Conducting films of polyphenylquinoxaline

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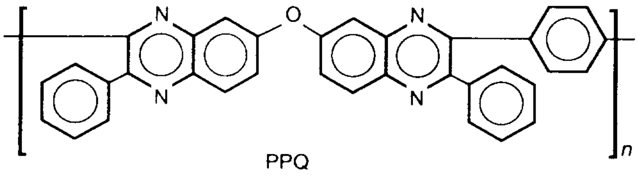
This paper reports the conductivities of polyphenylquinoxaline (PPQ) doped with aqueous H_2SO_4. The highest conductivity of doped PPQ is 4.5×10^{-2} S cm^{-1} obtained by the four-probe method at room temperature. The influence of concentration of aq. H_2SO_4 and doping time on the conductivity of doped PPQ is discussed. The structures of doped and undoped PPQ were confirmed by Fourier-transform infra-red, ultra-violet and X-ray photoelectron spectroscopies, electron spin resonance and elemental analysis. Also, the stability of the conductivity value was examined.

(Keywords: polyphenylquinoxaline; conducting films; proton doping)

INTRODUCTION

Since 1977, when the electrical conductivity of polyacetylene was first published, increasing attention has been directed to electrically conducting polymers derived from conjugated polymers. Most work has concentrated on only several kinds of polymers. Polyphenylquinoxaline (PPQ) possesses a step-ladder structure and exhibits good thermal stability, chemical resistance, electrical insulation and good processing characteristics[1,2]. Zhang Chi *et al.*[3] first reported the preparation of conducting PPQ films in solution by means of potentiostatic oxidation, and the conductivities of conducting PPQ show that PPQ can be transformed into a conductor by doping. Generally, there are two main methods of doping to produce conducting polymers. One way is by an oxidation–reduction reaction, as was described in ref. 3; the other is by proton doping. In our research, we discovered that PPQ exhibited a colour change of yellow–orange–red when treated with concentrated H_2SO_4. This phenomenon is consistent with the colour change in the doping procedure, which leads us to explore the possibility of preparing conducting PPQ by the method of proton doping.



PPQ

EXPERIMENTAL

Preparation of conducting PPQ films

PPQ film was prepared by polycondensation of aromatic tetraamine with aromatic dibenzil in cresol, and cast on a glass plate followed by complete cyclization according to ref. 1. The thickness of PPQ film was about 50 μm.

A PPQ film was soaked in aqueous H_2SO_4 and exhibited a colour change depending on the concentration of aq. H_2SO_4, which will be discussed below. The doped PPQ film was removed from aq. H_2SO_4. The excess aq. H_2SO_4 adhering to the surface of the PPQ film was absorbed by a filter, and the film was then dried in vacuum for one day.

Conductivity measurements

The conductivities of doped PPQ were measured by the four-probe method at room temperature.

Characterization

*FT*i.r. spectra of PPQ were obtained with a 2 μm thick PPQ film on a Perkin–Elmer 1760 *FT*i.r. spectrometer. The PPQ films for u.v.-vis. spectra on a Shimadzu UV-240 u.v.-visible recording spectrophotometer were prepared on silica glass. 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). Elemental analysis and e.s.r. were also performed and are discussed.

RESULTS AND DISCUSSION

Conductivity

The conductivities of doped PPQ depended on the concentration of aq. H_2SO_4 at room temperature. In this experiment, a series of aq. H_2SO_4 of different concentration was prepared to determine the influence of concentration on the conductivities of doped PPQ. The conductivities of PPQ doped for 24 h are shown in *Figure 1*. As we see in *Figure 1*, the conductivities increased with increase of concentration of aq. H_2SO_4 to a certain extent. The 9.1 M aq. H_2SO_4 yielded the highest conductivity of 4.5×10^{-2} S cm^{-1} of doped PPQ. This result showed that insulating PPQ can be transformed into a conductor by the use of proton doping. It should be pointed out that low concentrations of aq. H_2SO_4 would make the conductivities too low to be measurable and high concentrations would destroy PPQ films.

The doped PPQ exhibited a colour change depending on the concentration of aq. H_2SO_4. The doped PPQ

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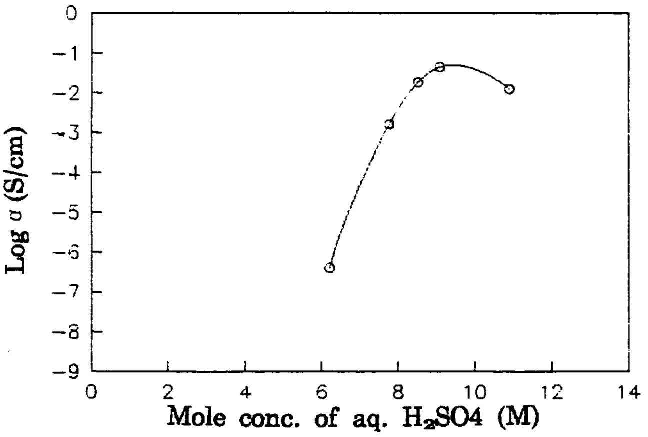

Figure 1 Dependence of the concentration of aq. H_2SO_4 on the conductivities of PPQ

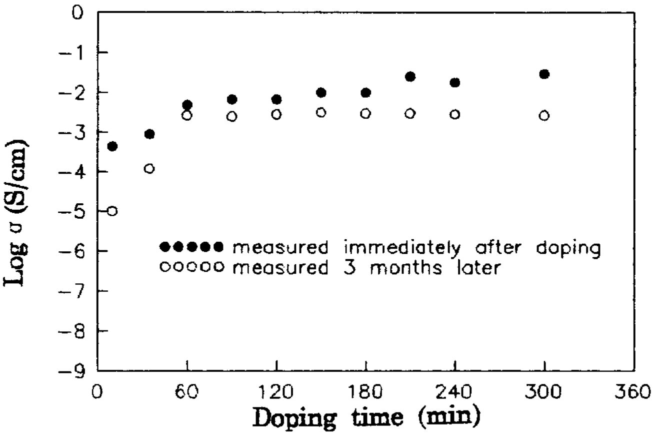

Figure 2 Doping time dependence on the conductivities of PPQ in 9.1 M aq. H_2SO_4

remained yellow in colour when doped in aq. H_2SO_4 with concentrations lower than 6 M, turned orange between 6 and 8 M, and became red in higher than 8 M aq. H_2SO_4.

Using 9.1 M aq. H_2SO_4 as dopant, we have studied the dependence of conductivity on doping time. The results are shown in *Figure 2*. The conductivities increased with the increase of doping time. When the doping time is longer than 60 min, the conductivities no longer varied with increase of doping time.

In heavily doped PPQ, the complete change in colour from yellow–orange–red was observed, while a colour change of yellow–orange took place in the intermediate case. The former showed higher conductivities than the latter.

The heavily doped PPQ recovered its original yellow colour when it was soaked in water and became insulating. This phenomenon together with structure characteristics, which will be described below, confirms the reversibility of protonic/deprotonic doping of PPQ.

The stability of the conductivities of doped PPQ was studied by remeasuring the conductivities of these PPQ films stored in a desiccator for 3 months. The conductivities decreased no more than one order of magnitude.

Characterization

Elemental analysis. Elemental analysis of PPQ was carried out and the results are listed in *Table 1*. The content of oxygen and sulfur increases with increase of doping time, whereas the content of carbon and nitrogen decreases. This suggested that the counterions (maybe SO_4^{2-} or HSO_4^-) were intercalated into the PPQ chain units, which confirmed the doping in PPQ.

X-ray photoelectron spectrometry. The N 1s binding energy of doped PPQ in 9.1 M aq. H_2SO_4 for different doping times obtained by x.p.s. is listed in *Table 2*. The N 1s spectra are shown in *Figure 3*. It can be seen that only the binding energy of nitrogen atoms is changed, indicating that doping occurred on the nitrogen atoms of the quinoxaline rings in PPQ chain units. As shown in *Figure 3*, there was only one N 1s peak at 399.3 eV in undoped PPQ, whereas a new N 1s* peak near 401.7 eV was observed after doping. Evidently, the N 1s* peak was ascribable to the nitrogen cation, which confirmed the doping in PPQ. It was interesting to notice that the atomic ratio of N 1s* to N 1s increased with increase of doping time. At high doping level, the N 1s peak disappeared, asserting that the nitrogen atoms in PPQ were all turned into nitrogen cations. Sample f, derived from sample e by soaking in distilled water for 2 min, exhibited a similar x.p.s. spectrum to undoped PPQ. This supported the fact that protonic/deprotonic doping in PPQ films is a reversible process, which is consistent with the doping character of conducting PPQ.

Fourier-transform infra-red spectroscopy. The *FT*i.r. spectrum of doped PPQ showed the same bands at 1605, 1475, 1350, 1202 and 699 cm^{-1} as undoped PPQ and wide absorption bands at 1202, 1043, 881 and 578 cm^{-1} were observed. This may be due to the intercalation of counterions in PPQ chain units (*Figure 4*). It indicated that the backbone structure of doped PPQ was similar to that of undoped PPQ. The *FT*i.r. spectrum of doped PPQ was exactly the same as that of undoped PPQ after soaking in distilled water for 2 min. This was in agreement with the results of x.p.s. and supports the reversibility of protonic/deprotonic doping of PPQ.

Ultra-violet/visible spectra and electron spin resonance spectra. The electronic spectra of undoped PPQ showed two peaks at 290 and 380 nm as shown in *Figure 5*. The higher one is assigned to quinoxaline rings[4]. After doping, no shift was observed for the peak at 290 nm; however, the peak at 380 nm shifted to 420 nm. It may indicate

Table 1 Elemental analysis of PPQ doped in 9.1 M aq. H_2SO_4

Doping time (min)	Elemental analysis (%)				
	C	N	H	S	O[a]
0	81.57	11.11	3.81	0	3.51
5	80.61	10.93	3.81	0.3	4.35
10	45.71	6.24	3.60	10.34	34.11
120	40.05	5.35	4.65	11.26	38.69
210	33.15	4.65	3.96	12.23	46.01

[a] [O] = 100 − [C] − [N] − [H] − [S]

Table 2 X.p.s. data of PPQ doped in 9.1 M aq. H_2SO_4

Doping time (min)	N 1s (eV)
0	399.3 –
5	399.7, 401.4
10	399.3, 401.6
120	399.4, 401.2
210	– 401.7

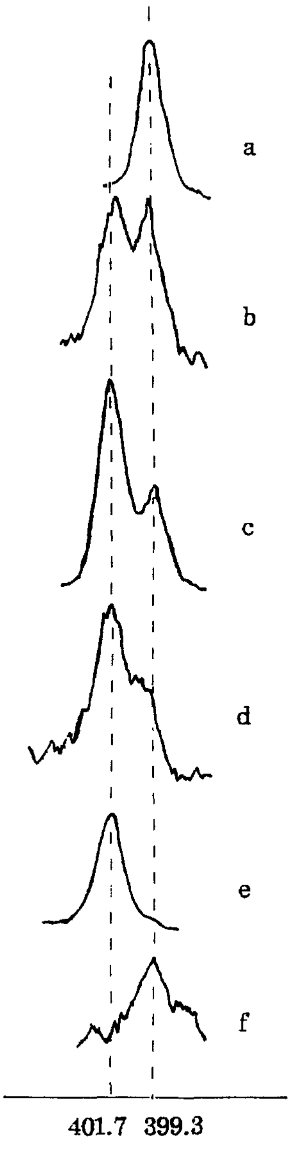

Figure 3 X.p.s. N 1s spectra of PPQ doped in 9.1 M aq. H_2SO_4 for different doping times: (a) undoped PPQ; (b) 5 min; (c) 10 min; (d) 2 h; (e) 3.5 h; (f) derived from (e) by soaking it in distilled water for 2 min

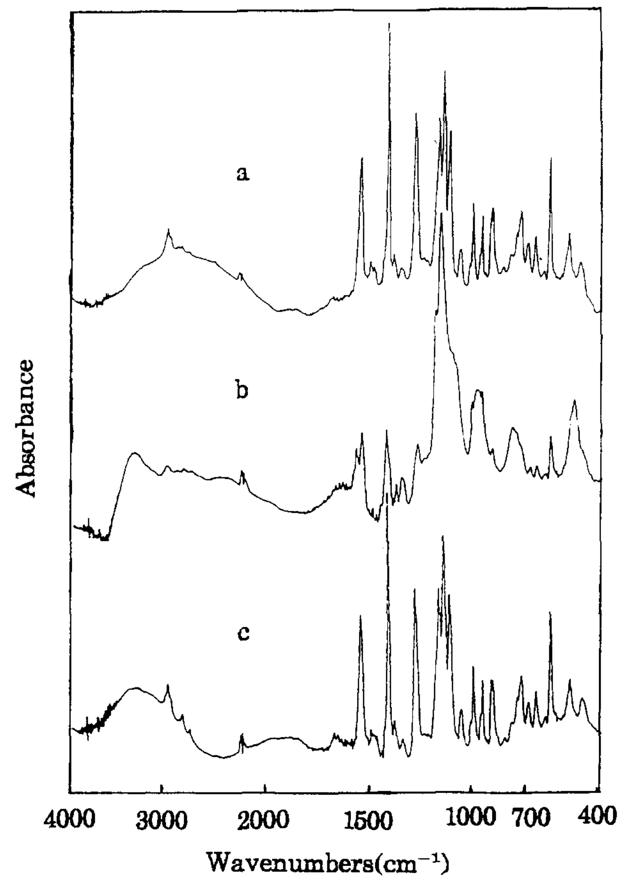

Figure 4 *FT*i.r. spectra of: (a) undoped PPQ; (b) doped PPQ; (c) derived from (b) by soaking it in distilled water for 2 min

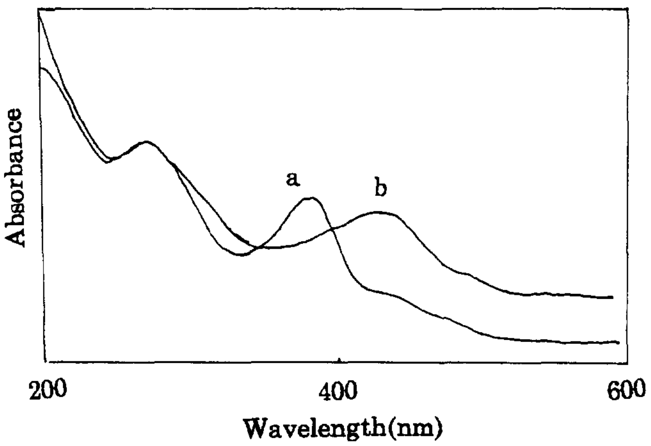

Figure 5 U.v.-vis. spectra of: (a) undoped PPQ; (b) doped PPQ

that doping occurred on quinoxaline rings, which was consistent with the results of x.p.s.

No signal was observed in e.s.r. spectra of doped PPQ. Therefore, it is expected that the bipolaron mechanism was proposed to interpret the conducting behaviour of H_2SO_4-doped PPQ.

CONCLUSIONS

PPQ can be conveniently transformed into a conductor by a method of proton doping. The highest conductivity at room temperature is $4.5 \times 10^{-2}\,S\,cm^{-1}$. The conductivities depend on the concentrations of aq. H_2SO_4 and doping time.

The doping of PPQ in aq. H_2SO_4 is accompanied by a yellow–orange–red colour change, and protonic/deprotonic doping is shown to be reversible.

The conductivities of doped PPQ decrease no more than one order of magnitude after all samples were stored in a desiccator for 3 months.

From structure characteristics of PPQ, it is determined that doping occurred on the nitrogen atoms of the quinoxaline rings in PPQ chain units. The bipolaron mechanism is proposed to interpret the conducting behaviour of H_2SO_4-doped PPQ.

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