & Technology Government of Malaysia, is gratefully acknowledged.

### REFERENCES

- Belanger, D.; Ren, X.; Davey, J.; Uribe, F.; Gottesfeld, S.; 2000. Characterization and long-term performance of polyaniline-based electrochemical capacitors", *J. Electrochem. Soc.*, 147: 2923-2929.
- Buckley, L. J.; Roylance, D. K. and Wnek, G. E.; 1987. Influence of dopant ion and synthesis variables on mechanical properties of polypyrrole films, *J. Polym. Sci., Part B: Polym. Phys.*, 25: 2179.
- Bunting, R. K., Swarat, K. and Yan, D.; 1997. Synthesis and characterization of a conducting polymer: An electrochemical experiment for general chemistry", *J. Chem. Edu.*, 74(4): 421.
- Cheung, K. M., Bloor, D. and Stevens, G. C.; 1990. The influence of unusual counterions on the electrochemistry and physical properties of polypyrrole, *J. Mat. Sci.*, 25: 3814-3837.
- Gardner, J. W.; Bartlett, P. N.; 1995. Application of conducting polymer technology in microsystems, *Sensors and Actuators A*, 51: 57-66.
- Gazotti, W. A.; Casalbore-Miceli, G.; Mitzakoff, S.; Geri, A.; Gallazzi, M. C. and DePaoli, M. A.; 1999. Conducting polymer blends as electrochromic materials. *Electrochim Acta*, 44(12): 1965-1971.
- Harris, P. D.; Arnold, W. M.; Andrews, M. K.; Partridge, A. C.; 1997. Resistance characteristics of conducting polymer films used in gas sensors, *Sensors and Actuators B*, 42: 177-184.

- Kassim, A.; Davis, F. J. and Mitchell, G. R.; 1994. The role of the counter-ion during electropolymerization of polypyrrole-camphor sulfonate films, *Synth. Met.*, 62: 41-47.
- Kassim, A.; Block, H.; Davis, F. J. and Mitchell, G. R.; 1992. Anisotropic films of polypyrrole formed electrochemically using a non-planar dopant, *J. Mat. Chem.*; 2 (9): 987-988.
- Kiani, M. S. and Mitchell, G. R.; 1992. The role of the counter-ion in the preparation of polypyrrole films with enhanced properties using a pulsed electrochemical potential, *Synth. Met.*, 48, 203-218.
- Kuwabata, S.; Okamoto, K.; Ikeda, O. and Yoneyama, H.; 1987. Effect of organic dopants on electrical conductivity of polypyrrole films, *Synth. Met.*, 18, 101-104.
- Kuwabata, S.; Nakamura, J. and Yoneyama, H.; 1990. Dependence of conductivity of polypyrrole film doped with p-phenol sulfonate on solution pH", *J. Electrochem. Soc.*, 137(7): 2147-2150.
- MacDiarmid, A. G.; 2002. Synthetic metals: a novel role for organic polymers, *Synthetic Metals*, 125: 11-22.
- Mermilliod, N. and Tanguy, J.; 1986. A study of chemically synthesized polypyrrole as electrode material for battery applications", *J. Electrochem. Soc.*, 133(6): 1073-1079.
- Mitchell, G. R., Davis, F. J. and Legge, C. H., 1988. The effect of dopant molecules on the molecular order of electrically-conducting films of polypyrrole, *Synth. Met.*, 26: 246-257.
- Nicolas, M.; Fabre, B. and Simonet, J.; 2001. Electrochemical sensing of F- and Cl- with a boric ester-functionalized polypyrrole, *J. Electroanal. Chem.*, 509, 1.
- Niwa, O. and Tamamura, T.; 1984. Electrochemical polymerization of pyrrole on polymer-coated electrodes, *J. Chem. Soc., Chem. Commun.*, 470: 817-818.
- Warren, L. F. and Anderson, D. P., 1987. Polypyrrole films from aqueous electrolytes: The effect of anions upon order, *J. Electrochem. Soc.*, 134(1): 101.
- Wernet, W.; Monkenbusch, M. and Wegner, G.; 1984. A new series of conducting polymers with layered structure: polypyrrole n-alkylsulfates and n-alkylsulfonates, *Makromol. Chem., Rapid Commun.*, 5: 157-164.
- Yan, F., Xue, G., Chen, J., and Lu, Y., 2001. Preparation of a conducting polymer/ferromagnet composite film by anodic-oxidation method, *Synth. Met.*, 123(1): 17-20.
- Zhou, M. and Heinze, J.; 1999. Electropolymerization of pyrrole and electrochemical study of polypyrrole: 1. Evidence for structural diversity of polypyrrole, *Electrochim. Acta*, 44, 1733-1748.
- Otero, T. F. and Sansinena, J. M., 1996. Influence of synthesis conditions on polypyrrole-poly(styrenesulphonate) composite electroactivity, *J. Electroanal. Chem.*, 412, 109-116.
- Palmisano, F.; De Benedetto, G. E. and Zamboni, C. G.; 1997. Lactate amperometric biosensor based on an electrosynthesized bilayers film with covalently immobilized enzyme", *Analyst*, 122: 365-369.
- Pernaut, J. M., Peres, R. C. D.; Juliano, V. F. and De Paoli, M. A.; 1989. Electrochemical study of polypyrrole/dodecyl sulphate, *J. Electroanal. Chem.*, 274, 225.
- Potember, R. S., Hoffman, R. C., Hu, H. S., Cocchiari, J. E., Viands, C. A., Murphy, R. A. and Poehler, T. O., 1987. Conducting organics and polymers for electronic and optical devices, *Polymer*, 28, 574-580.
- Rodriguez, J.; Grande, H. J. and Otero, T. F.; 1997. In: Salwa, H. S. (Editor), *Handbook of Organic Conductive Molecules and Polymers*. New York: John Wiley & Sons, 415.
- Saunders, B. R., Murray, K. S., and Fleming, R. J., 1992. Physical properties of polypyrrole films containing sulfonated metallophthalocyanine anions", *Synth. Met.*, 47, 167-178.
- Takeoka, S.; Hara, T.; Fukushima, K.; Yamamoto, K. and Tsuchida, E.; 1998. Antioxidative dopant for thermal-resisting polypyrrole and its mechanism", *Bull. Chem. Soc. Jpn.*, 71(6): 1471-1476.
- Toshima, N. and Hara, S.; 1995. Direct synthesis of conducting polymers from simple monomers, *Prog. Polym. Sci.*, 20: 155-183.
- Walton, D. J.; Hall, C. E. and Chyla, A.; 1992. Characterization of poly(pyrroles) by cyclic voltammetry, *Analyst*, 117: 1305-1311.
- Wang, L.; Li, X. and Yang, Y.; 2001. "Preparation, properties and applications of polypyrroles". *Reactive and Functional Polymers*, 47(2): 125-139.