

Halogen-induced charge transfer polymerization of pyrrole in aqueous media

E. T. Kang, T. C. Tan, K. G. Neoh and Y. K. Ong

Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511, Republic of Singapore
(Received 12 March 1986)

Simultaneous polymerization and doping of pyrrole have been carried out in the presence of a halogenic electron acceptor, bromine (Br_2) or iodine (I_2), in aqueous dispersion or in a two-phase solvent system. The morphology of the polypyrrole (PPY) so produced is granular and porous. The electrical conductivity of the PPY- I_2 charge transfer (CT) complex is of the order of $10^1 \text{ ohm}^{-1} \text{ cm}^{-1}$ while that of the PPY- Br_2 complex is about one order of magnitude less. Both complexes are stable in the atmosphere. The physicochemical properties of the PPY- I_2 and PPY- Br_2 CT complexes prepared under various experimental conditions are examined in detail.

(Keywords: polypyrrole; charge transfer polymerization; halogen doping; electrical conductivity; thermal analysis)

INTRODUCTION

The report on the exceptional electrical properties of doped polyacetylene in 1977¹ has contributed to a rapidly increasing interest in conducting conjugated polymers during the past few years. Intensive studies have been made on conjugated organic polymers such as poly(*p*-phenylene)², poly(phenylene sulphide)³, poly(diacetylene)⁴, polythiophene⁵, polypyrrole⁶ and their derivatives. Indeed, conducting polymers have emerged as a new class of electrical/electronic materials⁷. Of these polymers, the heterocyclic polymers are usually prepared in the form of highly conducting polyheterocyclic cations in the process of electrochemical polymerization⁸⁻¹⁰. In particular, highly conductive polypyrrole (PPY) film obtained via the electrochemical oxidation and polymerization of pyrrole and *N*-substituted pyrrole derivatives in the presence of various counteranions and electrolytes have been under intensive investigation^{8,11-13}. The availability of conductive pyrrole polymers in film form from the electrochemical preparation has encouraged us to search for a chemical method of preparation.

Previous attempts by other investigators at the chemical preparation of pyrrole polymers have resulted mainly in insulating materials¹⁴⁻¹⁶. Room-temperature conductivity of the PPY films obtained from the typical chemical oxidation of pyrrole is of the order of $10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$.¹⁶ Moreover, these films are not completely stable in air even at room temperature¹⁶. These initially insulating films can be doped by bromine (Br_2) and iodine (I_2) to achieve stable conductivity values of the order of $10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$.¹⁶ Very recently, Bocchi *et al.*¹⁷ have reported on the chemical polymerization of conducting polypyrrole in aqueous FeCl_3 solution and by various oxidizing agents, such as halogens and other metal salts. In this paper, we report on a relatively simple method for the simultaneous polymerization and doping of pyrrole in the presence of a halogen, such as Br_2 or I_2 . The resulting PPY- I_2 and PPY- Br_2 charge transfer (CT) complexes are quite

conductive and are completely stable in ambient air. The morphology and physicochemical properties of these complexes prepared under various conditions are examined by means of scanning electron microscopy (SEM), u.v.-visible absorption and infra-red (i.r.) absorption spectroscopy, differential scanning calorimetry (d.s.c.), chemical analysis, thermogravimetric analysis (t.g.a.), conductivity (σ) and density measurements.

EXPERIMENTAL

Polymer synthesis and doping

The monomer, pyrrole (Merck, reagent grade), used for the present study was purified by cold vacuum distillation before use. Well cleaned glass equipment was used, but no attempt was made to remove moisture/grease films or other trace impurities. All solvents were of reagent grade and were used as received. All work was carried out in ambient air, unless specified otherwise. The PPY- I_2 CT complexes were synthesized in aqueous dispersion as follows. One gram of solid iodine (sublimed, Aldrich Chemical Co.) was introduced into a 250 cm³ beaker containing about 125 ml of deionized water. Since iodine is only sparingly soluble in water, most of the iodine remains as submerged solids. Then 1.5 ml of pyrrole was introduced onto the surface of the water. The beaker was covered with aluminium foil and kept in the dark either at room temperature or at 4°C for at least 48 h. As pyrrole diffused/dispersed slowly into the aqueous medium, the solution changed gradually from the original pink colour of I_2 to dark green, characteristic of the CT complex formation, and eventually became almost colourless. A thick, black, spongy layer was obtained at the bottom of the beaker. The black spongy material was removed, rinsed thoroughly with copious amounts of methanol, acetonitrile, carbon tetrachloride and 95% ethanol (in that order). It was then soaked in a large excess of absolute ethanol for at least 24 h or boiled in absolute ethanol (78.5°C) for at least 1 h. The soaking or boiling

0032-3861/86/121958-05\$03.00

© 1986 Butterworth & Co. (Publishers) Ltd.

1958 POLYMER, 1986, Vol 27, December

procedure was repeated until no unreacted monomer or acceptor could be detected in the ethanol wash by u.v.-visible absorption spectroscopy. The black porous material was subsequently dried by pumping at a rotary vacuum of 10^{-2} torr for at least 8 h. This black material was later identified to be the PPY-I₂ CT complex (see text). The PPY-I₂ CT complex so produced is spongy and somewhat rubbery in texture. The yield was about 35–40%. Pyrrole was also polymerized in the presence of sulphuric acid initiator according to the method of Salmon¹⁶, except that 0.5 g of iodine was also added to the reaction mixture in the present experiment. The polymer existed as a black swollen gel in the solution. The gel was then removed and washed thoroughly as described above for the preparation of the PPY-I₂ CT complex.

In the synthesis of PPY-Br₂ CT complex, 1 ml of bromine (BDH Chemicals, reagent grade) was dissolved in 50 ml of carbon tetrachloride in a 250 cm³ beaker. Then 75 ml of deionized water was added to form a two-phase system. Monomer (1.5 ml) was introduced on to the top surface of the water layer. The system was covered with aluminium foil and allowed to stand in the dark for at least 60 h. A thick black polymer cake was obtained at the interface between the water and CCl₄ layer. A thin brittle film (black) was also found floating on the water surface. Owing to its thin and brittle nature, the top film was not analysed further. The thick polymer cake was removed from the interface and subjected to a washing sequence as prescribed for the PPY-I₂ complex. It was then soaked in copious amounts of absolute ethanol for a prolonged period of time before being dried in dynamic vacuum. The yield was about 45–50%.

Polymer characterization

The u.v.-visible absorption spectra were measured using a Shimadzu UV-260 spectrophotometer equipped with a microprocessor. The i.r. absorption measurements were carried out on a Perkin-Elmer model 682 spectrophotometer with the polymer dispersed in KBr. SEM micrographs were obtained using a Philips SEM-505 scanning electron microscope. D.s.c. was performed using a Perkin-Elmer model DSC-2C calorimeter with a heating/cooling rate of 10 K min⁻¹ under a constant flow of nitrogen. T.g.a. was performed on a Netzsch model STA 409 simultaneous t.g.-d.t.a. apparatus at a heating rate 10 K min⁻¹ in nitrogen. The composition of the CT complexes was determined by elemental analysis. For electrical conductivity measurements, the polymer samples were pressed into thin circular pellets (about 0.05–0.1 cm in thickness and 1.2 cm in diameter) in a stainless-steel press at a pressure of about 300 kg cm⁻². Electrical conductivities were measured using the standard four-probe and two-probe techniques. Densities of the polymeric complexes at 25°C were determined by the flotation method in an ethanol/tetrabromoethane mixture. The density of the solution mixture was measured using a Paar model DMA 46 calculating digital density meter.

RESULTS AND DISCUSSION

Morphology of the polymeric complexes

Figures 1 and 2 show the respective SEM micrographs of the PPY-I₂ and PPY-Br₂ CT complexes obtained

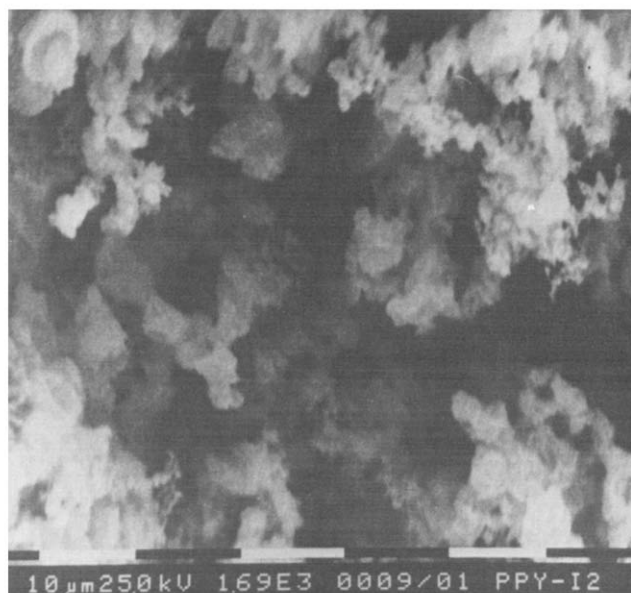


Figure 1 Scanning electron micrograph of PPY-I₂ complex synthesized in aqueous dispersion

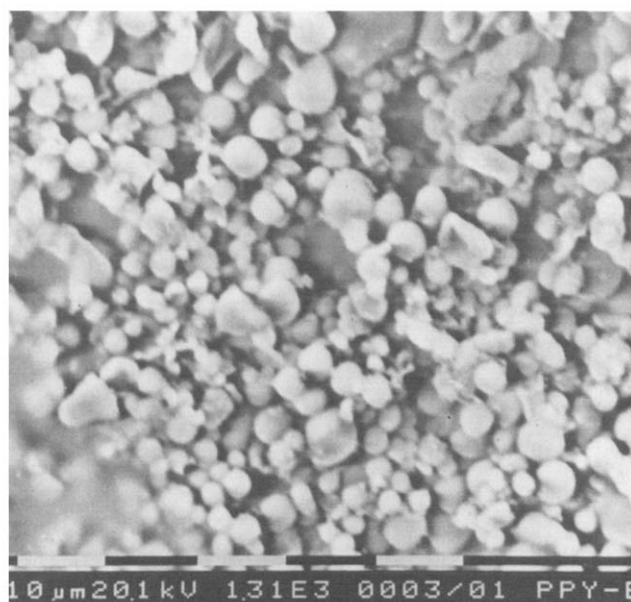


Figure 2 Scanning electron micrograph of PPY-Br₂ complex synthesized in H₂O/CCl₄ two-phase solvent system

from CT polymerization in aqueous media. The PPY-I₂ complex is highly porous and spongelike and is somewhat elastic in texture. Upon crushing and grinding, the spongelike structure disintegrates into granules. The PPY CT complex synthesized in the presence of sulphuric acid initiator according to the method of Salmon¹⁶, but with I₂ also added to the reaction mixture (PPY-I₂S), has only a granular morphology. As shown in Figure 2, the PPY-Br₂ CT complex is composed mainly of loosely packed granules/particulates of about 1 to several micrometres in dimension. The complex also lacks the rubbery texture of the PPY-I₂ complex.

U.v.-visible and infra-red absorption spectra

The u.v.-visible absorption spectra of both the PPY-I₂ and PPY-Br₂ CT complexes reveal two relatively broad bands. One band centres at around 420 nm and is characteristic of polypyrrole^{6,16}. The other intense broad

band which appears in the red and extends well into the near-i.r. region probably results from the CT interaction between the polymer and the dopant, since undoped PPY does not have any appreciable absorption in the near-i.r.¹⁶ The i.r. absorption spectra for the PPY-I₂ and PPY-Br₂ are shown in Figures 3a and 3b, respectively, while that of the PPY-I₂S is shown in Figure 3c. The i.r. spectra in all three cases show a featureless decrease in absorption from 4000 to about 1700 cm⁻¹. This long absorption tail has been assigned to be the tail of an absorption peak located in the near-i.r. for oxidized PPY^{6,18}. The absorption tail precludes the observation of the expected N-H stretching mode absorption between 3300 and 3500 cm⁻¹. However, the bands at about 1540, 1300, 1170, 1030 and 900 cm⁻¹ are all characteristic of PPY¹⁸. Comparison of the absorption spectra between PPY-I₂ and PPY-Br₂ reveals some differences in the relative absorbance of the respective PPY bands. This

probably reflects the difference in the degree of CT interaction between the polymer and the dopant in the two complexes. A small band at around 1700 cm⁻¹ can be clearly seen in PPY-Br₂ and PPY-I₂S (but less so in PPY-I₂) and is probably due to the presence of the pyrrolidinone carbonyl group, the presence of which has been reported for chemically synthesized PPY¹⁵. Finally, the bands at 1110 and 610 cm⁻¹ for the PPY-I₂S spectra (Figure 3c) are characteristic of the sulphate anion¹⁶.

Chemical compositions and electrical properties

Results of the elemental analyses of the PPY-halogen CT complexes produced under various experimental conditions and their respective electrical conductivities are summarized in Table 1. The elemental analysis data indicate that the CT complexes are primarily polymerized pyrrole units plus the halogen dopant.

For the PPY-I₂ CT complex, there is no significant difference between the sample polymerized at room temperature and that at 4°C, as far as chemical compositions are concerned, although low-temperature polymerization appears to give a somewhat higher conductivity. Re-exposure of a well washed PPY-I₂ complex to I₂ vapour can result in further uptake of the dopant (sample 3). However, no significant increase in conductivity was observed and the sample lost the excess iodine gradually when exposed again to the ambient air. Thus, the ratio of about four pyrrole units to one molecule of I₂ in samples 1 and 2 may represent the stable, optimum stoichiometric composition for the PPY-I₂ CT complex. The result has been further confirmed by thermal analysis (see below). The ratio of about 3-4 pyrrole units to one anion has also been reported for a number of PPY-anion salt complexes obtained from electrochemical polymerization^{6,11}. Polymerization of PPY in the simultaneous presence of H₂SO₄ and I₂ (sample 4) results in the uptake of about 0.18 moles of sulphate ion for every mole of pyrrole, a value comparable with that reported for the chemical polymerization of pyrrole by H₂SO₄ alone¹⁶. However, the uptake of sulphate ion has greatly reduced the amount of I₂ incorporation. As a result, a substantially lower conductivity than that of the PPY-I₂ complex was observed for the PPY-I₂S CT complex.

In the case of PPY-Br₂ complex, the conductivity is lower than that of the PPY-I₂ CT complex by about an order of magnitude. The stable, optimum stoichiometric composition for the PPY-Br₂ complex corresponds to a pyrrole:Br₂ ratio of about 2.3:1. This pyrrole:Br₂ ratio is comparable to that found in the bromine-doped complex, using an originally insulating PPY film obtained from chemical polymerization in the presence of an acid

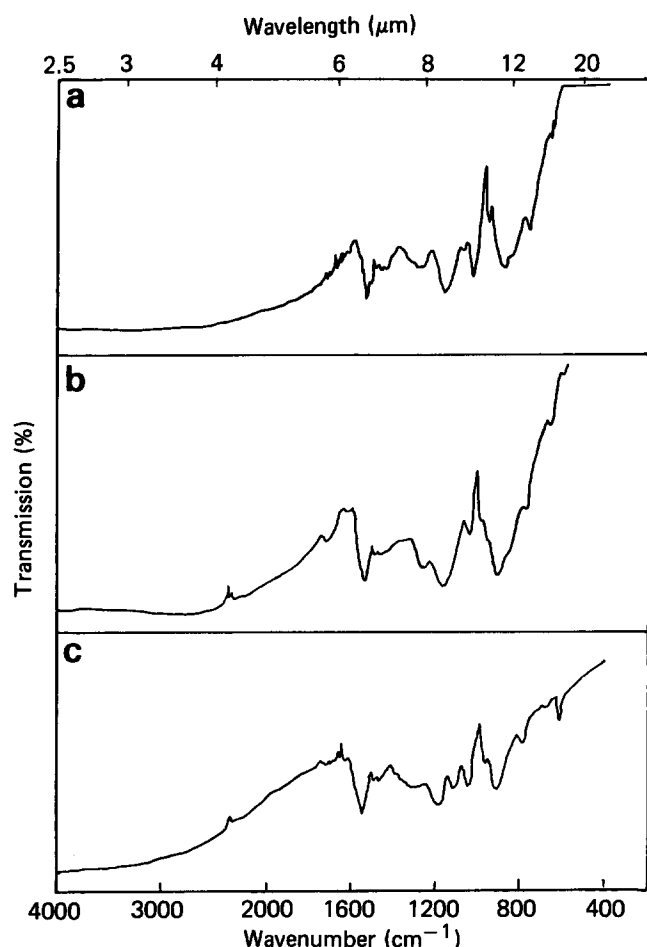


Figure 3 Infra-red absorption spectra of (a) PPY-I₂ complex, (b) PPY-Br₂ complex and (c) PPY-I₂S complex

Table 1 Chemical composition and electrical conductivity of the PPY-I₂ and PPY-Br₂ complexes

| Sample no. | System | Polymerization medium | Chemical composition (normalized to 1.0N) | Conductivity σ (ohm ⁻¹ cm ⁻¹) at 27°C |
|------------|---------------------------------|--|--|---|
| 1 | PPY-I ₂ | H ₂ O, 27°C | C _{4.1} H _{2.6} N _{1.0} O _{1.0} (I ₂) _{0.25} | 7 |
| 2 | PPY-I ₂ | H ₂ O, 4°C | C _{4.1} H _{2.7} N _{1.0} O _{0.95} (I ₂) _{0.26} | 8 |
| 3 | PPY-I ₂ ^a | H ₂ O, 27°C | C _{4.0} H _{2.3} N _{1.0} O _{1.1} (I ₂) _{0.44} | 8 |
| 4 | PPY-I ₂ S | H ₂ O/H ₂ SO ₄ , 27°C | C _{4.2} H _{3.1} N _{1.0} O _{1.1} (SO ₄) _{0.18} (I ₂) _{0.02} | 10 ⁻¹ |
| 5 | PPY-Br ₂ | H ₂ O/CCl ₄ , 27°C | C _{4.3} H _{3.1} N _{1.0} O _{1.2} (Br ₂) _{0.44} | 5 × 10 ⁻¹ |
| 6 | PPY-I ₂ ^b | H ₂ O, 27°C | - | 3 × 10 ⁻⁶ |

^a Obtained by re-exposure of a well washed, stable PPY-I₂ CT complex to an I₂ atmosphere

^b PPY-I₂ sample exposed to 5 M NH₄OH solution for 36 h

catalyst alone¹⁶. For comparison, the latter has a ratio of about 2.2 pyrrole units to one molecule of bromine.

The oxygen content in all samples was determined by difference. They are comparable to that of the PPY produced by the chemical oxidation of pyrrole¹⁶. This suggests, therefore, the presence of a substantial amount of pyrrolidinone structure¹⁵ in the present polymeric complexes. Furthermore, we cannot exclude the possibility that the polymer samples have also been doped, to a small extent, by oxygen, as in the case of neutral and oxidized PPY films obtained from electrochemical polymerization⁶. The H mole ratio in the PPY-I₂ CT complex is substantially below the theoretical value of 3 to justify the primarily α,α' linkages of the pyrrole moiety⁶. The deficiency in H may serve to indicate the simultaneous presence of α and β linkages for some of the pyrrole units of this complex, probably as a result of crosslinking or chain branching. However, the C:H:N ratio for the PPY-Br₂ CT complex is close to the expected ratio for a long linear chain of disubstituted pyrrole rings, i.e. 4:3:1.

We wish to emphasize that both the PPY-I₂ and PPY-Br₂ CT complexes synthesized by the present method are stable in the atmosphere. The electrical conductivity in both cases shows only a weak temperature dependence, at temperatures above room temperature, and remains relatively stable up to about 150°C in the case of PPY-I₂ complex and about 120°C in the case of PPY-Br₂ complex (see below). However, a substantial loss in conductivity ($>10^6$) was observed when the PPY-I₂ CT complex was contacted with 5 M NH₄OH solution for about 36 h (sample 6). This compensation behaviour is not unlike that of other conjugated polymers, such as polyacetylene¹⁹ or polyphenylacetylene²⁰, doped with electron acceptors.

The densities of the PPY-I₂ (sample 1) and PPY-Br₂ (sample 5) complexes produced via the present CT polymerization technique were determined, using the flotation method in ethanol/tetrabromoethane mixture, to be 1.99 g cm⁻³ and 1.78 g cm⁻³, respectively.

Thermal properties

The d.s.c. scans of the PPY-I₂ and PPY-Br₂ CT complexes are shown in Figure 4. The scan for the PPY-I₂ CT complex does not show any obvious transition between 30 and 250°C, consistent with the scans reported for the PPY obtained from electrochemical polymerization¹⁸, except for the presence of an exothermic reaction, barely visible between 110 and 150°C, and a relatively sharp endothermic peak at about 183°C in the present sample. It is interesting to note that the peak at 183°C not only coincides with the boiling point of iodine (184°C) but also corresponds to the onset of major weight loss for the PPY-I₂ CT complex (see t.g.a. data below). Thus, the endothermic peak at 183°C may be associated with the physical vaporization or removal of I₂ from the PPY-I₂ CT complex. The conclusion is further supported by the fact that in the second heating, after the sample is allowed to cool from 250°C to room temperature, the scan becomes featureless. The thermal response of the PPY-Br₂ CT complex is somewhat more complicated. The d.s.c. scan is featureless at the boiling point of Br₂ (59°C), but shows a relatively broad exothermic peak centred at about 140°C and a superficial transition at about 197°C. The exothermic process is irreversible and

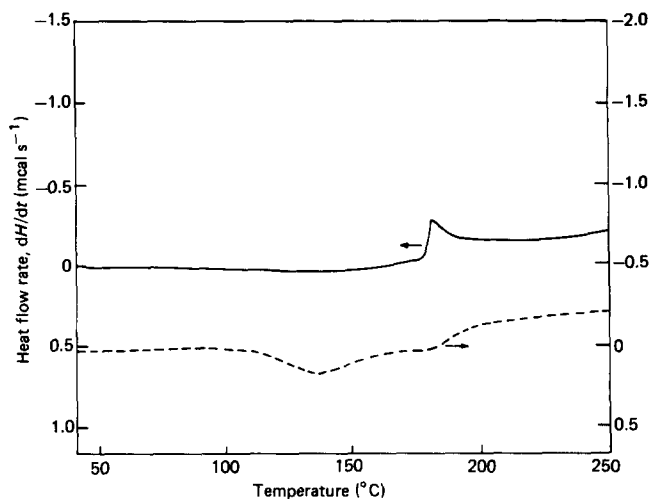


Figure 4 D.s.c. scans of PPY-I₂ (—) and PPY-Br₂ (---) complexes prepared at 27°C

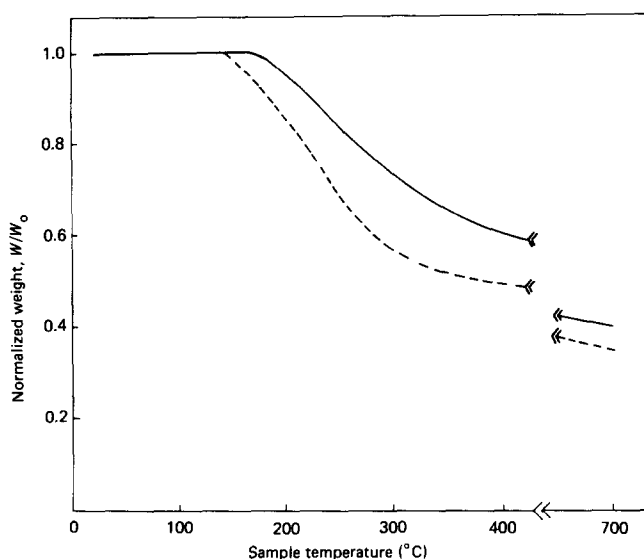


Figure 5 Thermogravimetric scans of PPY-I₂ (—) and PPY-Br₂ (---) complexes prepared at 27°C

does not recover when the sample is cooled. The temperature of this exothermic peak at about 140°C also corresponds to the onset of major weight loss in t.g.a. (see below). Thus, this exothermic process may be associated with the thermal decomposition reaction of the PPY-Br₂ complex.

The thermogravimetric scans in nitrogen of the PPY-I₂ and PPY-Br₂ CT complexes from room-temperature polymerization are shown in Figure 5. Both complexes suffer only about 65–70% loss of their original weight when heated from room temperature to a temperature as high as 750°C. The PPY-I₂ complex is stable to heating up to slightly above the vaporization temperature of iodine (184°C), when it begins to lose weight gradually. For scans carried out in air, the complex also exhibits the same thermal stability below 184°C. Similarly, the PPY-Br₂ complex is thermally stable up to the decomposition temperature of about 140°C. In both cases, the weight losses are associated with a loss in electrical conductivity. The thermal stability of the present PPY-halogen CT complex differs significantly from the thermal behaviour of most of the halogen-doped conducting polymers, obtained in the conventional solid-gas phase interactions. Iodine-doped polyacetylene, for example,

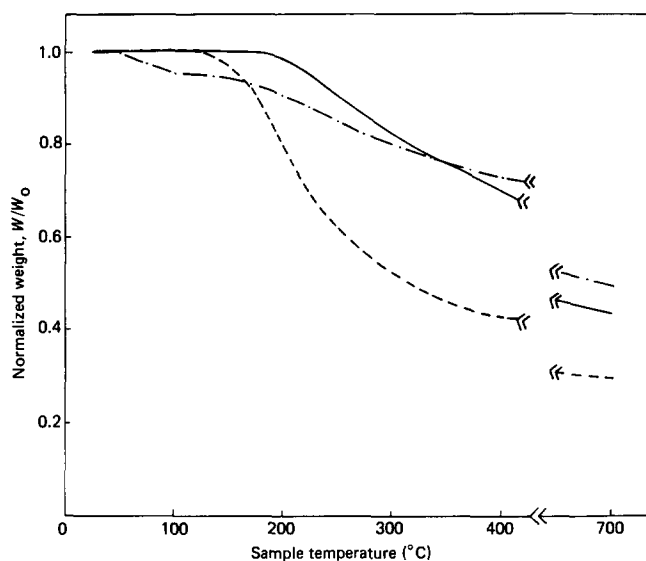


Figure 6 Thermogravimetric scans of PPY-I₂ complex prepared at 4°C (—), PPY-I₂ complex with excess I₂ (---) and PPY-I₂S complex (- · - · -)

shows a rather poor thermal stability and suffers a weight loss immediately upon heating above room temperature²¹. The thermal instability of the polyacetylene-iodine complex may readily result from the morphological complexity of the pristine polymer and the chemical and physical heterogeneity usually associated with the vapour-phase doping²². Thus, the PPY-I₂ and PPY-Br₂ CT complexes obtained from the present CT polymerization technique must be of greater chemical and physical homogeneity, as a result of more uniform interaction between the dopant and the polymer.

For comparison, Figure 6 shows the t.g.a. scans in nitrogen of the PPY-I₂ CT complex synthesized at 4°C, the PPY-I₂S CT complex and the PPY-I₂ CT complex with 'excess' iodine obtained through further contact of a 'stoichiometric' PPY-I₂ complex with I₂ vapour (sample 3, Table 1). The thermal behaviour of the PPY-I₂ CT complex prepared at 4°C is similar to that prepared at room temperature. However, for the PPY-I₂ sample with 'excess' iodine, the weight loss commences at a temperature as low as 115°C, with a more substantial loss occurring after 180°C. This observation readily indicates that for a PPY-I₂ CT complex with an I₂/pyrrole mole ratio greater than 0.25, the excess iodine molecules are only loosely complexed with the polymer. The PPY-I₂S complex loses initially about 5% of its weight when heated to above 60°C, followed by a major decomposition reaction at about 180°C. However, among all the complexes studied, it suffers the least total weight loss when exposed to high temperature. In fact, the PPY-I₂S complex still retains almost 50% of its original weight when heated to a temperature as high as 750°C. Finally, we wish to point out that the gradual weight loss observed among the present PPY-halogen CT complexes differs somewhat from that of PPY films obtained from electrochemical polymerization. The latter show a much more rapid weight loss when heated above the decomposition temperature¹⁸.

CONCLUSIONS

A relatively simple method has been found for the simultaneous chemical synthesis and doping of polypyrrole in aqueous media and in the presence of a halogenic electron acceptor, such as bromine or iodine. The lone pair of electrons on the pyrrole nitrogen might have made the molecule sufficiently electron donating to facilitate partial electron transfer to the halogenic electron acceptor, the pyrrole moiety becoming simultaneously sufficiently polarized for polymerization of the monomer to occur. Presumably the ionic nature of this interaction is not affected to a significant extent by the protic character of the aqueous media, since halogens are only sparingly soluble and solvation of the anions may be minimal. The polymer-dopant CT complexes so produced are of good thermal stability. The PPY-I₂ CT complex is spongelike and somewhat rubbery in texture and has a conductivity of the order of 10¹ ohm⁻¹ cm⁻¹. The PPY-Br₂ CT complex is granular in nature and has a conductivity of about 0.5 ohm⁻¹ cm⁻¹. Both complexes show remarkable stability in the atmosphere. The same CT polymerization techniques are currently being explored for the synthesis of other conducting polyheterocyclics in our laboratory.

REFERENCES

- Chiang, C. K., Fincher, C. R., Jr, Park, Y. K., Heeger, A. J., Shirakawa, H., Louis, E. J., Gau, S. C. and MacDiarmid, A. G. *Phys. Rev. Lett.* 1977, **39**, 1098
- Street, G. B. and Clarke, T. C. *IBM J. Res. Dev.* 1981, **25**, 51
- Robalt, J. F., Clarke, T. C., Kanazawa, K. K., Reynolds, J. R. and Street, G. B. *J. Chem. Soc., Chem. Commun.* 1980, 347
- Block, H. *Adv. Polym. Sci.* 1979, **33**, 94
- Kaneto, K., Yoshino, K. and Inuishi, Y. *Solid State Commun.* 1983, **46**, 389
- Street, G. B., Clarke, T. C., Krounbi, M., Kanazawa, K., Lee, V., Pfluger, P., Scott, J. C. and Weiser, G. *Mol. Cryst. Liq. Cryst.* 1982, **83**, 253
- De Young, H. G. *High Tech.* 1983, **3**(1), 65
- Diax, A. F. *Chem. Sci.* 1981, **17**, 145
- Tourillon, G. and Garnier, F. J. *Electroanal. Chem.* 1982, **135**, 173
- Bargon, J., Mohmand, M. and Waltman, R. *IBM J. Res. Dev.* 1983, **27**, 330
- Kanazawa, K. K., Diaz, A. F., Geiss, R. H., Gill, W. D., Kwak, J. F., Logan, J. A., Rabolt, J. F. and Street, G. B. *J. Chem. Soc., Chem. Commun.* 1979, 854; Diaz, A. F., Kanazawa, K. and Gardini, G. P. *J. Chem. Soc., Chem. Commun.* 1979, 635
- Diaz, A. F. and Castillo, J. I. *J. Chem. Soc., Chem. Commun.* 1980, 397
- Diaz, A. F., Castillo, J. I., Logan, J. A. and Lee, W. Y. *J. Electroanal. Chem.* 1981, **129**, 115
- Gardini, G. P. *Adv. Heterocycl. Chem.* 1973, **15**, 67
- Jones, R. A. and Been, G. P. 'The Chemistry of Pyrroles', Academic Press, San Francisco, 1977
- Salmon, M., Kanazawa, K. K., Diaz, A. F. and Krounbi, M. J. *Polym. Sci., Polym. Lett. Edn.* 1982, **20**, 187; Nalwa, H. S., Dalton, L. R., Schmidt, W. F. and Rabe, J. G. *Polym. Commun.* 1985, **26**, 240
- Bocchi, V. and Gardini, G. P. *J. Chem. Soc., Chem. Commun.* 1986, 148
- De Paoli, M. A., Waltman, R. J., Diaz, A. F. and Bargon, J. J. *Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 1687
- Clarke, T. C. and Street, G. B. *Synthetic Metals* 1979/80, 119
- Kang, E. T. *Eur. Polym. J.* 1985, **21**, 919
- Osterholm, J. E., Yasuda, H. K. and Levenson, L. L. *J. Appl. Polym. Sci.* 1983, **28**, 1265
- Tomkiewicz, Y., Schultz, T. D., Brown, H. B., Clark, T. C. and Street, G. B. *Phys. Rev. B* 1981, **23**, 5137