Chemical synthesis and characterization of polypyrrole–chlorine complex

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Simultaneous chemical polymerization and oxidation of pyrrole have been initiated by chlorine (Cl_2) in various organic solvents. The polypyrrole–chlorine (PPY–Cl_2) complex so produced is granular in nature and has a room-temperature direct-current (d.c.) electrical conductivity (σ) that varies from $<10^{-7}$ to 0.5 S cm^{-1} depending on the solvent medium used for polymerization. The PPY–Cl_2 complex prepared in acetonitrile has the highest conductivity and, for this sample, a plot of ln σ *versus* (temperature)$^{-1/4}$ gives a straight line over the 120–300 K region. The physicochemical and thermal properties of this sample were also examined in some detail. Substantial addition of the halogen to the pyrrole ring may have occurred during polymerization. Electrochemical characterization of the complex in powder form was also carried out using a specially modified electrode.

(Keywords: polypyrrole; chemical synthesis; chlorine oxidant; conductivity; solvent media)

INTRODUCTION

Electrically conducting polymers have attracted a great deal of attention in recent years because of their unusual electronic properties[1]. Of these polymers, oxidized polypyrrole (PPY) and related polyheterocycles are of particular interest owing to their relative stability and well characterized stoichiometry[2]. 'Pyrrole blacks' with proposed molecular weights of 800–1000 have been prepared in the presence of various oxidizing reagents since the beginning of this century[3]. Recently, however, highly conducting pyrrole polymers have usually been prepared in the form of polycations via electrochemical polymerization and oxidation[4–6]. The room-temperature conductivity of these PPY cations ranges from 1 to 100 S cm^{-1}.

Rather conductive PPY complexes have also been synthesized chemically in the presence of various Fe(III) oxidants, such as $Fe(ClO_4)_3$ and $FeCl_3$ (refs. 7–9). We reported recently on the simultaneous chemical polymerization and oxidation of pyrrole by iodine (I_2) and bromine (Br_2) in aqueous media and in organic solvents[10,11]. The PPY–I_2 and PPY–Br_2 complexes so produced are stable in the atmosphere and have electrical conductivity and conduction behaviour comparable to that of the electrochemically prepared PPYs[12]. In this report, we describe a similar chemical method for the simultaneous polymerization and oxidation of pyrrole by chlorine (Cl_2). The resulting PPY–Cl_2 complex is characterized by infra-red (i.r.) absorption spectroscopy, differential scanning calorimetry (d.s.c.), thermogravimetric analysis (t.g.a.), chemical analysis and electrical conductivity measurements. Cyclic voltammetry has also been carried out on the powder samples of PPY–Cl_2, using a specially modified electrode, to study their oxidation and reduction behaviour.

EXPERIMENTAL

Polymer synthesis and oxidation

Pyrrole monomer (Merck, reagent grade) used in the present studies was purified by distillation under reduced pressure and stored under an inert atmosphere. All solvents were of reagent grade and were used as received. The solvent media tested were water, methanol, chloroform, carbon tetrachloride, toluene, tetrahydrofuran and acetonitrile. All polymerization work was carried out under a nitrogen atmosphere at either room temperature or at 0°C. Chlorine gas was bubbled into 200 ml of solvent until saturation. Pyrrole (1.5 ml) was then introduced into the solution with rigorous stirring. In all cases, the solution turned dark and eventually a dark powdery precipitate appeared. In most cases film formation on the reactor walls was also observed. The dark precipitate, which was later identified to be the polypyrrole–Cl_2 complex, was removed by filtration and rinsed thoroughly with copious amounts of absolute ethanol. The precipitate was then dried by pumping under reduced pressure of 10^{-2} Torr for about 6 h.

The amount of precipitate formed is dependent on the chlorine concentration and the types of monomer and solvent used. For example, with acetonitrile as solvent, the amount of polymer precipitated increased with increase in chlorine concentration. When *N*-substituted monomers, such as *N*-methylpyrrole, *N*-butylpyrrole and *N*-phenylpyrrole, were used in acetonitrile, only *N*-methylpyrrole gave rise to a black precipitate, while dark solutions with no precipitate were obtained for the latter two monomers. The ultra-violet–visible (u.v.–vis.) absorption spectra of these solutions indicate the presence of a broad absorption tail extending well into the red and near-i.r. region. This suggests the presence of low-molecular-weight PPY species. When water was used

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as a medium for polymerization, a minimal amount of precipitate was formed and this precipitate was soluble in ethanol. Hence no further analysis was carried out with this precipitate.

Polymer characterization

The chemical compositions of the polymeric complexes were determined by elemental analysis. Since the complexes are insoluble in all organic solvents tested, the molecular weight of the polymer cannot be determined by the traditional chromatographic techniques at this stage. The i.r. absorption spectra measurements were carried out on a Perkin–Elmer model 682 spectrophotometer with the polymer samples dispersed in KBr pellets. For electrical conductivity measurements, the polymer samples were pressed into thin circular discs of about 0.05–0.1 cm thickness and 1.2 cm diameter in a stainless-steel press at a pressure of about 300 kg cm^{-2}. Electrical conductivities were measured using the standard collinear four-probe technique. The measuring circuit consisted of a Keithley 614 digital electrometer and a Hewlett–Packard model 6212B d.c. power supply. The current passed was 10 mA. Conductivities below room temperature were measured *in situ* in a liquid nitrogen cryostat and in the presence of an inert atmosphere. Thermogravimetric analyses (t.g.a.) were carried out using a Netzsch model STA 409 simultaneous t.g.–d.t.a. apparatus, at a heating rate of 10°C min^{-1} in nitrogen. Differential scanning calorimetry (d.s.c.) was performed using a Perkin-Elmer DSC-2C calorimeter with a heating/cooling rate of 10°C min^{-1} under a constant flow of nitrogen. Cyclic voltammograms of a mixture of PPY–Cl_2 complex and graphite in aqueous 1 M NaCl were determined using the specially modified electrode shown schematically in *Figure 1*. A detailed description of this electrode and its performance have been reported in an earlier publication[13]. The electrochemical studies were carried out in a Hokuto Denko one-compartment electrochemical cell equipped with a platinum counter-electrode and a Ag/AgCl reference electrode. A function generator provided the desired voltage sweep rates to the cell through a potentiostat.

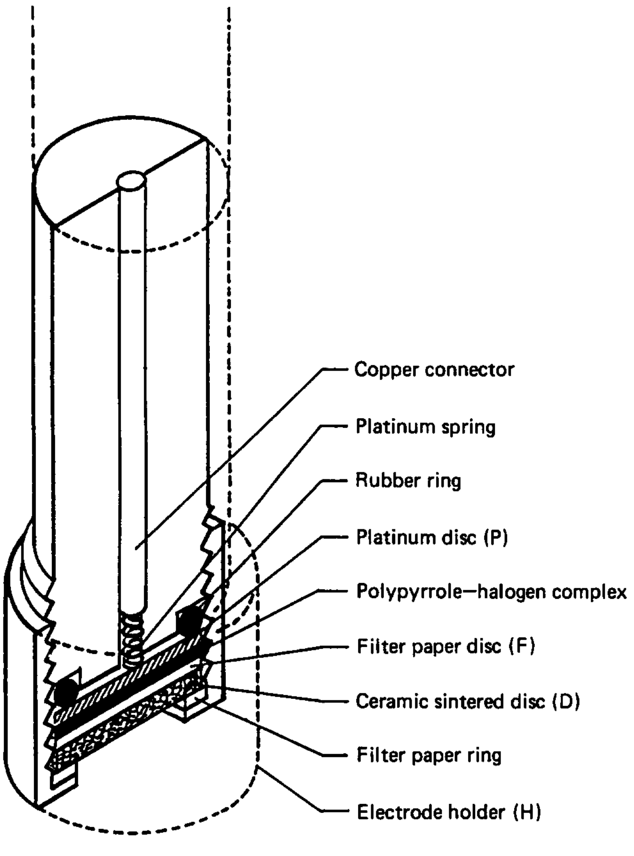

Figure 1 Detailed construction of the working electrode used in electrochemical studies

RESULTS AND DISCUSSION

The results of the analysis of the PPY–Cl_2 complex obtained in acetonitrile will be discussed in detail, while the effects of solvent will be given in a later section.

Chemical compositions and electrical properties

Results of the elemental analysis of the PPY–Cl_2 complexes prepared in acetonitrile solutions and their respective room-temperature electrical conductivities σ are summarized in *Table 1*. The elemental analysis data indicate that the present complexes are primarily polymerized pyrrole (or *N*-methylpyrrole) units plus the chlorine dopant. There is no significant difference between the samples synthesized at room temperature and at 0°C as far as chemical composition and electrical conductivity are concerned.

The C:H:N ratio of the PPY–Cl_2 complexes is close to the theoretical value 4:3:1 for a linear chain of disubstituted pyrrole rings and is similar to the PPY–I_2 and PPY–Br_2 complexes obtained earlier[11]. The ratio of about three pyrrole units to one chlorine molecule appears to represent the stable stoichiometric composition for the complex. This pyrrole:halogen ratio is lower compared to the PPY–I_2 and PPY–Br_2 complexes prepared in a similar manner, which showed a ratio of approximately 4:1.[11] Our recently obtained Cl 2p X-ray photoelectron spectroscopy (XPS) core-level spectrum of the PPY–Cl_2 complex indicates the presence of both covalent (C–Cl) as well as ionic (Cl^-) species (*Figure 2*). The relatively weak π–π^* satellite structure in this spectrum readily suggests a loss of some conjugation with the addition of Cl to the ring by covalent bonding. The XPS results are consistent with the elemental analysis data and the i.r. absorption spectra, which show a

Table 1 Chemical composition and electrical conductivity[a] of polypyrrole–chlorine complex prepared in acetonitrile (CH_3CN) solutions

Polymer–acceptor complexes	Polymerization temperature (°C)	Chemical composition	Conductivity σ (S cm^{-1})
Polypyrrole–chlorine	27	$C_{4.0}H_{2.9}N_{1.0}(Cl_2)_{0.33}O_{0.72}$	0.5
Polypyrrole–chlorine	0	$C_{4.0}H_{2.9}N_{1.0}(Cl_2)_{0.37}O_{0.55}$	0.4
Poly(*N*-methylpyrrole)–chlorine	27	$C_{4.0}H_{2.2}N_{1.0}(CH_3)_{1.0}(Cl_2)_{0.10}O_{0.84}$	$<10^{-7}$

[a] At room temperature, 27°C

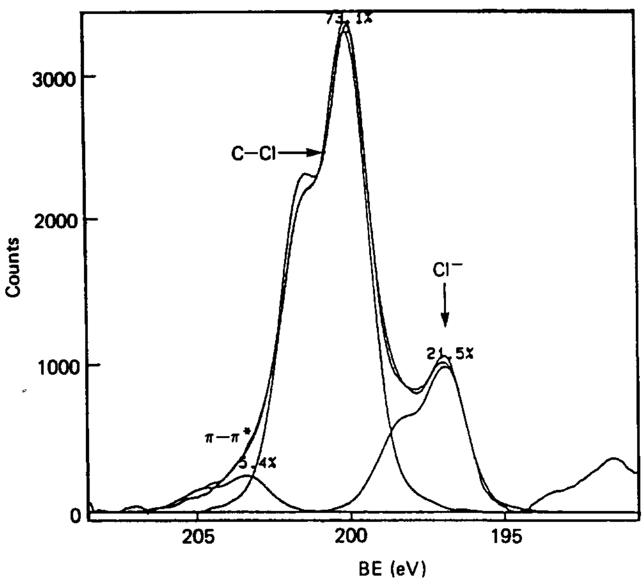

Figure 2 Cl2p XPS core-level spectrum of PPY–Cl_2 complex

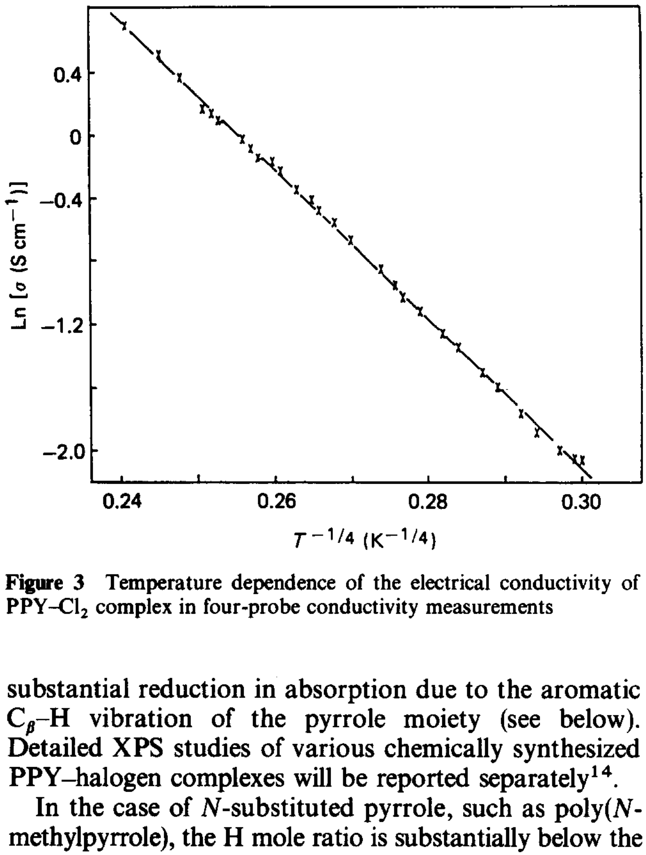

Figure 3 Temperature dependence of the electrical conductivity of PPY–Cl_2 complex in four-probe conductivity measurements

substantial reduction in absorption due to the aromatic C_β–H vibration of the pyrrole moiety (see below). Detailed XPS studies of various chemically synthesized PPY–halogen complexes will be reported separately[14].

In the case of *N*-substituted pyrrole, such as poly(*N*-methylpyrrole), the H mole ratio is substantially below the theoretical value of 3 to justify the primary α,α' linkages of the pyrrole moiety. Furthermore, the Cl_2 uptake in this sample is substantially below that of the PPY samples. Thus crosslinking or other side reactions may have occurred to a significant extent in this complex. As a result, the complex does not exhibit high electrical conductivity.

The room-temperature conductivity of the present PPY–Cl_2 complex is about a factor of 50 lower than that of the PPY–Br_2 and PPY–I_2 complexes[12]. This lower value of conductivity may be attributed to a higher degree of loss of effective conjugation, as a result of ring halogenation. The conductivity was measured as a function of temperature T and the plot of $\ln \sigma$ *versus* $T^{-1/4}$ is given in *Figure 3*. An apparent linear fit of the experimental data was obtained throughout the temperature range from 120 to 300 K. The $T^{-1/4}$ dependence has also been widely observed for electrochemically polymerized and oxidized PPY films[15–17] as well as in chemically synthesized PPY–I_2 and PPY–Br_2 complexes[12]. This relationship has been interpreted in terms of Mott's model[18] of variable-range hopping between localized states near the Fermi surface. However, in view of the recently reported inadequacy of the ordinary four-probe conductivity measurement in overcoming the intergranular, interfibrillar and intercrystallitic contact resistance of highly conductive polymer samples[19], the physical significance of the $T^{-1/4}$ dependence in the present complex should be interpreted with care.

Thermal properties

The d.s.c. and t.g.a. scans of the PPY–Cl_2 complex are shown in *Figure 4*. At 55°C, a small weight loss was detected, while the major weight loss occurred after 135°C. The initial weight loss is not accompanied by any loss in electrical conductivity. In fact, a reversible thermally activated conductivity was observed until about 140°C when an irreversible decrease in conductivity occurred simultaneously with the major weight loss. The d.s.c. scans show that exothermic reactions occur just prior to the onset of the major weight loss, while a sharp endothermic peak at 175°C precedes the point where this weight loss is most rapid. We wish to emphasize that the present PPY–Cl_2 complex synthesized in acetonitrile is stable in the atmosphere and at room temperature.

Infra-red absorption spectra

The i.r. absorption spectrum of the PPY–Cl_2 complex is given in *Figure 5* and is superimposable on that of the PPY complexes synthesized by the electrochemical method[20]. The i.r. spectrum reveals a rather featureless decrease in absorption from 4000 to 1700 cm^{-1}. This long absorption tail probably resulted from the tail of the

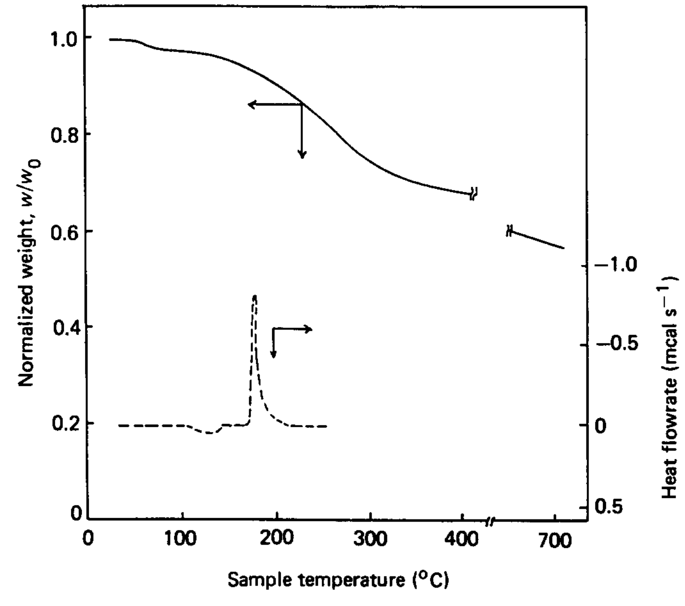

Figure 4 T.g.a. and d.s.c. scans of PPY–Cl_2 complex in N_2

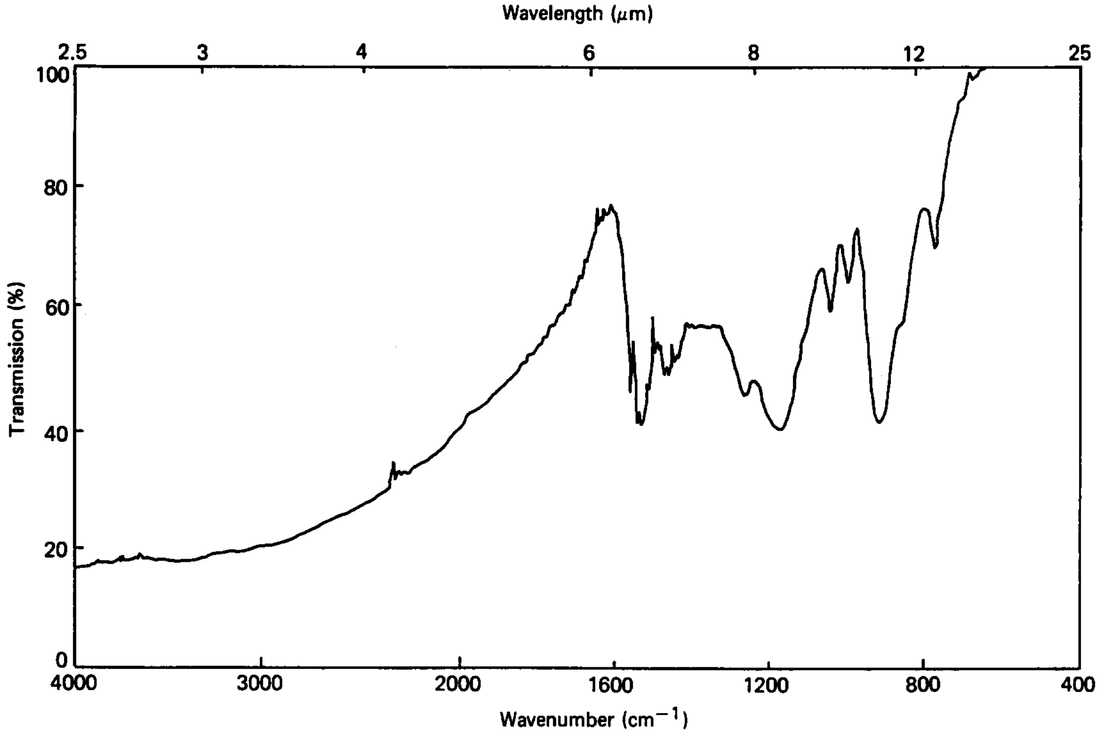

Figure 5 Infra-red absorption spectrum of PPY–Cl_2 complex prepared in acetonitrile

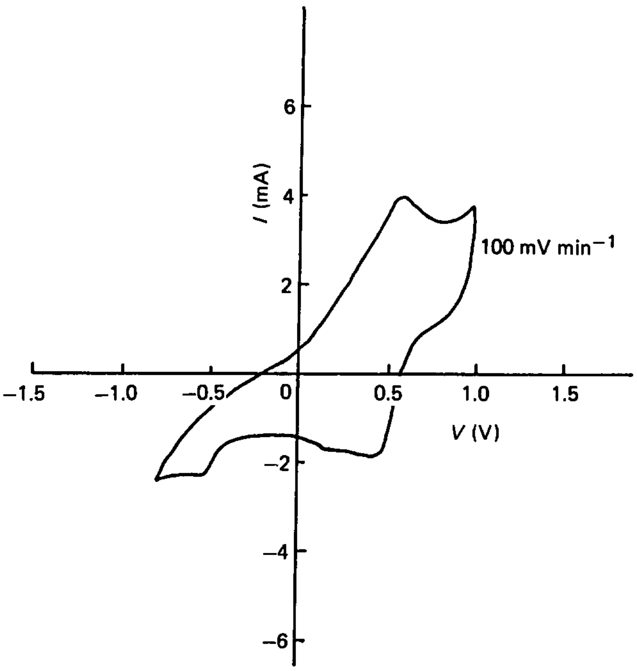

Figure 6 Voltammogram of 1:1 mixture of graphite and PPY–Cl_2 complex in 1 M NaCl

absorption band located in the red and near-i.r. region. An i.r. absorption tail of similar nature has been reported for chemically[10,11] as well as electrochemically[20] synthesized and oxidized polypyrrole and is characteristic of oxidized and highly conducting PPYs. The bands at about 1540, 1280, 1180, 1040 and 900 cm^{-1} are characteristic of PPY[20]. However, the absorption peak at 1040 cm^{-1} due to the aromatic C_β–H in-plane vibration[21] is substantially reduced compared to the spectra from our earlier work with PPY–I_2 and PPY–Br_2 complexes[10,11]. This observation together with the presence of a covalent C–Cl bond in the XPS spectrum readily indicate that a substantial number of pyrrole rings must have been halogenated by chlorine. The halogenation is probably accompanied by a substantial loss of conjugation, since the H mole ratio in the present PPY complex remains close to the theoretical value of 3 for a linear chain of disubstituted pyrrole (see *Table 1*).

Electrochemical characterization

The voltammogram of a 1:1 (by weight) mixture of PPY–Cl_2 and graphite powder is given in *Figure 6*. The graphite powder in the mixture would not affect the voltammogram since pure graphite has been found to produce no observable oxidation and reduction peaks at sweep rates of 100 mV min^{-1} or less. The voltammogram in *Figure 6* shows a well defined oxidation peak but the resolution for the reduction peak is poor. This is in contrast to the voltammograms reported earlier for PPY–I_2 and PPY–Br_2, which showed well defined oxidation and reduction peaks[13]. This poor resolution is probably attributable to the fact that a large portion of the chlorine is covalently bonded in the present PPY–Cl_2 complex. This is further supported by our recent studies of PPY–Br_2 complex prepared in the presence of a large excess of bromine. This complex also shows a substantial reduction in the absorption intensity of the C_β–H vibration band, probably as a result of halogenation at the β-carbons, and the voltammogram is usually unstable with a substantial loss in the resolution of the oxidation and reduction peaks[13].

Solvent effects

Attempts were also made to prepare the PPY–Cl_2 complex in other solvents: water, methanol (CH_3OH), toluene (C_7H_8), chloroform (CH_3Cl), carbon tetrachloride (CCl_4) and tetrahydrofuran (THF). In all cases, with the exception of water, a precipitate was obtained that was insoluble in ethanol and most organic solvents. The colour of the precipitate is dark violet when THF was used and black with the other solvents. As can be seen from *Figure 7*, the solvent medium for polymerization and oxidation has a strong effect on the conductivity. The most conductive complex was obtained when acetonitrile was used, while essentially insulator-like materials were obtained with protic solvents like methanol. The i.r. absorption spectrum of the PPY–Cl_2 complex obtained in CH_3OH is shown in *Figure 8*. Comparing this spectrum with that shown in *Figure 5*, a notable difference is the much-reduced intensity of the absorption tail between 4000 and 1700 cm^{-1} for the complex prepared in CH_3OH. Furthermore, when CH_3OH is used as solvent, the i.r. absorption spectrum shows a band near 1700 cm^{-1}, which is probably associated with the presence of the carbonyl group. A similar effect of conductivity decrease accompanied by a reduction in intensity of the absorption tail between 4000 and 1700 cm^{-1} has also been observed in the PPY–I_2 complex prepared in protic solvents[11]. It has also been reported that the composition of the chemically synthesized and oxidized PPY can vary substantially with the method of preparation as well as the reaction medium[3,21,23]. It appears that the presence of aprotic solvents facilitates the chemical oxidation and polymerization by halogen, as in the case of electrochemical oxidation and polymerization[4].

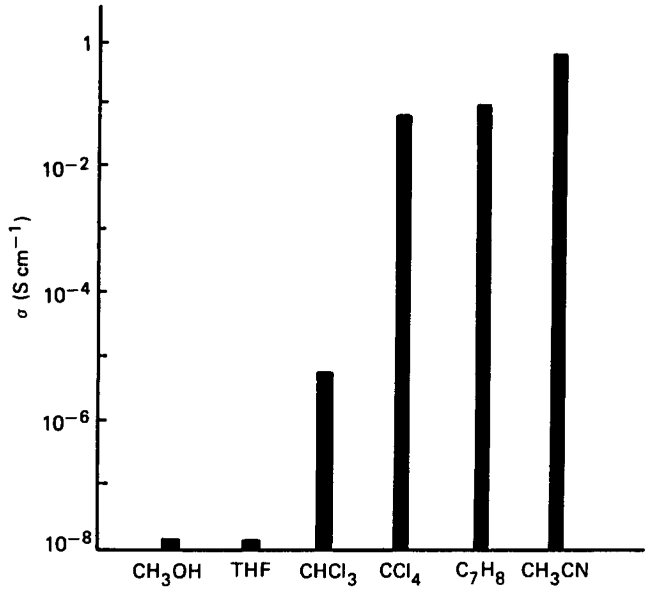

Figure 7 Effect of solvent medium on conductivity of PPY–Cl_2 complex

CONCLUSIONS

Simultaneous chemical polymerization and oxidation of pyrrole by chlorine have been achieved. The room-temperature d.c. electrical conductivity and the chemical structure of the PPY–Cl_2 complex are dependent on the solvent medium. Of the solvents investigated, acetonitrile provides the medium for the synthesis of PPY–Cl_2 complex with the highest conductivity ($\sigma \sim 0.5$ S cm^{-1}). From the characterization of this complex using chemical, electrochemical and spectroscopic methods, it appears that halogenation of the pyrrole ring with some loss of conjugation may have occurred. This can then help to account for the lower electrical conductivity observed in the present complex than in the case of PPY–I_2 and PPY–Br_2 complexes synthesized in a similar manner.

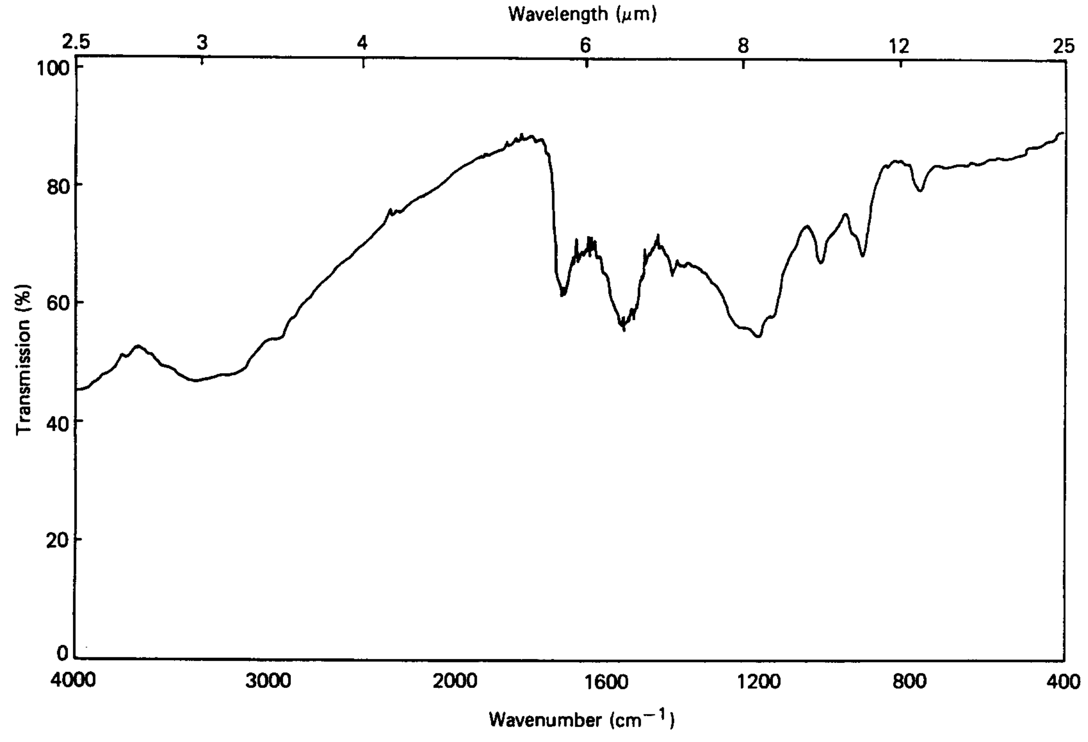

Figure 8 Infra-red absorption spectrum of PPY–Cl_2 complex prepared in methanol

REFERENCES

1 See, for example, Skotheim, T. (Ed.), 'Handbook of Conducting Polymers', Vols. I & II, Marcel Dekker, New York, 1986

2 Diaz, A. F. and Kanazawa, K. K. in 'Extended Linear Chain Compounds', Vol. 3, (Ed. J. S. Miller), Plenum, New York, 1983, p. 417

3 Gardini, G. P. *Adv. Heterocycl. Chem.* 1973, **15**, 67

4 Diaz, A. F., Kanazawa, K. K. and Gardini, G. P. *J. Chemical Soc., Chem. Commun.* 1979, 635

5 Diaz, A. F., Castillo, J. I., Logan, J. A. and Lee, W. Y. *J. Electroanal. Chem.* 1981, **129**, 115

6 Wegner, G., Wernet, W., Glatzhofer, D. T., Ulanski, J., Krohnke, C. H. and Mohammadi, M. *Synth. Metals* 1987, **18**, 1

7 Mermilliod, N. M., Tanguy, J. and Petiot, F. *J. Electrochem. Soc.* 1986, **133**, 1073

8 Audebert, P. and Bidan, G. *Synth. Metals* 1986, **14**, 71

9 Bocchi, V. and Gardini, G. P. *J. Chem. Soc., Chem. Commun.* 1986, 148

10 Kang, E. T., Tan, T. C., Neoh, K. G. and Ong, Y. K. *Polymer* 1986, **27**, 1958

11 Kang, E. T., Neoh, K. G., Tan, T. C. and Ong, Y. K. *J. Macromol. Sci.–Chem.* 1987, **A24**(6), 631

12 Kang, E. T., Neoh, K. G. and Ti, H. C. *Solid State Commun.* 1986, **60**, 457

13 Kang, E. T., Tan, T. C. and Neoh, K. G. *Europ. Polym. J.* in press

14 Kang, E. T., *et al.* to be published

15 Kanazawa, K. K., Diaz, A. F., Gill, W. D., Grant, P. M. and Street, G. B. *Synth. Metals* 1980, **1**, 329

16 Watanabe, A., Tanaka, M. and Tanaka, J. *Bull. Chem. Soc. Japan* 1981, **54**, 2278

17 Pfluger, P., Weiser, G., Scott, J. C. and Street, G. B. in 'Handbook of Conducting Polymers', Vol. II (Ed. T. Skotheim), Marcel Dekker, New York, 1985, p. 1369

18 Mott, N. F. and Davis, E. A. 'Electronic Processes in Non-Crystalline Materials', Clarendon Press, Oxford, 2nd Edn., 1979, p. 34

19 Wan, M., Wang, P., Cao, Y., Quan, R., Wang, F., Zhao, X. and Gong, Z. *Solid State Commun.* 1983, **47**, 759

20 Street, G. B., Clarke, T. C., Krounbi, M., Kanazawa, K. K., Lee, V., Pfluger, P., Scott, J. C. and Weiser, G. *Mol. Cryst. Liq. Cryst.* 1981, **83**, 253

21 Mohammadi, A., Hasan, M. A., Liedberg, B., Lundstrom, I. and Salaneck, W. R. *Synth. Metals* 1986, **14**, 189

22 Salmon, M., Kanazawa, K. K., Diaz, A. F. and Krounbi, M. *J. Polym. Sci. Lett.* 1982, **20**, 187

23 Becchi, L., Chierici, L., Gardini, G. P. and Mondelli, R. *Tetrahedron* 1970, **26**, 4073