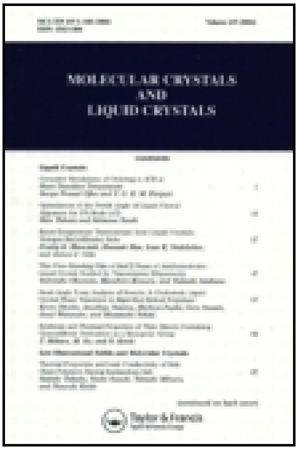

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# Chemical Polymerization and Oxidation of Pyrrole by Halobenzoquinones

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# Chemical Polymerization and Oxidation of Pyrrole by Halobenzoquinones

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The halobenzoquinones, *p*-fluoranil, *p*-chloranil and *o*-bromanil have been successfully used for the simultaneous chemical polymerization and oxidation of pyrrole. The electrical conductivity ($\sigma$) of the polypyrrole(PPY)-*p*-chloranil complex is about 2-10 S/cm while ($\sigma$) for the PPY-*p*-fluoranil and PPY-*o*-bromanil complexes is in the range of $10^{-3}$-$10^{-2}$ S/cm. XPS measurements indicate the presence of halogen anions in all three PPY-halobenzoquinone complexes and that the oxidation process may have proceeded further than pure molecular charge transfer complex formation. The physicochemical properties of these complexes are reported in some detail.

*Keywords: polymerization and oxidation, halobenzoquinones, pyrrole, electroactive*

## INTRODUCTION

One of the most promising conducting polymer systems appears to be polypyrrole (PPY) and related polyheterocycles. In particular, PPY complexes, such as PPY-$BF_4$, obtained via the electrochemical oxidation and polymerization are highly conductive and relatively stable.[1-4] Chemical methods of preparation with acid or peroxide initiators have resulted in fairly oxidative insulating materials with room temperature electrical conductivity ($\sigma$) typically in the order of $10^{-11}$ S/cm.[5] The initially insulating PPY films can be doped with halogenic electron acceptors such as bromine and iodine to achieve conductivity of the order of $10^{-5}$ S/cm.[5] PPY films with $\sigma$ in the order of 10 S/cm have been synthesized chemically in the presence of a Lewis acid catalyst, such as $FeCl_3$ and $RuCl_3$.[6-8] We have recently described a relatively simple and novel method for simultaneous chemical polymerization and oxidation of pyrrole by halogens[9] and by the organic electron acceptors, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone(DDQ) and tetrachloro-*o*-benzoquinone (*o*-

chloranil).[10] The PPY-complexes so produced have electrical conductivity and conduction behaviour comparable to those prepared electrochemically or in the presence of a Lewis acid. Accordingly, the chemical polymerization and oxidation of pyrrole have been extended to include three other halobenzoquinones: tetrafluoro-*p*-benzoquinone(*p*-fluoranil), tetrachloro-*p*-benzoquinone(*p*-chloranil) and tetrabromo-*o*-benzoquinone(*o*-bromanil). The physicochemical properties of these PPY-halobenzoquinone complexes are characterized by elemental analysis, X-ray photoelectron spectroscopy (XPS), infrared (IR) absorption spectroscopy, thermogravimetric (TG) analysis and electrical conductivity measurements. The results from this work together with the earlier data on PPY-*o*-chloranil complex should provide a detailed representation of chemically synthesized PPY-halobenzoquinone complexes.

## EXPERIMENTAL

### Polymer Synthesis and Oxidation

Pyrrole monomer (Merck, reagent grade) used in the present studies was purified by distillation under reduced pressure. All solvents were of reagent grade and were used as received. The organic acceptors were obtained from Aldrich Chemical Co. and were recrystallized from appropriate solvents before use. PPY-acceptor complexes were synthesized in the bulk by reacting pyrrole directly with the acceptor under a nitrogen atmosphere, and with vigorous agitation according to the method used for the synthesis of PPY-DDQ and PPY-*o*-chloranil complexes.[10] The reaction mixture turned dark almost instantaneously and, depending on the nature of the acceptor and its concentration, the reaction might be quite violent. In all cases, the reaction mixture was cooled in a water bath. A black precipitate was formed and after at least 12 hours, the precipitate was washed with copious amount of organic solvents to remove the excess reactants. The powdery precipitate was then dried under dynamic vacuum for about 4 hours.

### Polymer Characterization

The chemical compositions of the polymeric complexes were determined by elemental analysis. XPS measurements of the various PPY-acceptor complexes were made on a VG Scientific ESCALAB MkII spectrometer with a MgKα X-ray source (1253.6 eV photons). The polymer samples in powder form were mounted on the standard sample studs by using double-sided adhesive tape. All core-level spectra were referenced to the Cls neutral carbon peak at 284.6 eV. From the XPS measurements, the stoichiometry of the acceptor at the surface of each complex can also be determined from the ratios of the spectral areas after correction with the appropriate elemental sensitivity factor. 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 in diameter, and both standard four-probe and two-probe methods were used. For the more conductive samples, the temperature dependence of electrical conductivity was also determined using a liquid nitrogen cryostat. The heating rate used was about 1°C/min. The IR absorption measurements were carried out on a Perkin-Elmer Model 682 spectrophotometer with the polymer samples dispersed in KBr pellets. TG scans were carried out using a Netzsch simultaneous TG-DTA apparatus, Model STA 409, at a heating rate of 10°C/min in nitrogen.

## RESULTS AND DISCUSSION

### Chemical Composition and XPS Measurements

It was found that the product yield, based on the initial monomer concentration, increased with the acceptor:monomer mole ratio in the reaction mixture. However, a high acceptor:monomer ratio has the tendency of resulting in non-uniform and inhomogeneous reactions, since all of the present bulk polymerization and oxidation reactions are rather rapid and somewhat violent in nature. Thus, a low acceptor:monomer ratio (0.2:1 or less) is usually preferred. For a particular initial acceptor:monomer ratio, the yield for the PPY-*p*-chloranil complex is always substantially lower than the PPY-*o*-bromanil and PPY-*p*-fluoranil complexes. Elemental analysis of the complexes indicate the following compositions: for PPY-*p*-fluoranil complex, $C_{4.2}H_{3.0}H_{1.1}(C_6F_4O_2)_{0.19}$; for PPY-*p*-chloranil complex, $C_{4.2}H_{2.7}N_{1.0}(C_6Cl_4O_2)_{0.25}$; and for PPY-*o*-bromanil complex, $C_{4.2}H_{2.8}N_{1.0}(C_6Br_4O_2)_{0.24}$. The stoichiometry of one acceptor molecule to 4-5 pyrrole units is consistent with those of the PPY-*o*-chloranil and PPY-DDQ complexes[10] and other oxidized PPYs, synthesized either chemically[8,9] or electrochemically.[1-3] The surface stoichiometries for the PPY-*p*-fluoranil and PPY-*o*-bromanil complexes as determined from XPS measurements agree fairly well with the bulk values. This is not so for the PPY-*p*-chloranil complexes which appear to have a slightly higher acceptor concentration at the surface as compared to the value for the bulk. Since the interaction between PPY and the halobenzoquinones has probably proceeded further than pure molecular charge transfer complex formation (see below), no attempts were made to study the structure of undoped PPY.

The XPS halogen core-level spectra of the PPY-halobenzoquinone complexes are given in Figure 1. Each spectrum can be deconvoluted into two major components with a shake-up satellite at the high binding energy tail. For each spectrum, the largest peak (e.g. the peak at about 200 eV for the Cl2p spectrum) is assigned to the covalently bonded halogen while the smaller peak at lower binding energy is attributable to the halogen anion. The O1s XPS core-level spectra for all complexes also reveal a peak component which is shifted about −1.5 eV from the neutral carbonyl peak at about 532 eV and is probably attributable to the benzoquinone anion. This appears to be consistent with the IR absorption data (see below). However, one cannot rule out also the contribution from the dopant oxygen to this low binding energy component, as the low oxidation potential of PPY would cause it to oxidize readily in the air.[4] The total fraction of anionic species is the largest in the PPY-*p*-chloranil complex. This may partially account for the higher conductivity (see below) of this sample as compared to PPY-*p*-fluoranil and PPY-*o*-bromanil. The $\sigma$ of this PPY-*p*-chloranil complex is also higher than that of the

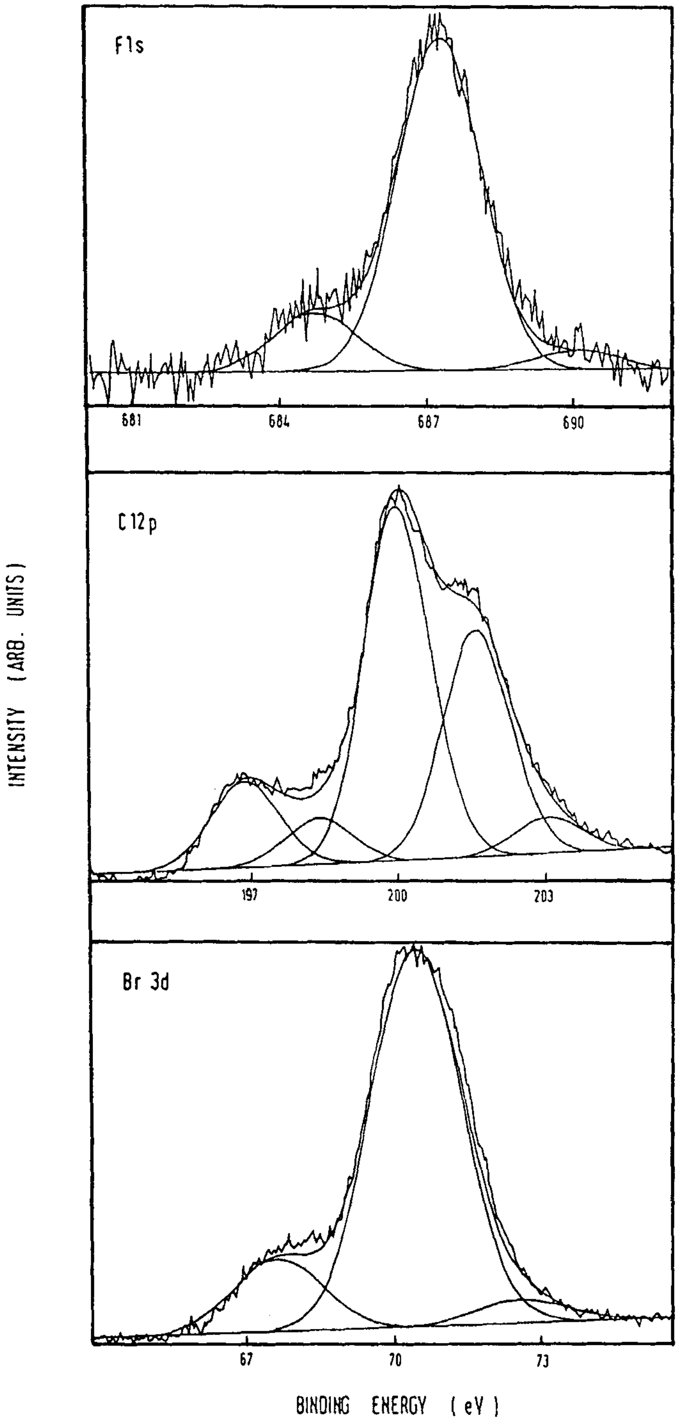

FIGURE 1 XPS halogen core-level spectra for (a) PPY-*p*-fluoranil (b) PPY-*p*-chloranil and (c) PPY-*o*-bromanil complexes.

PPY-*o*-chloranil complexes reported earlier,[10,11] probably for the same reason. The presence of halogen anions suggests that some cleavage of the C—Cl, C—Br and C—F bonds of the acceptors must have occurred, with possible formation of new linkages between the sites of cleavage and pyrrole. The N1s XPS core-level spectra of the samples are skewed substantially towards the high binding energy side and is consistent with the presence of positively charged nitrogen. In the charge transfer interactions involving pyridine and *p*-chloranil, the presence of chloride anions and pyridinium cations has been attributed to the formation of linkages between positively charged pyridinium nitrogen atoms and the C atoms of the acceptor at the sites of cleavage.[12]

### The Absorption Spectroscopy

The IR absorption spectra for the PPY-*p*-fluoranil, PPY-*p*-chloranil and PPY-*o*-bromanil complexes are shown in Figure 2(a), (b) and (c) respectively. These spectra are consistent with the presence of a linear chain of $\alpha$, $\alpha'$-disubstituted pyrrole rings[13] and the absorption bands at about 1540, 1300, 1180, 1040 and 900 $cm^{-1}$ are all characteristic of oxidized PPY.[10,13] The presence of strong 1040 $cm^{-1}$ peak attributable to $C_\beta$—H vibration[13] in each of these spectra indicates that the acceptors do not interact to a significant extent with the $\beta$-carbons of the pyrrole unit. These spectra also show a featureless decrease in absorption from 4000 to 1800 $cm^{-1}$ and this decrease has been assigned to the tail of the absorption peak located in the near-IR for oxidized PPY.[14,15] With the exception of a weak absorption band at about 1700 $cm^{-1}$ and attributable to the residual C=O group, there is an absence of bands due to the halobenzoquinones in these spectra. This is similar to the spectra reported for other PPY-organic acceptor complexes[10] and for electrochemically oxidized PPY,[14] and is consistent with the presence of strong charge transfer interactions.[16] Furthermore, a substantial reduction in the carbonyl absorption is probably consistent with the formation of benzoquinone anion.[17]

### Electrical Conductivity

Of the three halobenzoquinones used in the present work, the PPY-*p*-chloranil complex exhibits the highest electrical conductivity. The electrical conductivity of the complex synthesized with a large excess of pyrrole (monomer:acceptor ratio of 1:0.017) is about 2 S/cm. This value is about three orders of magnitude higher than that of the corresponding PPY-*o*-chloranil complex.[10] The conductivity of the PPY-*p*-chloranil complex can be increased to about 10 S/cm by using a substantially higher acceptor to monomer ratio in the reaction mixture, but the complex becomes less stable. The conductivity of the PPY-*p*-fluoranil and PPY-*o*-bromanil complexes is about $10^{-2}$ and $5 \times 10^{-3}$ S/cm respectively and hence is closer to the value obtained for the PPY-*o*-chloranil complex.[10]

The electrical conductivity of the complexes does not seem to be directly related to the complexing ability of the acceptors. Among the halobenzoquinone acceptors studied, the complexing ability decreases in the order DDQ > fluoranil > chloranil > bromanil.[16] Furthermore, although fluoranil, bromanil and chloranil have about the same reduction potential, the reduction potential of DDQ is substantially lower.[18]

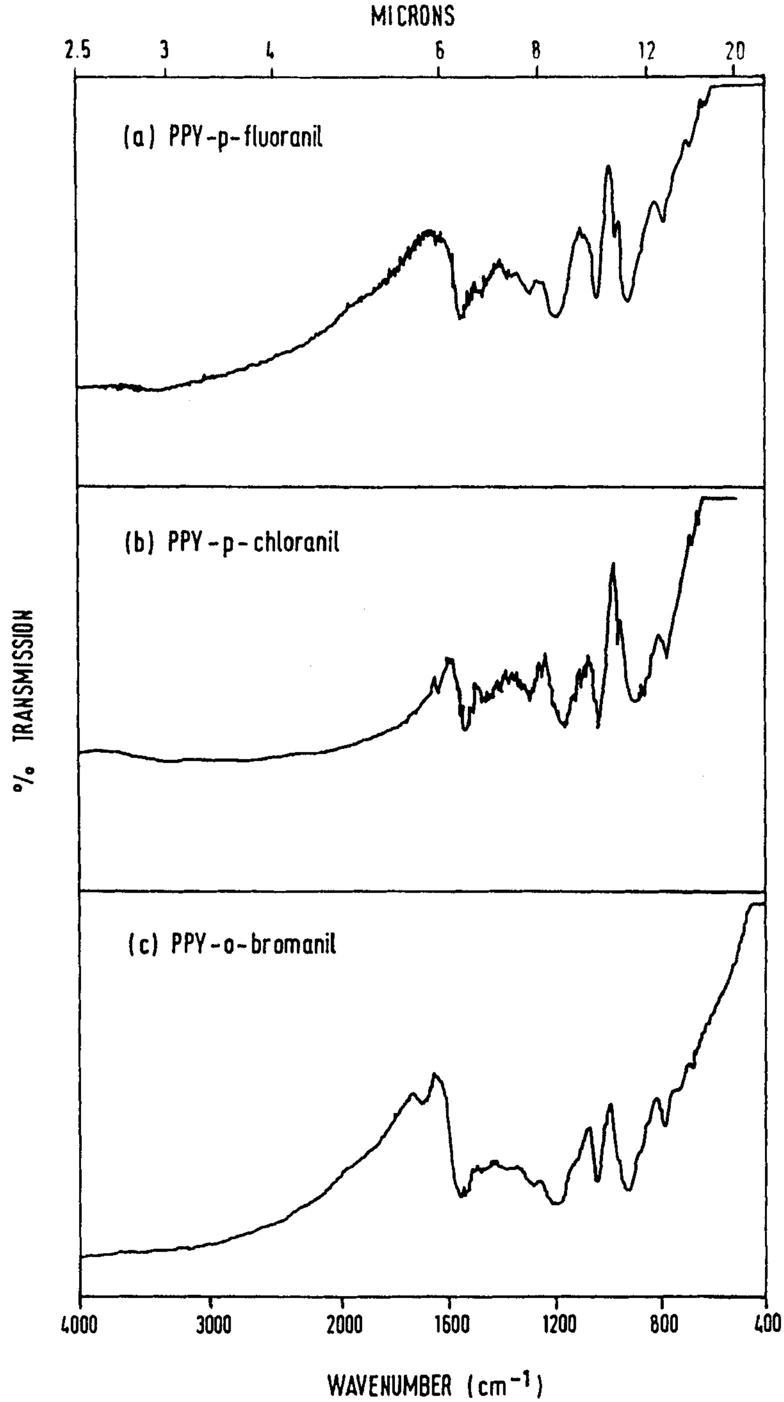

FIGURE 2 IR absorption spectra of (a) PPY-*p*-fluoranil (b) PPY-*p*-chloranil and (c) PPY-*o*-bromanil complexes.

On the other hand, $\sigma$ of the PPY-halobenzoquinone complexes decreases in the order PPY-*p*-chloranil > PPY-DDQ > PPY-*p*-fluoranil > PPY-*o*-bromanil, PPY-*o*-chloranil. This can probably be attributed to the fact that all the halobenzoquinone acceptors have undergone chemical reactions with the polymer beyond the formation of pure charge transfer complexes, as suggested by the cleavage of the halogens from the acceptors to form halogen anions. The difference in the nature and extent of these reactions can be expected to influence the electrical conductivity of the resulting complex.

The ln $\sigma$ vs $T^{-1/4}$ plot for the PPY-*p*-chloranil complex near and below room temperature as obtained from four-probe conductivity measurements is shown in Figure 3. An apparent linear fit of the experimental data is obtained throughout the temperature range of 150 to 300 K. This behaviour has also been widely observed in electrochemically polymerized and oxidized PPY films.[13,15] as well as in chemically synthesized PPY-halogen complexes.[9] Based on these results, the conduction mechanism in PPY has been interpreted in terms of Mott's model[19] of variable range hopping between localized states near the Fermi surface. In view of the recently reported inadequacy of the ordinary four-probe conductivity measurements in overcoming the interfibrillar, intergranular and intercrystallitic contact

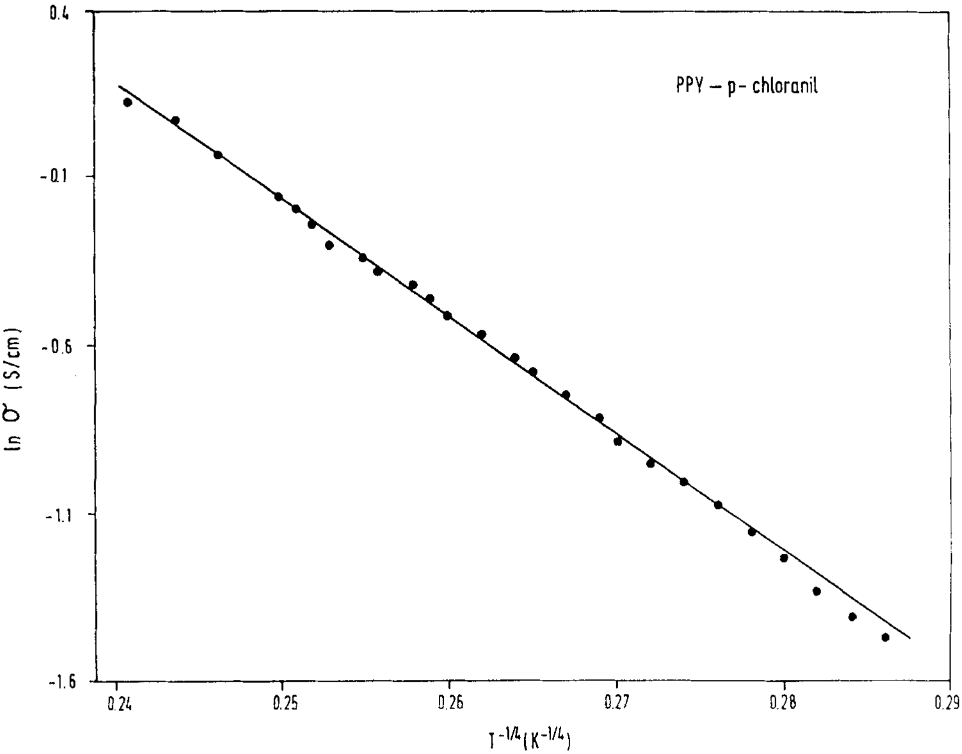

FIGURE 3 Temperature dependence of the electrical conductivity of PPY-*p*-chloranil complex in four-probe conductivity measurements.

resistance of the polymer samples with metallic conductivity,[20,21] the physical significance of the $T^{-1/4}$ dependence in the present complex can be fully interpreted only in the presence of more substantial solid state experimental data.

### Thermogravimetric Analysis

The TG scans of the PPY-halobenzoquinone complexes are shown in Figure 4. The PPY-*p*-fluoranil complex shows a slow but steady weight loss immediately upon heating, whereas, the PPY-*p*-chloranil complex and the PPY-*o*-bromanil complex show a small initial weight loss followed by a plateau and then another weight loss step commencing at about 200°C. The larger initial weight loss of the PPY-*p*-fluoranil complex reflects its lower degree of stability upon heating, since *p*-fluoranil sublimes readily even at room temperature. At 700°C the PPY-*p*-chloranil complex still retains about 60% of the original weight. A much smaller amount of residue is obtained with the PPY-*o*-bromanil complex and this is probably associated with

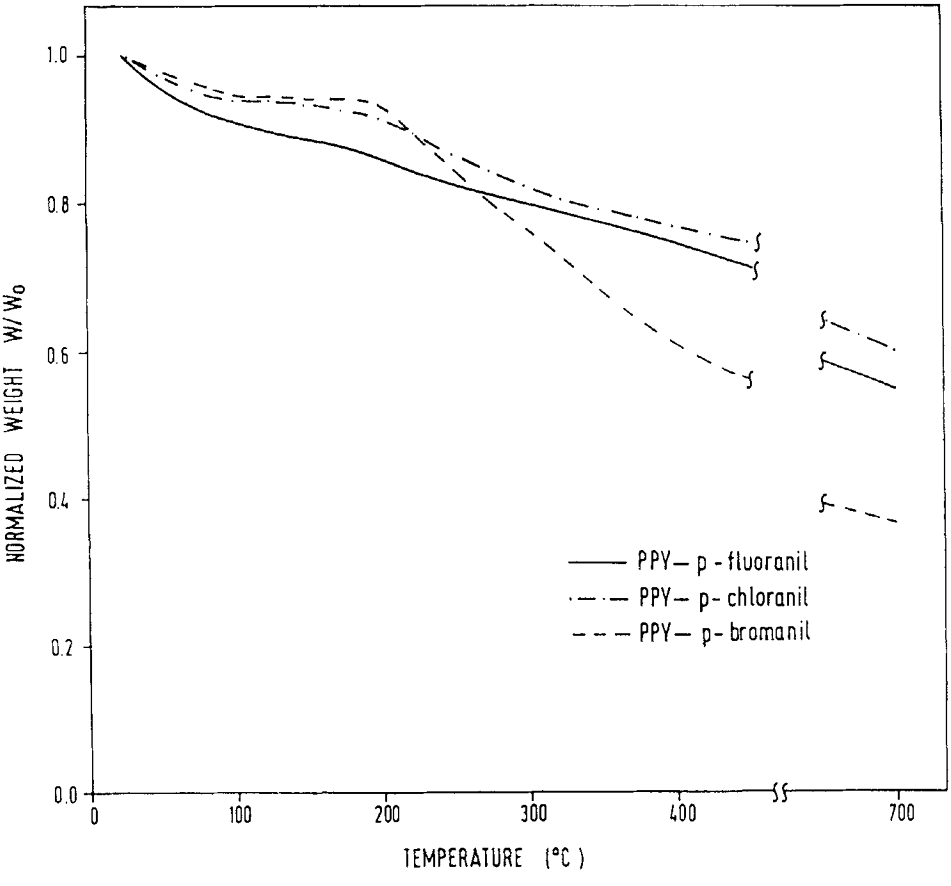

FIGURE 4 Thermogravimetric scans of PPY-*p*-fluoranil, PPY-*p*-chloranil and PPY-*o*-bromanil complexes.

the higher weight fraction of acceptor incorporated into the complex. The weight loss behavior observed in all of the present complexes, especially the high proportion of materials retained at high temperature, is grossly similar to that of other chemically prepared PPY-organic acceptor complexes.[10] Finally, the weight loss behavior observed appear to be also consistent with a degradation mechanism thereby the acceptor species, especially the loosely complexed ones, are gradually removed or dissociated from the polymer complex when heated above room temperature.

## CONCLUSION

The relatively simple method used for the simultaneous chemical polymerization and oxidation of pyrrole by *o*-chloranil[10] has been extended to three other halobenzoquinones:*p*-chloranil, *p*-fluoranil and *o*-bromanil. The PPY-halobenzoquinone complexes so produced are semiconductive in nature. The PPY-*p*-chloranil complex exhibits a conductivity of at least 2 S/cm, which is substantially higher than those of the other PPY-halobenzoquinone complexes. XPS analysis shows that a significant fraction of the halogen in each complex exists as negatively charged anionic species and suggests the formation of linkage between the pyrrole and acceptor. The nature of the acceptor also affects the fraction of halogen present as anions and the thermal stability of the complex.

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