Conducting polyphenylquinoxaline

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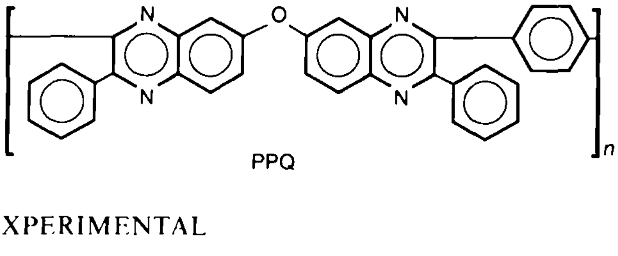
This paper first reports the preparation of conducting polyphenylquinoxaline (PPQ) film in polymer solution by means of potentiostatic oxidation. The conductivities of the conducting PPQ films vary from 10^{-7} to 10^{-12} S cm^{-1} depending on dopant anions. The structure of the conducting PPQ with different dopant anions was confirmed by infra-red and X-ray photoelectron spectroscopy. It is interesting to note that the conducting PPQ films are highly sensitive to moisture in air, and hydration and dehydration are accompanied by a reversible change in colour. Electronic spectra and morphology of the conducting PPQ films were also studied.

(Keywords: polyphenylquinoxaline; electrochemical oxidation; electrical conductivity)

INTRODUCTION

Since 1977 when the electrical conductivity of polyacetylene was first published, a lot of work has been devoted to the synthesis of new organic conducting or semiconducting materials. A new development in the field of electrically conducting polymers is the emergence of conducting, soluble and high-temperature polymers as a class of materials. Many of these polymers possess molecular order due to their rigid, planar, ladder or stepladder chain structure. These polymers, which are normally excellent electrical insulators, can be converted into conducting materials by chemical or electrochemical oxidation or reduction during doping[1-3].

Polyphenylquinoxaline possesses a stepladder structure and exhibits good thermal stability, electrical insulation and chemical resistance. It possesses good processing characteristics[4,5] and has unique applications in the aerospace and electronics industries. This paper reports for the first time that polyphenylquinoxaline (PPQ) can be made conductive by the use of an electrochemical oxidation method. The conductivities of the conducting PPQ films vary from 10^{-7} to 10^{-12} S cm^{-1} depending on dopant anions. The structure of the conducting PPQ was characterized. The results of this study are described below.



PPQ

EXPERIMENTAL

Preparation of materials

PPQ was prepared according to the literature[4] and supporting electrolytes Et_4NClO_4, Bu_4NAsF_6, Et_4NBF_4 and Bu_4NPF_6 were synthesized and purified following a known procedure[6].

Electrochemical oxidation

This was carried out for PPQ in 1,1,2,2-tetrahcloroethane (TCE) in the presence of supporting electrolytes by means of controlled potential electrolysis using a two-electrode system. Both the working and counter-electrode were platinum-plate electrodes, each with an area of 1.0×4.5 cm^2. Before electrolysis, 0.30 mmol of PPQ was dissolved in a mixture of 10 ml TCE and 0.16 mmol of supporting electrolyte and then the solution was kept at constant voltage ~20 V. When the potential was applied, a red film began to deposit on the anode and its thickness increased gradually with increasing time. When the electrolysis was stopped after an approximate time (1–2 h), the film that had deposited on the electrode was washed with chloroform and dried in vacuum. Then the film was stripped from the electrode. The red film changes into yellow as soon as it is exposed in air. The yellow films of PPQ(ClO_4^-), PPQ(AsF_6^-) and PPQ(BF_4^-) turn red again when placed back in vacuum, in silica gel desiccator or upon heating to 80–120°C in air. This change in colour is reversible.

Conductivity measurements

The oxidized PPQ films were compacted under a pressure of 70 kg cm^{-2} to form a dense film for conductivity measurements. The d.c. conductivity was measured by means of a TR 8401 Vibrating Reed Electrometer (Takeda Riken) to determine the voltage drop across a reference resistance in a series d.c. circuit.

Characterization

I.r. and u.v.-vis. spectra of doped and undoped PPQs were obtained with KBr powder compacts. The i.r. spectra of these samples were recorded using a Bruker IFS 11-3V type i.r. spectrometer. The u.v.-vis. spectra of these samples were recorded on a Hitachi 340 spectrophotometer. X.p.s. data were obtained on a Kratos model ES-300X photoelectron spectrophotometer, excited by Mg K_α X-rays ($E_X = 1235.6$ eV). The C_{1s} peak from impurity carbon was used for binding energy calibration (285.0 eV). SEM photographs of the samples were obtained using a Hitachi S-530 scanning electron microscope.

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RESULTS AND DISCUSSION

Structure

Electrochemical doping of polymer in solution by means of potentiostatic anodic oxidation is a new method for preparing conducting polymers. We are the first to have prepared conducting PPQ films with different dopant anions by this technique. The i.r. spectra of the conducting PPQ show the same bands at 3055, 1605, 1475, 1340, 1202 and 695 cm^{-1} as undoped PPQ and the characteristic absorption of the dopant anions (*Figure 1*). The bands at 1088 and 624 cm^{-1} of conducting PPQ film obtained in PPQ–Et_4NClO_4–TCE solution are characteristic of ClO_4^- ion (*Figure 1b*). These bands are replaced by new ones at 707 cm^{-1} (*Figure 1c*), 1060 cm^{-1} (*Figure 1d*) or 824 cm^{-1} (*Figure 1e*) corresponding to AsF_6^-, BF_4^- or PF_6^- ion respectively, if Bu_4NAsF_6, Et_4NBF_4 or Bu_4NPF_6 are used instead of Et_4NClO_4. The i.r. spectra of conducting PPQ films show the same absorption as PPQ and in all cases dopant anions, ClO_4^-, AsF_6^-, BF_4^- or PF_6^- are present. This means that the structure of conducting PPQ is similar to undoped PPQ, but there are positive charges in the polymer chain.

X.p.s. of the doped and undoped PPQ are compared in an attempt to identify the primary site of polymer–dopant interactions. As shown in *Figure 2* in PPQ(ClO_4^-) the N_{1s} binding energy for most nitrogen atoms increases from 399.3 to 402.0 eV, which is ascribable to the nitrogen cation. The peak of Cl_{2p} (207.5 eV) confirms the presence of ClO_4^- ion in the PPQ(ClO_4^-). The fact that the binding energy of carbon and oxygen does not change indicates that they remain unchanged. It follows that the positive charges are located on the nitrogen atom in PPQ(ClO_4^-) film, and the dopant anion ClO_4^- is present. The same conclusion can also be obtained from the X.p.s. results of PPQ(AsF_6^-), PPQ(BF_4^-) and PPQ(PF_6^-) (*Table 1*). It is found that the area of the nitrogen cation peak relative to that of the nitrogen peak of conducting PPQ film varies with dopant anions (*Figure 3*). That is, the oxidation state of the nitrogen atom in conducting PPQ films is different with different dopant anions. The oxidation state of nitrogen in PPQ(ClO_4^-) is highest in the conducting PPQ films, and PPQ(PF_6^-) is the lowest. The oxidation state of the conducting PPQs change in the following order: PPQ(ClO_4^-) > PPQ(AsF_6^-) > PPQ(BF_4^-) > PPQ(PF_6^-).

An elemental analysis of PPQ(ClO_4^-) is listed in *Table 2*. The molecular formula of the structural unit of the yellow PPQ(ClO_4^-) film is $(C_{34}H_{20}N_4O)(ClO_4)_{3.4}(H_2O)_{8.4}$. That is, the molar ratio of nitrogen and ClO_4^-

Table 1 X.p.s. data of the conducting PPQ films (eV)[a]

Conducting PPQ film	N_{1s}	X^-
PPQ	399.3	
PPQ(ClO_4^-)	402.0 399.3	207.9 (Cl_{2p})
PPQ(AsF_6^-)	402.3 399.8	1329.2 (As_{2p}) 686.6 (F_{1s})
PPQ(BF_4^-)	401.7 399.8	194.0 (B_{1s}) 686.6 (F_{1s})
PPQ(PF_6^-)	402.1 399.1	136.0 (P_{2p}) 686.4 (F_{1s})

[a] $X^- = ClO_4^-$, AsF_6^-, BF_4^-, PF_6^-

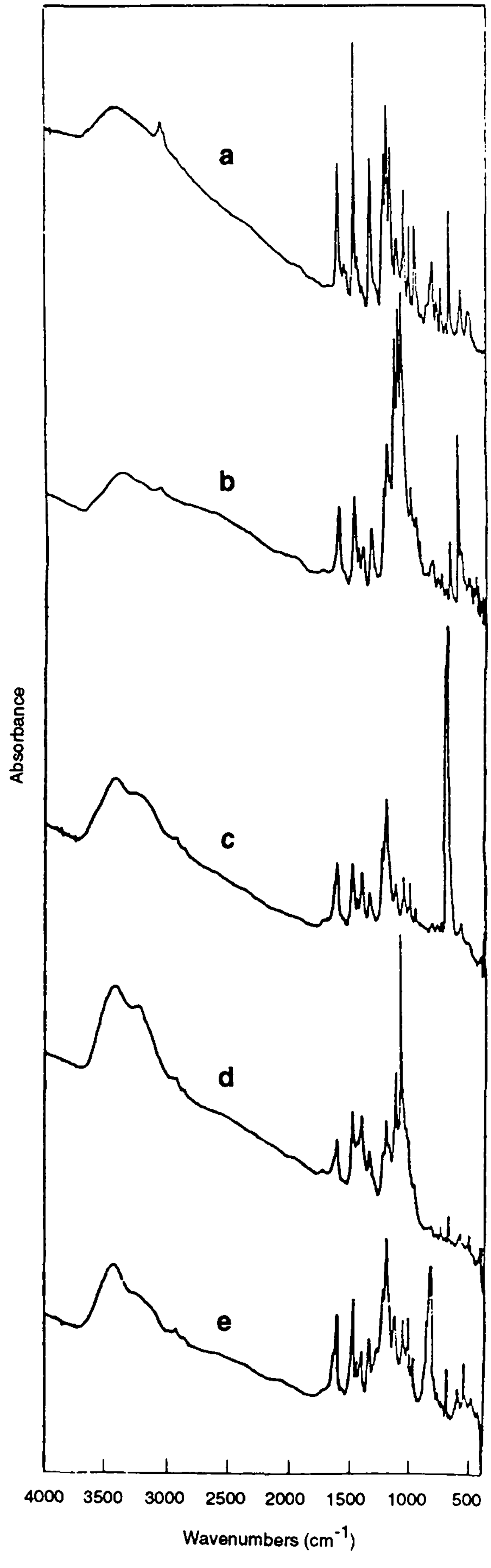


Figure 1 I.r. spectra of conducting PPQ films: (a) PPQ, (b) PPQ(ClO_4^-), (c) PPQ(AsF_6^-), (d) PPQ(BF_4^-), (e) PPQ(PF_6^-)

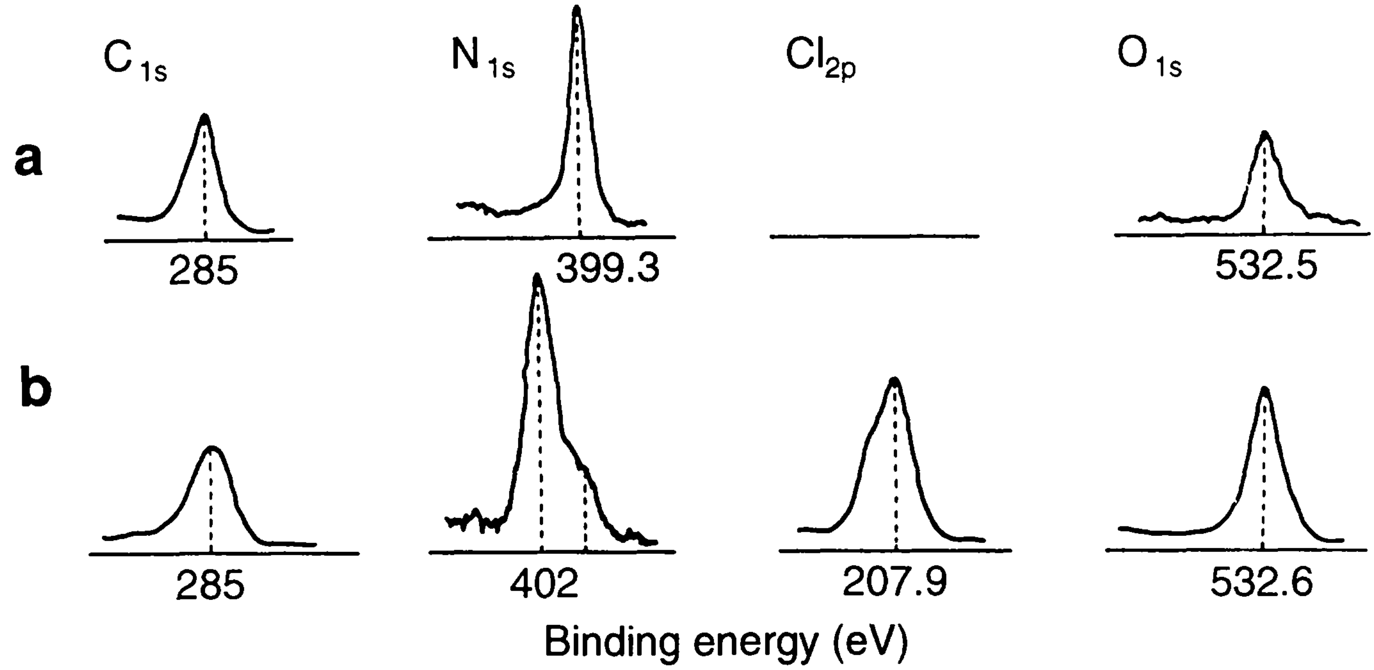
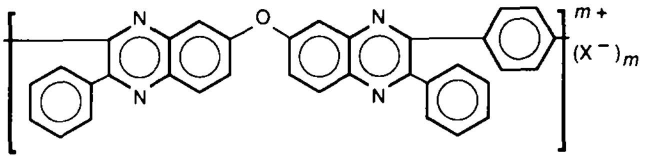


Figure 2 X.p.s. of PPQ(ClO_4^-) film (b) compared with undoped film (a)

Table 2 Elemental analysis of the yellow PPQ(ClO_4^-) film

Element	C	H	N	Cl
Content (%)	41.63	3.74	5.56	11.93

ion is 1 to 0.85 in PPQ (ClO_4^-). This result agrees well with that of the N_{1s} spectrum of PPQ(ClO_4^-) by using X.p.s. (*Figure 2b*). According to these results we propose a structure for conducting PPQ as follows:



where $X^- = ClO_4^-$, AsF_6^-, BF_4^-, PF_6^-; *m* is the number of positive charges in a structural unit of PPQ. When $X^- = ClO_4^-$, $m = 3.4$. In this structure, the positive charges are located on nitrogen atoms. Because the conducting PPQ films easily hydrate in air, there are H_2O in each chain unit of the structure. For example, there are 8.4 moles of H_2O in each structural unit of PPQ(ClO_4^-).

Conductivity

PPQ is an insulator with excellent thermal and chemical stability. We have found that PPQ can be conductive when doped by electrochemical oxidation of PPQ-TCE solution in the presence of supporting electrolytes. The conductivities of conducting PPQ films with different dopant anions are summarized in *Table 3*. A marked enhancement in conductivity was observed with ClO_4^-, AsF_6^-, or BF_4^- ions. The conductivities of PPQ(ClO_4^-), PPQ(AsF_6^-) and PPQ(BF_4^-) range from 10^{-7} to 10^{-8} S cm^{-1}, which is 10–11 orders of magnitude higher than that of undoped PPQ. The conductivity of PPQ(PF_6^-) film is much lower than the above three. This resulted from the lowest oxidation state of PPQ(PF_6^-) in the conducting PPQ films.

The conductivity of the films was as high as 10^{-4} S cm^{-1} at the beginning of measurement. It decreased with prolonged measurement time and reached a constant value as listed in *Table 3*. We believe that the conductivity of the films mainly results from an ionic conductivity contribution. This is also proved by the fact that the conductivity of PPQ(ClO_4^-) film is increased sharply with increase of relative humidity (to be published elsewhere). The electronic conductivity of the film was very low because the ether linkage limits the conjugation length in electrochemically oxidized PPQ. The nature of conductivity of the film needs further study.

It was found that the conducting PPQ films were quite stable at ambient temperature. The PPQ(ClO_4^-) film sample maintained its conductivity for more than 1 year in a silica gel desiccator or for 3 months in air.

Ultra-violet visible spectra

The electronic spectra of the conducting PPQ show a new shoulder band near 460 nm compared with that of undoped PPQ (*Figure 4*). This may be the result of charge-transfer intercalation of dopant anions during electrochemical doping of PPQ. This phenomenon has also been observed in charge-transfer intercalation of other conducting polymers[7]. With varied anions, the strength of the new band relative to the band at 390 nm is different. PPQ(AsF_6^-) is the strongest of them, PPQ(BF_4^-) and PPQ(ClO_4^-) are the next, and the weakest is PPQ(PF_6^-). The order is in agreement with that of conductivity.

Morphology

Scanning electron microscopy of the conducting PPQ films shows that the surface facing the electrolyte is rough and varies with the dopant anion (*Figure 5*). PPQ(ClO_4^-) film shows a honeycomb-like surface (*Figure 5a*). The surface of PPQ(AsF_6^-) film is very rough and irregular (*Figure 5b*). PPQ(BF_4^-) film shows a net-like surface (*Figure 5c*). The surface of PPQ(PF_6^-) film is finer and

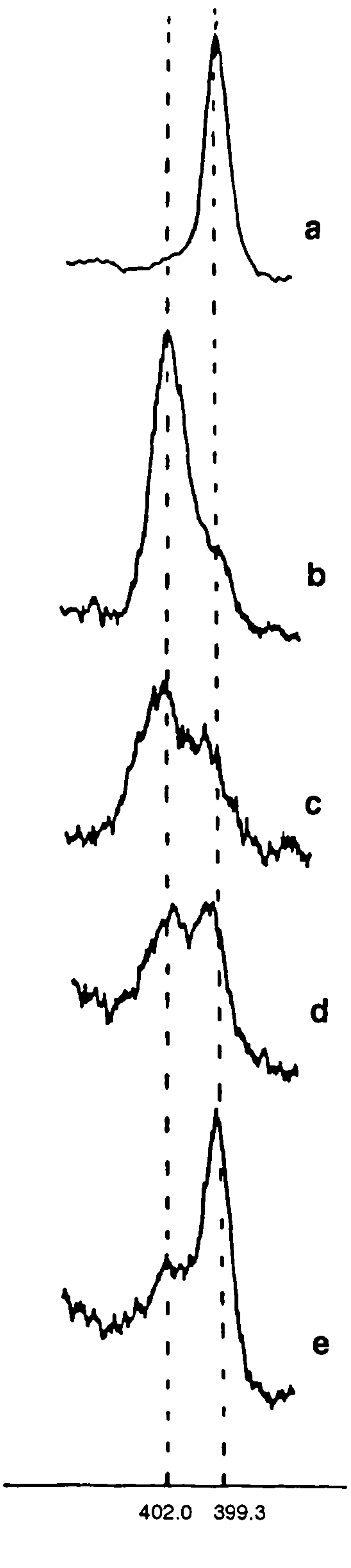


Figure 3 X.p.s. N_{1s} spectra of conducting PPQ films: (a) PPQ, (b)PPQ(ClO_4^-), (c) PPQ(AsF_6^-), (d) PPQ(BF_4^-), (e) PPQ(PF_6^-)

Table 3 Conductivity of the conducting PPQ films

Conducting PPQ film	Conductivity[a] ($S\ cm^{-1}$)
PPQ(ClO_4^-)	4.9×10^{-8}
PPQ(AsF_6^-)	6.3×10^{-7}
PPQ(BF_4^-)	3.8×10^{-7}
PPQ(PF_6^-)	1.2×10^{-12}

[a] Measured in air at room temperature, r.h. 50%

closer, and there are no holes on it (*Figure 5d*). The loose morphology structures of PPQ(ClO_4^-), PPQ(AsF_6^-) and PPQ(BF_4^-) films make it easy for ions of the film to hydrate in air and to move. It is very difficult for an ion to hydrate and move in PPQ(PF_6^-) film, owing to its compact morphology. The effect of dopant anions on the morphology of the conducting PPQ films is consistent with that on conductivity.

Change in colour

The conducting PPQ films exhibit unique changes in colour. At the beginning of electrolysis, PPQ(ClO_4^-), PPQ(AsF_6^-) and PPQ(BF_4^-) films are red; PPQ(PF_6^-) film is orange. As electroysis goes on, the PPQ(ClO_4^-) and PPQ(BF_4^-) films are still red; there are some orange

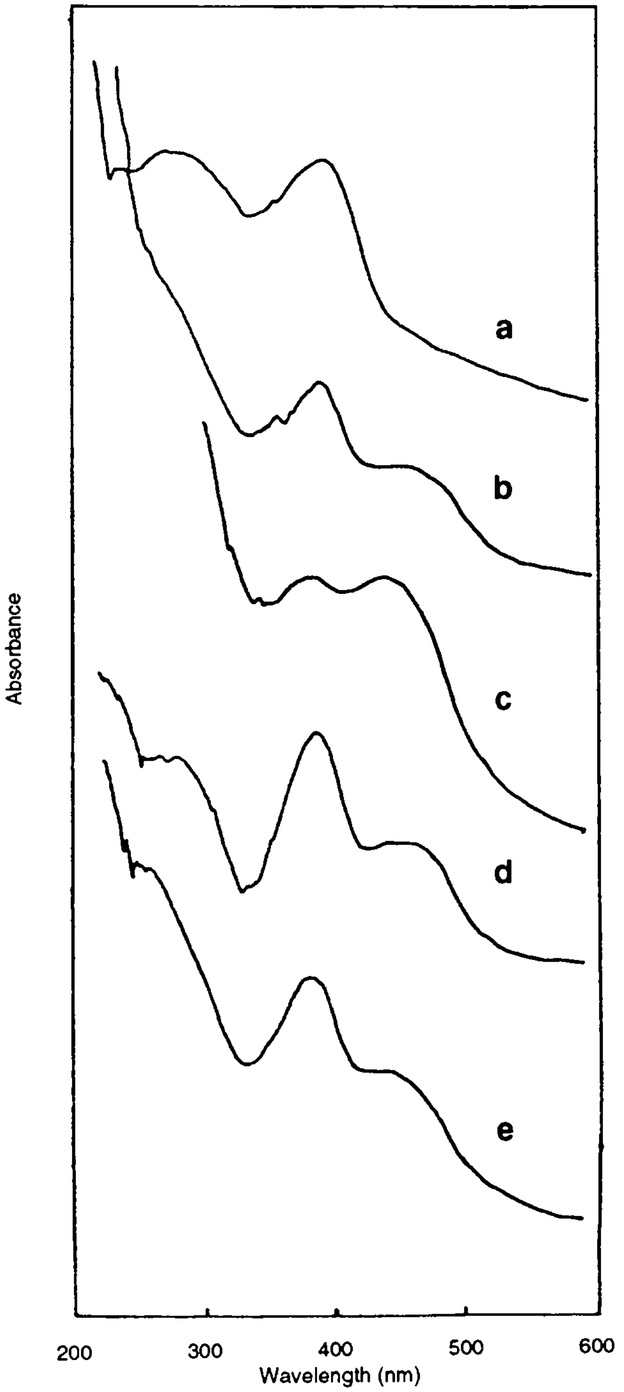


Figure 4 U.v.-vis. spectra of conducting PPQ films: (a) PPQ, (b) PPQ(ClO_4^-), (c) PPQ(AsF_6^-), (d) PPQ(BF_4^-), (e) PPQ(PF_6^-)

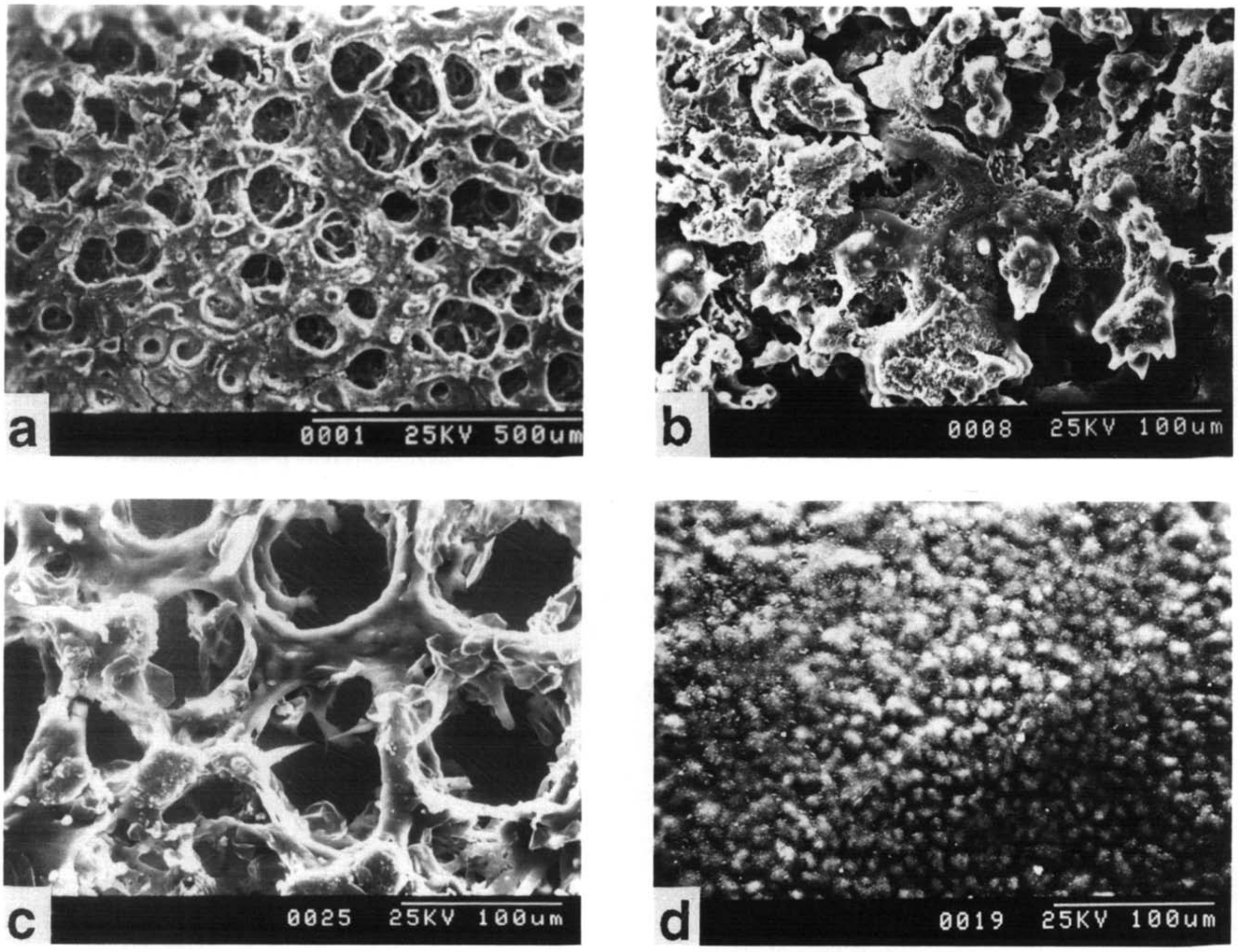


Figure 5 Morphology of surface facing the electrolyte of conducting PPQ films: (a) PPQ(ClO_4^-), (b) PPQ(AsF_6^-), (c) PPQ(BF_4^-), (d) PPQ(PF_6^-)

Table 4 Data results of the conducting PPQ films

Conducting PPQ film	T_{endo} (°C)[a]	Weight loss (%)
PPQ(ClO_4^-)	58	15.4
PPQ(AsF_6^-)	65, 101	27.4
PPQ(BF_4^-)	65, 94	29.7
PPQ(PF_6^-)		

[a] T_{endo} is the endothermic peak temperature

spots on the red PPQ(AsF_6^-) film; and the PPQ(PF_6^-) film changes to yellow. The red PPQ(ClO_4^-), PPQ(AsF_6^-) and PPQ(BF_4^-) films change to yellow when exposed in air; the yellow PPQ(ClO_4^-), PPQ(AsF_6^-) and PPQ(BF_4^-) films become red again in vacuum. This change in colour of the conducting PPQ films is reversible. The yellow PPQ(PF_6^-) film shows no change in colour even in vacuum.

We believe that this change in colour is caused by moisture in air. This conclusion is proved by d.t.a. results (*Table 4*). When the yellow films are heated in air, d.t.a. of yellow PPQ(ClO_4^-), PPQ(AsF_6^-) and PPQ(BF_4^-) films show that one or two endothermic peaks at 50–110°C are accompanied by weight loss, and at the same time the yellow films change to red. The d.t.a. curve shows that the weight loss of the yellow PPQ(ClO_4^-) film is 15.4%, which is equal to the water content in the yellow film calculated from elemental analysis (15.3%). This indicated that the yellow film loses water during the change in colour. It follows that the water in yellow film is all gone when the colour changes. There is no more water in the red film. We believe that water in the yellow film is solvated to the dopant anions. The yellow PPQ(PF_6^-) films does not show an apparent endothermic peak in the same temperature range. The conducting PPQ(ClO_4^-), PPQ(AsF_6^-) and PPQ(BF_4^-) films are highly sensitive to moisture in air. The reversible change in colour of the film is caused by hydration and dehydration.

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