JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 212–216

Characterization of polypyrrole films incorporating various anions

HECAI SUN

Department of Chemistry, Suzhou University, Suzhou, P.R. China

BIANTING SUN*

School of Chemistry, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

Received 27 June 1991; revised 2 January 1992

The conductivity of polypyrrole films has been enhanced by electrochemical post-deposition doping with various anions. The change of conductivity was found to depend on the type and concentration of the anion. Results for the polypyrrole films doped with anions of H_2SO_4, $(C_2H_5)_4N(O_3SC_6H_4CH_3)$, KI, $CH_3C_6H_4SO_3H \cdot H_2O$ (*p*-toluene sulphonic acid monohydrate), $AlCl_3$, $KBrO_3$ and HNO_3 showed that in the case of H_2SO_4, $(C_2H_5)_4N(O_3SC_6H_4CH_3)$ and $CH_3C_6H_4SO_3H \cdot H_2O$ the conductivity can be enhanced by up to a factor of two, from a value of $67\,S\,cm^{-1}$ up to 165, 102 and $95\,S\,cm^{-1}$, respectively. Doping with I^- had a negligible effect on the conductivity which was about $71\,S\,cm^{-1}$, while in the case of $AlCl_3$, $KBrO_3$ and HNO_3 the conductivity of the polypyrrole decreased significantly for certain anion concentrations.

1. Introduction

Polypyrrole prepared by electrochemical methods is characterized not only by its high conductivity, but also by its stability [1]. In order to improve its properties for a wider range of applications, doping of the polymer films by incorporation of electrochemically active species (including catalysts) is attractive for producing improved electrode materials [2].

Diaz *et al.* reported that the wide variation in conductivity of the polypyrrole films grown in various electrolytes was due primarily to the nature of the anion of the electrolyte in the polymer [3], and that modification by introducing substituents into the cationic pyrrole polymer or by varying the accompanying anion, resulted in significant changes in the electrochemical and conducting properties of the films [4]. Chemical modification of a polypyrrole electrode surface was reported by Diaz *et al.* [5]. A change in the cyclic voltammetric behaviour of the electrode in acetonitrile solution of 0.1 M Et_4NBF_4 was observed after treatment with 1 : 4 nitric acid/acetic anhydride at 0 °C. The conductivity of polypyrrole films was found to be affected by acid and base treatment due to an ion-exchange of the dopants in the polymer with the acid radical anion or hydroxide ion [6–10]. Polypyrrole films are very sensitive to the presence of hydroxide ion.

In a recent study, we further investigated the influence of electrochemical doping on the conductivity of polypyrrole films. It was found that the conductivity of polypyrrole was dramatically changed if charged negative species were electrochemically doped into polypyrrole in the oxidized state. In the present study, the effect of electrochemical post-deposition doping of polypyrrole films by several anion species has been investigated. The effect of anion type and concentration on the conductivity of the films has been studied and will be discussed.

2. Experimental details

A Pyrex U-tube (10 cm × 2.5 cm) was employed as the electrochemical cell, a square polypyrrole film (2 cm × 2 cm, Lutamer West Germany) as anode, and a copper plate of the same area as cathode. Solutions of various concentrations H_2SO_4 (AJAX Chemicals, Australia), $(C_2H_5)_4N(O_3SC_6H_4CH_3)$ (Aldrich Chemical Company, Inc. USA), $CH_3C_6H_4SO_3H \cdot H_2O$ (Aldrich Chemical Company, Inc. USA), KI (AJAX Chemical, Australia), $AlCl_3$ (May & Baker Ltd, Dagenham, England), $KBrO_3$ (AJAX Chemicals Ltd. Sydney–Melbourne, Australia) and HNO_3 (May & Baker Australia Pty, Ltd) were employed as electrolytes. The experiments were carried out at room temperature and at a constant voltage of 3.0 V. A constant doping time of 1 h was selected so as to conveniently compare the influence of various dopants on the conductivity of the polypyrrole films. After the electrochemical doping process, the polypyrrole films were washed with distilled water and then vacuum dried at room temperature. The four-probe technique using the Van Der

---

* Author to whom all correspondence should be addressed.

0021-891X

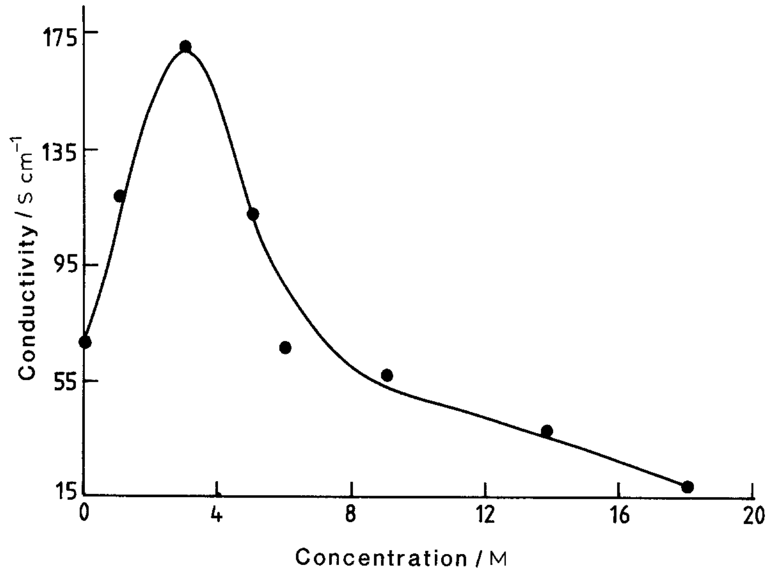

Fig. 1. The influence of H_2SO_4 concentration on the conductivity of the polypyrrole film.

Pauw method was employed to measure the conductivity of the polypyrrole films [11].

3. Results and discussion

Figs 1, 2 and 3 show the change of conductivity of the polypyrrole modified by sulphuric acid, tetraethyl ammonium *p*-toluene sulphonate and potassium iodide, respectively, with dopant concentration. It can be seen that the figures exhibit a similar trend with regard to the influence of the three dopants on the conductivity of the polypyrrole, the conductivity being initially enhanced with increasing electrolyte concentration. The values of conductivity reach a maximum value for dopant concentrations of 3 M for H_2SO_4, 0.15 M for $(C_2H_5)_4N(O_3SC_6H_4CH_3)$ and 0.5 M for KI, the peak values of conductivity being 165, 102 and 71 S cm^{-1}, respectively. Beyond the peak values, the conductivity of polymer is seen to decrease with increasing electrolyte concentration. In the case of *p*-toluene sulphonic acid doping, however, an increase in the conductivity of the polypyrrole is observed with increasing dopant concentration as shown in Fig. 4. The highest conductivity value of 94 S cm^{-1} was obtained at a concentration of 1.2 M. Due to the limited solubility of the electrolyte, the maximum concentration of $CH_3CH_4SO_3H \cdot H_2O$ employed was 1.2 M.

When aluminium chloride, potassium bromate and nitric acid were used as dopants, the conductivity of polypyrrole films was seen to decrease as shown in Figs 5, 6 and 7. The difference among the three is that the conductivity of the polypyrrole is much more sensitive to $AlCl_3$ than to $KBrO_3$ or HNO_3. The conductivity dropped dramatically for the first dopant dopant concentration change of 0.15 M $AlCl_3$, and then levelled off. The conductivity of the polypyrrole film treated with HNO_3 decreased linearly with

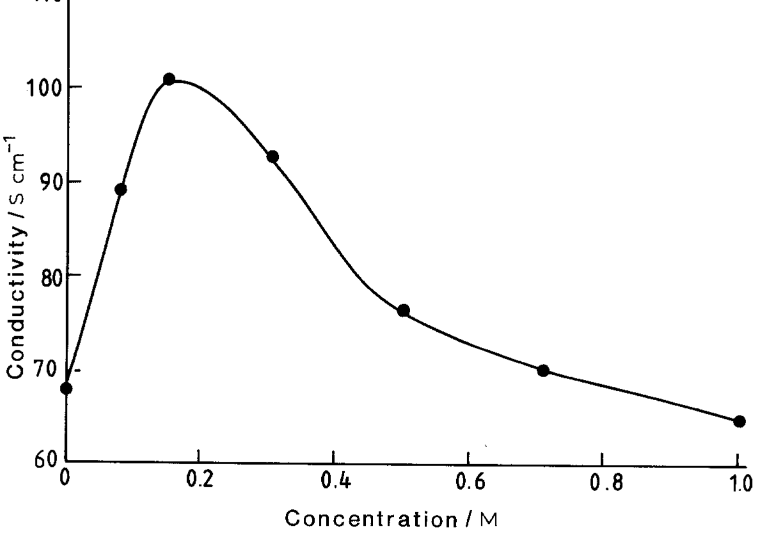

Fig. 2. The influence of $(C_2H_5)_4N(O_3SC_6H_4CH_3)$ concentration on the conductivity of polypyrrole film.

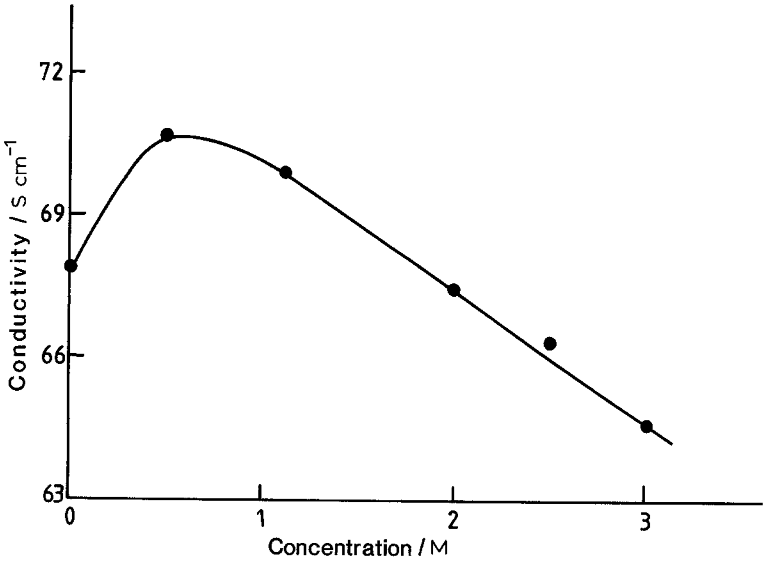

Fig. 3. The influence of KI concentration on the conductivity of the polypyrrole film.

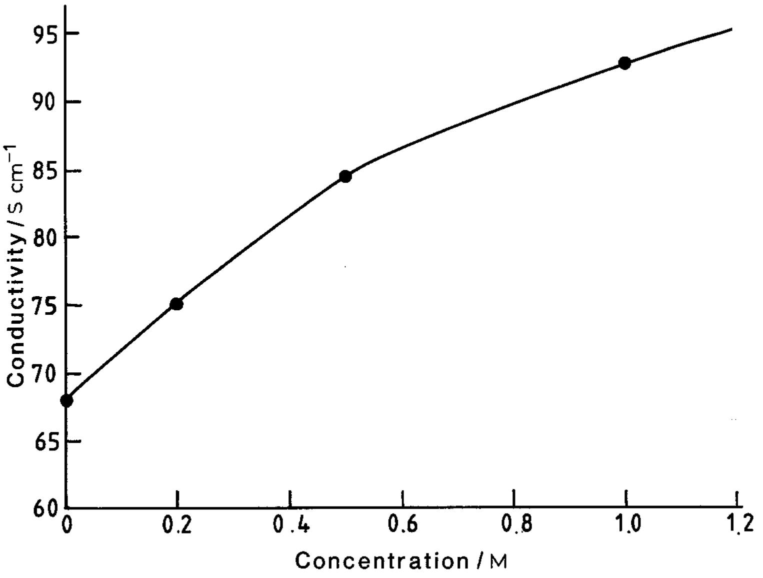

Fig. 4. The influence of $CH_3C_6H_4SO_3H \cdot H_2O$ concentration on the conductivity of the polypyrrole film.

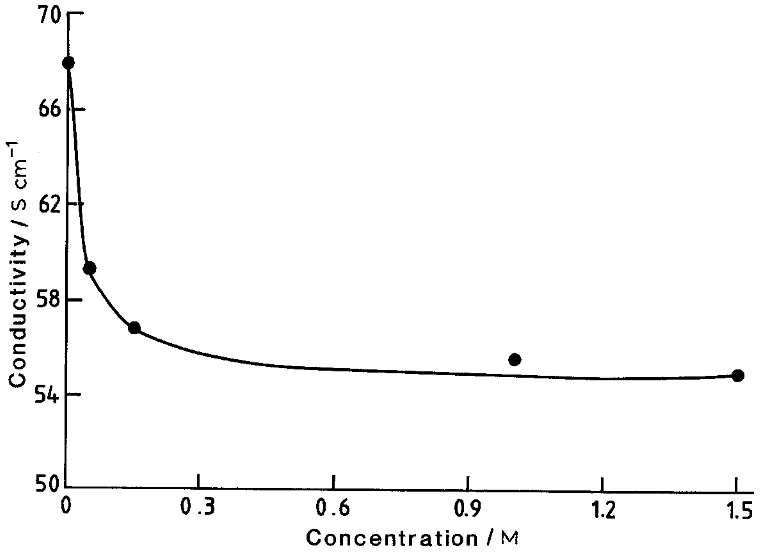

Fig. 5. The influence of $AlCl_3$ concentration on the conductivity of the polypyrrole film.

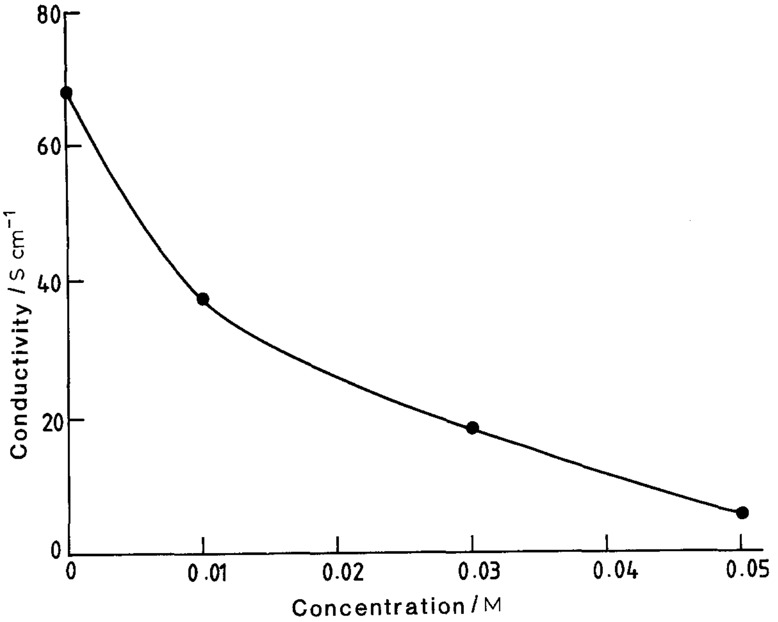

Fig. 6. The influence of $KBrO_3$ concentration on the conductivity of the polypyrrole film.

increasing dopant concentration, dropping to 0 S cm^{-1} at a concentration of 2 M HNO_3.

The influence of the dopants on the conductivity of the polypyrrole films is probably associated with the valence of the anions incorporated in the films and the interaction between the polypyrrole films and the dopant. Because of the large π conjugation system of the charged positive polypyrrole film and the electron donor properties of the doped anion species, $(FG)^{n-} \rightarrow PPyr^{n+}$ interactions are likely. If a stable and favourable chemical micro-environment for the $(FG)^{n-}$ between the anion incorporated, $(FG)^{n-}$ and the polypyrrole films exists, the following hypothesis may be proposed: (i) The higher the value of n, the more stable the chemical micro-environment. (ii) The chemical donor–acceptor model proposed by Gutmann *et al.* [12] can be applied to the $(FG)^{n-}$-polypyrrole film, i.e. there is a chemical donor–acceptor interaction between $(FG)^{n-}$ and the polypyrrole film. The charged positive polypyrrole with its large π conjugate system is the electron acceptor and $(FG)^{n-}$ behaves as an electron donor, so that the $(FG)^{n-} \rightarrow PPyr^{+}$ can be hypothesized. (iii) Bredas *et al.* [13], using quantum chemistry calculations, proposed that the nitrogen atom in polypyrrole is not only a strong π donor (−0.35 eV), but also a stronger σ acceptor (0.66 eV). If the nature of the electron donor is considered, then the greater the value of n, the stronger the interaction between $(FG)^{n-}$ and $PPyr^{+}$. The experimental observations may be explained by this basic hypothesis because the interaction is favourable with regard to electrostatic effects as well as for the hypothetical chemical mode.

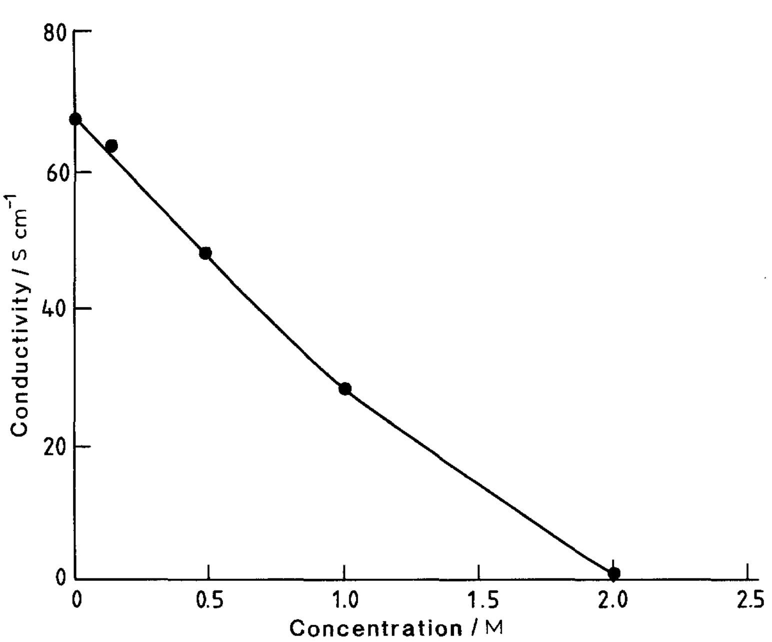

Fig. 7. The influence of HNO_3 concentration on the conductivity of the polypyrrole film.

For dopant concentrations of 3 M, 0.15 M and 0.5 M for H_2SO_4, $(C_2H_5)_4N(O_3SC_6H_4CH_3)$ and KI, respectively, the conductivity peak value of polypyrrole is closely related to the model structure of the $(FG)^{n+} \rightarrow PPyr^+$ because the polypyrrole film with its N atoms of the strong σ, accept electrons of the anion donor so that the electrons of the overall system can be freely conducted. However, when the concentration of H_2SO_4 and $(C_2H_5)_4N(O_3SC_6H_4CH_3)$ is further increased, the extent of oxidation and halogenation increases, thus, the chains in the polymer are probably oxidized and halogenated so that conductivity of the polypyrrole film drops. The reason for the decreasing conductivity of the polypyrrole film with increasing dopant concentration, $AlCl_3$, $KBrO_3$ and HNO_3, is believed to be due to an oxidation–reduction reaction between the polypyrrole film and the dopants so that the polypyrrole chains are halogenated or oxidized, thus increasing the film resistance.

4. Conclusion

The conductivity of electrochemically doped polypyrrole films is affected by the type and concentration of dopant. The dopants, H_2SO_4, $(C_2H_5)_4N(O_3SC_6H_4CH_3)$, KI and $CH_3C_6H_4SO_3H \cdot H_2O$, initially caused an increase in the conductivity of the film, but beyond a certain dopant concentration, the conductivity decreased. When the polypyrrole films were doped with $AlCl_3$, $KBrO_3$ and HNO_3, however, the conductivity of the film decreased with increasing dopant concentration.

The conductivity obtained depends not only on a suitable dopant which causes a stable chemical microenvironment between the $(FG)^{n-}$ and polypyrrole film, but also on the concentration of the dopants. The change in the conductivity of the polypyrrole film, also depends on the extent of chain orientation and cross linking in the polymer after doping.

Acknowledgements

Authors would like to thank Associate Professor M. Skyllas-Kazacos, the School of Chemical Engineering and Industrial Chemistry, University of New South Wales, Australia for her valuable guidance and support in this study.

References

[1] (a) A. F. Diaz, J. I. Castillo, A. J. Logan and W. Y. Lee, *J. Electronal. Chem.* **129** (1981) 115; (b) Bianting Sun, J. J. Jones, R. P. Burford and M. Skyllas-Kazacos, *J. Electrochem. Soc.* **136** (1989) 698.

[2] R. A. Bull, F. R. Fan and A. J. Bord, *J. Electrochem. Soc.* **131** (1984) 687.

[3] A. F. Diaz and K. K. Kanazawa, *in* 'Extended Linear Chain Compound', Vol. 3, (edited by J. S. Miller), Plenum Press, New York (1983) 417.

[4] M. Salmon, A. F. Diaz, A. J. Logan, M. Krounbi and J. Bargon, *Mol. Cryst. Liq. Cryst.* **3** (1982) 265.

[5] A. F. Diaz, Wen-Yang Lee, A. Logan and D. C. Green, *J. Electroanal. Chem.* **108** (1980) 377.

[6] A. F. Diaz, J. M. Vallejo and A. M. Duran, *IBM. J. Res. Develop.* **25** (1981) 42.

[7] H. Münstedt, *Polymer* **27** (1986) 899.

[8] H. Münstedt, H. Naarmann, G. Köhler, *Mol. Cryst. Liq. Cryst.* **118** (1985) 129.

[9] O. Inganäs, R. Erlandssan, C. Nylander and I. Lundström, *J. Phys. Chem. Solids* **45**(45) (1984) 427.

[10] Bianting Sun, J. J. Jones, R. P. Burford and M. Skylas-Kazacos, *J. Mater. Sci.* **24** (1989) 4024.

[11] A.R. Blythe, *Polym. Testing* **4** (1984) 195.

[12] V. Gutmann, G. Gritzner and K. Danksagmüller, *Inorg. Chem. Acta* **17** (1976) 81.

[13] J. L. Bredas, B. Themans, J. G. Frepiat, J. M. Andre, R. R. Chace, *Phys. Rew. B. Condens. Matter* **29**(12) (1984) 6761.