

Effects of Acceptor Level on Chemically Synthesized Polypyrrole-Halogen Complexes

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Synopsis

Electrically conductive polypyrrole (PPY)-halogen complexes have been synthesized by simultaneous chemical polymerization and oxidation of pyrrole. The ratio of pyrrole monomer to halogen (chlorine, bromine, or iodine) used in the synthesis was varied and the physicochemical and electrical properties of the resulting complexes were studied in detail. With all three halogens, the yield of the complex is affected by the initial amount of halogen used, with the properties of the polypyrrole-bromine complex showing the strongest dependence on the acceptor level. For this complex, both the percentage of bromine incorporated and the ratio of covalent to ionic bromide increase upon increasing the initial bromine concentration, while the electrical conductivity shows a maximum. Experimental evidence suggests that some halogen substitution at the pyrrole ring must have occurred in the PPY-Br₂ and PPY-Cl₂ complexes, but not in the PPY-I₂ complex.

INTRODUCTION

Electrically conductive materials derived from pyrrole usually have been prepared by electrochemical polymerization¹⁻⁴ or by chemical synthesis in the presence of an acid or peroxide initiator.^{5,6} In the case of electrochemically oxidized polypyrrole (PPY) films, a wide range of anions (e.g., BF₄⁻, ClO₄⁻, C₇H₇SO₃⁻, etc.) have been used, with the anion stoichiometry in the range of 0.25-0.33 anions per pyrrole ring.²⁻⁴ However, the type of anion incorporated affects the electrochemical behavior and thermal stability of the polymer and can produce as much as four orders of magnitude variation in the electrical conductivity (σ) of the film.⁴

PPY synthesized chemically using acid or peroxide initiators has resulted mainly in insulating films with σ typically in the order of 10⁻¹¹ S/cm.^{5,7} These films are not completely stable in air even at room temperature.⁵ These initially insulating films can be doped by bromine (Br₂) and iodine (I₂) to achieve stable conductivity of the order of 10⁻⁵ S/cm.⁵ Conductive PPY complexes have also been synthesized chemically in the presence of various Fe(III) oxidants such as Fe(ClO₄)₃ and FeCl₃.⁸⁻¹⁰ We have also reported recently on a relatively simple and novel method for the simultaneous chemical polymerization and oxidation of pyrrole by halogens (Br₂, I₂, or Cl₂) in aqueous media¹¹ and in organic solvents.¹² The PPY-halogen complexes so produced are stable in the atmosphere and the electrical conductivity and conduction behavior of the PPY-I₂ and PPY-Br₂ complexes are comparable to that of electrochemically synthesized PPYs.¹³ In this communication, we

describe the effect of varying halogen to pyrrole monomer ratio during polymerization on the properties of the resulting PPY-halogen complexes. The various PPY-halogen complexes are characterized by elemental analysis, electrical conductivity measurements, infrared (IR) absorption spectroscopy, thermogravimetric analysis, X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry.

EXPERIMENTAL

The chemical synthesis of the PPY-halogen complexes has been described in detail in earlier publications.^{11,12} In the current investigation, acetonitrile was used as the reaction medium and the halogens used were Cl₂, Br₂ and I₂. The concentration of pyrrole was kept constant while varying the amount of halogen. The yield of the resulting PPY-halogen complex was measured. The mole ratio of halogen to pyrrole monomer used was varied from 0.45:1 to 2.03:1 for bromine and iodine. As for chlorine, the amount of chlorine dissolved in acetonitrile was varied by varying the time of bubbling a constant flowrate of chlorine gas through the acetonitrile solution. The amount of chlorine dissolved was determined gravimetrically. Since the PPY-halogen complexes are granular in nature, these powders were compressed into pellets of 1.2 cm in diameter and 0.05 cm to 0.1 cm in thickness for the measurement of σ using the standard collinear 4-probe method. Thermal stability was tested using a Netzsch STA409 simultaneous thermogravimetric-differential thermal analyzer. For each run, about 8 mg of sample was used with 100 mL/min of N₂ and a heating rate of 10°C/min. The infrared (IR) absorption spectra measurements were carried out on a Perkin-Elmer Model 682 spectrophotometer with the polymer samples dispersed in KBr pellets. The electrochemical studies were carried out in a Hokuto Denko one-compartment cell equipped with a platinum counter electrode and a Ag/AgCl reference electrode. A specially modified working electrode was used for handling powder samples and a detailed description of this electrode and its performance have been reported in an earlier publication.¹⁴ The XPS data were obtained on an ESCA 750 with a monochromatized MgK α X-ray source (1253.6 eV photons) through the courtesy of Toray Research Center, Inc., Shiga, Japan.

RESULTS AND DISCUSSION

Chemical Compositions

The yield of the PPY-I₂ and PPY-Cl₂ complexes increases with increasing halogen used for polymerization while the yield of the PPY-Br₂ complex increases and then decreases. Tables I, II, and III summarize the synthesis conditions and properties of the resulting PPY-Br₂, PPY-I₂ and PPY-Cl₂ complexes, respectively. The elemental analysis results in Table I show that as the Br₂: pyrrole monomer ratio is increased, the percentage of Br₂ incorporated into the complex increases and the number of Br₂ molecules per pyrrole unit increases from 0.17 to 0.38. At low Br₂: pyrrole monomer ratio, the C:H:N ratio is close to the theoretical value of 4:3:1 for a linear chain of pyrrole rings with α , α' linkages.² However, as the Br₂ content increases, the complex becomes hydrogen deficient relative to this idealized structure, sug-

TABLE I
 Synthesis Conditions and Properties of Polypyrrole-Bromine Complexes

Sample	Reagent mole ratio Br ₂ : monomer	Wt PPY·Br ₂ Wt monomer	Chemical composition	Wt % Br ₂ in complex	σ, S/cm	Ionic bromide ^a	
						Covalent bromide	
(PPY-Br ₂)-1	0.45:1	0.48	C _{4,0} H _{3,1} N _{0,99} O _{0,45} (Br) _{0,34}	26.3	9		6.7:1
(PPY-Br ₂)-2	0.68:1	0.81	C _{4,0} H _{3,1} N _{1,0} O _{0,58} (Br) _{0,38}	27.8	25		4.4:1
(PPY-Br ₂)-3	1.35:1	1.21	C _{4,0} H _{2,8} N _{0,99} O _{0,46} (Br) _{0,48}	29.7	4		1.2:1
(PPY-Br ₂)-4	2.03:1	0.75	C _{4,0} H _{2,5} N _{0,96} O _{0,34} (Br) _{0,76}	45.3	1		0.44:1

^a Determined by X-ray photoelectron spectroscopy.

TABLE II
 Synthesis Conditions and Properties of Polypyrrole-Iodine Complexes

Sample	Reagent mole ratio I_2 : monomer	$\frac{\text{Wt PPY}-I_2}{\text{Wt monomer}}$	Chemical composition	Wt % I_2 in complex	σ , S/cm	$\frac{\text{Ionic iodide}^a}{\text{Covalent iodide}}$
(PPY- I_2)-1	0.45:1	0.14	$C_{4.0}H_{3.2}N_{0.92}O_{0.39}(I)_{0.40}$	42.1	↑	↑
(PPY- I_2)-2	0.68:1	0.25	$C_{4.0}H_{3.0}N_{0.96}O_{0.44}(I)_{0.40}$	42.2	0.5-2	~ 100% ionic
(PPY- I_2)-3	1.35:1	0.58	$C_{4.0}H_{3.2}N_{0.97}O_{0.30}(I)_{0.48}$	46.7	↓	↓
(PPY- I_2)-4	2.03:1	0.98	$C_{4.0}H_{3.7}N_{0.95}O_{0.50}(I)_{0.56}$	49.6		

^aDetermined by X-ray photoelectron spectroscopy.

TABLE III
 Synthesis Conditions and Properties of Polypyrrole-Chlorine Complexes

Sample	Reagent mole ratio Cl_2 : monomer	$\frac{\text{Wt PPY}-\text{Cl}_2}{\text{Wt monomer}}$	Chemical composition	Wt % Cl_2 in complex	σ , S/cm	$\frac{\text{Ionic chloride}^a}{\text{Covalent chloride}}$
(PPY- Cl_2)-1	0.64:1	0.60	$\text{C}_{4.0}\text{H}_{2.8}\text{N}_{1.0}\text{O}_{0.72}(\text{Cl})_{0.66}$	23.4	0.5	← ~ 0.3:1 →
(PPY- Cl_2)-2	2.20:1	0.98	$\text{C}_{4.0}\text{H}_{2.2}\text{N}_{1.0}\text{O}_{0.51}(\text{Cl})_{0.84}$	29.3	0.2	

^a Determined by X-ray photoelectron spectroscopy.

gesting that either cross-linking has occurred and/or some of the hydrogen at the β position has been substituted by bromine. Further evidence of this H deficiency is suggested by the IR absorption spectra (see Fig. 1 below). The nitrogen also decreases slightly relative to the carbon as the bromine content increases.

When iodine is used as acceptor, the same degree of variation of acceptor:pyrrole monomer ratio produces a much smaller variation in the percentage of acceptor incorporated into the complex and hence in the number of anions per pyrrole unit (Table II). The C:H:N ratio of the PPY-I₂ complexes shows a greater deviation from the idealized 4:3:1 ratio. The H/C ratio is higher than 3/4 while the N/C ratio is less than 1/4 regardless of the initial iodine/pyrrole ratio. Mendoli et al.¹⁵ have reported that the N/C ratio decreases from 1/4 when potential increases above 0.8 V (against SCE) during the electrolytic oxidation of pyrrole. They suggest that overoxidation can lead to ring opening and hydrolysis, and thus the loss of nitrogen atoms. It is possible that a similar mechanism may occur in our system when either iodine or a high

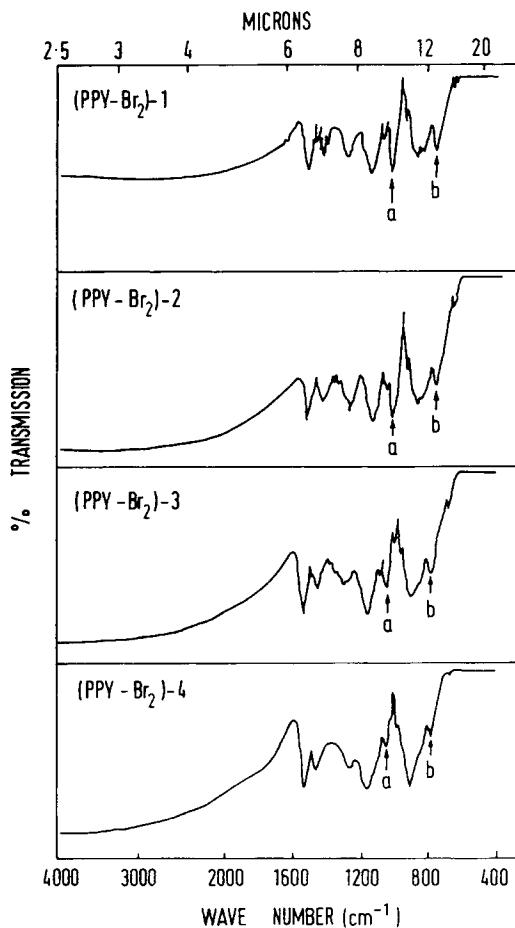


Fig. 1. IR absorption spectra for PPY-Br₂ complexes (peak a is at 1040 cm⁻¹, peak b is at 760 cm⁻¹).

concentration of bromine is available for reaction with pyrrole in acetonitrile. When chlorine is used as acceptor, varying the chlorine concentration in the reaction medium also produces only a small variation in the Cl_2 incorporated into the complex (Table III). The number of chlorine molecules to one pyrrole unit is between 0.33 to 0.42. With low Cl_2 concentration in the reaction medium, the H/C ratio is slightly lower than 3/4 and as the acceptor concentration increases, the hydrogen becomes more deficient. Again, cross-linking or ring halogenation may have occurred.

Elemental analysis indicates a trace amount of oxygen in all our complexes. The Cls XPS core-level spectra suggest the presence of trace amounts of carbonyl structure in the present complexes. However, the carbonyl structure is not readily visible in the IR absorption spectra (see Fig. 1). This discrepancy can be explained by the fact that the carbonyl absorption peak at around 1700 cm^{-1} may have been masked by the broad absorption tail of the polymer complex and that the carbonyl structure is probably more characteristic of the surface rather than the bulk state. Furthermore, the possibility of the present complexes being doped to a small extent by oxygen, as in the case of neutral and oxidized PPY films obtained from electrochemical polymerization,¹⁶ cannot be ruled out.

Electrical Conductivity

The electrical conductivity of the PPY- Br_2 complex is affected by the acceptor level. First σ increases with increasing Br_2 content and then decreases. The maximum σ of the four samples is 25 S/cm. It is postulated that the decrease in σ with increasing Br_2 loading is attributable to the bromination of the pyrrole ring. This is entirely consistent with the fact that polybromopyrroles obtained from chemical and electrochemical polymerization have σ values substantially lower than that of PPYs.⁹ The maximum σ of the PPY- I_2 complexes is more than an order of magnitude lower than that of PPY- Br_2 . For PPY- I_2 complexes, σ ranges from 0.5 to 2 S/cm regardless of the amount of I_2 used. It appears that acetonitrile may be the best reaction medium for the synthesis of PPY- Br_2 complexes but for the synthesis of PPY- I_2 complexes, the use of aqueous media yields substantially more conductive material. For example, PPY- I_2 complex with σ in the range of 25 to 30 S/cm and nearly ideal C:H:N have been obtained.¹³ The lower values of σ of the present PPY- I_2 complexes may be related to the N/C ratio being less than 1/4, when acetonitrile is used as the polymerization medium. The postulated mechanism of ring opening will lead to a loss of effective conjugation which would adversely affect the conductivity of the polymer.¹⁵ The value of σ for the PPY- Cl_2 complexes is also of the order of 0.5 S/cm. This lower value of σ as compared to the PPY- Br_2 complexes with high ionic to covalent halide ratio may be associated with substantial ring halogenation of the pyrrole moiety.

IR Absorption Spectra and XPS

Since it appears that the formation of covalent halide will strongly affect σ , the ratio of ionic halide to covalent halide was determined. This ratio was

obtained from the XPS data and is presented in Tables I, II and III for PPY-Br₂, PPY-I₂, and PPY-Cl₂ complexes, respectively. Figure 2 shows the Br3d XPS core-level spectrum of a PPY-Br₂ complex with relatively low covalent bromine content (Sample (PPY-Br₂)-2). It should be emphasized that since the surface compositions, as viewed by XPS may differ somewhat from the bulk compositions, the XPS results should be regarded only as approximate when extended to bulk properties. Table I shows that as the initial amount of Br₂ used is increased, its chemical state in the PPY-Br₂ complex changes from predominantly ionic to predominantly covalent bromide. This trend is accompanied by a progressive reduction in both the 1040 cm⁻¹ (peak a) and 760 cm⁻¹ peaks (peak b) of the IR absorption spectra as shown in Figure 1. The 1040 cm⁻¹ peak has been assigned to the C_β-H in-plane vibration while the peak below 900 cm⁻¹ is assigned to the C_β-H out-of-plane vibration.¹⁷ The reduction in the intensity of these two peaks suggests the hydrogen at the β-carbons may be substituted by bromine, which would also be consistent with the increased proportion of covalent bromide. Another notable feature in Figure 1 is the decrease in absorption from 4000 to 1700 cm⁻¹. This long absorption tail has been assigned to be the tail of the absorption peak located in the near IR region.^{12,16} An IR absorption tail of similar nature has also been reported for electrochemically synthesized PPY¹⁶ and is characteristic of oxidized and highly conductive PPY. For samples with low acceptor level, such as ((PPY-Br₂)-1), this absorption tail is not as well developed. The conductivity of this sample remains lower than the maximum value even though the C_β-H vibrations absorption are strongest among the four samples studied. Thus, it appears that σ is associated with both the absorption tail and the C_β-H peaks of the IR absorption spectra.

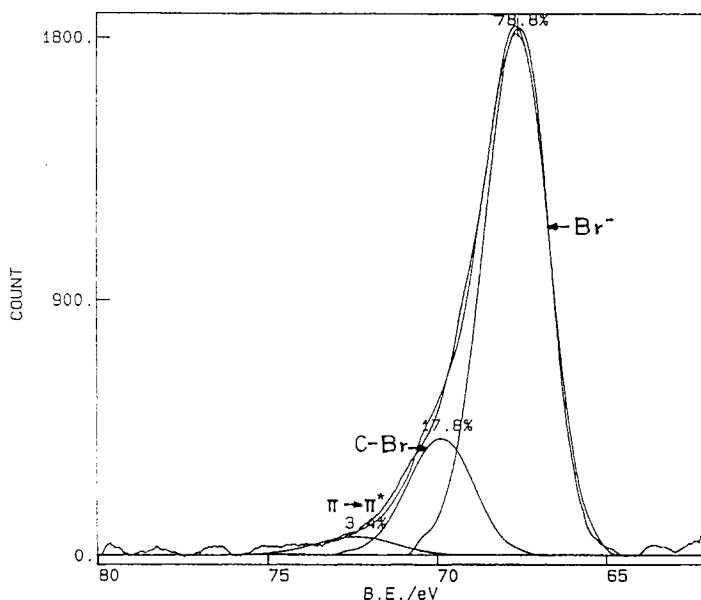


Fig. 2. Br3d XPS core-level spectrum of PPY-Br₂ complex (sample (PPY-Br₂)-2)

The XPS data for PPY-I₂ complexes suggest that the iodine species is present almost exclusively as ionic iodide for all four samples. On the other hand, for PPY-Cl₂ complexes, regardless of the amount of Cl₂ used, the chlorine exists predominantly as covalent chloride. The ratio of ionic to covalent chloride is about 0.3:1. The IR absorption spectra for PPY-I₂ and PPY-Cl₂ complexes are consistent with the XPS results and show that the 1040 cm⁻¹ peak is always well defined for the former but is much reduced for the latter, regardless of the acceptor concentration.

Thermal Properties

The thermal stability of the PPY-halogen complexes is dependent on the halogen used and the acceptor level. All the PPY-halogen complexes are stable at ambient conditions (~ 25°C, ~ 70% relative humidity). Upon heating the PPY-Br₂ complexes in N₂, the sample having the lowest Br₂ content, (PPY-Br₂)-1, shows the least weight loss and this weight loss commences at the highest temperature (Fig. 3). As the Br₂ content, and thus the amount of covalently bonded bromine increase, the rate of weight loss and total weight loss increase. The different PPY-I₂ and PPY-Cl₂ complexes do not show substantial differences in the thermal stability. The thermal decomposition mechanism of PPY-I₂ complex has been postulated to be the decomposition of I₅⁻ to I₃⁻ and I₂,¹⁸ as in the case of I₂-doped polyacetylene.¹⁹ The decomposition mechanisms for PPY-Br₂ and PPY-Cl₂ complexes are not clear at present but are expected to differ from that of PPY-I₂ because of the presence of covalent as well as ionic halide in the former cases.

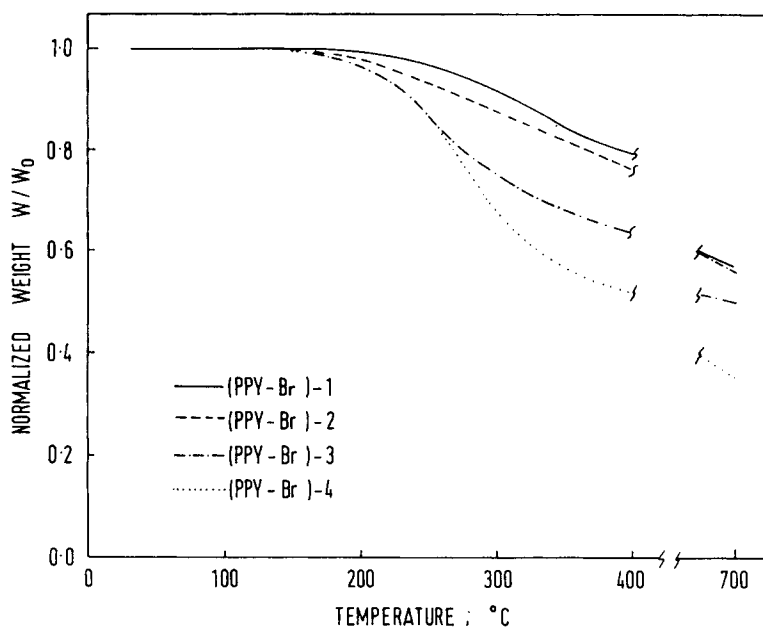


Fig. 3. Effect of temperature on the normalized weight loss, W/W_0 , of PPY-Br₂ complexes. — (PPY-Br₂)-1; --- (PPY-Br₂)-2; - · - (PPY-Br₂)-3; · · · · (PPY-Br₂)-4.

Electrochemical Characterization

The cyclic voltammograms of (PPY-Br₂)-1 and (PPY-Br₂)-4 are given in Figure 4. These voltammograms were obtained in 0.5-M aqueous NaBr at a sweep rate of 10 mV/min. The two major differences between the two voltammograms are the shift in the redox potential of the (PPY-Br₂)-4 sample to a more positive value than that for (PPY-Br₂)-1 and the poor resolution of the oxidation peak of the former sample. Audebert and Bidan⁹ have shown that chemically and electrochemically synthesized polyhalopyrroles have more positive redox potentials than that of PPY. Since a large fraction of the Br₂ in the (PPY-Br₂)-4 sample may have been covalently bonded to the β position of the pyrrole ring, the shifting of the redox potential toward a more positive value and the resulting poorer resolution in the voltammogram may be due to the combined redox effects of PPY as well as polybromopyrrole. The voltammogram of the (PPY-Br₂)-4 could be better resolved supposedly by cycling at potentials well above 1.0 V. This has to be

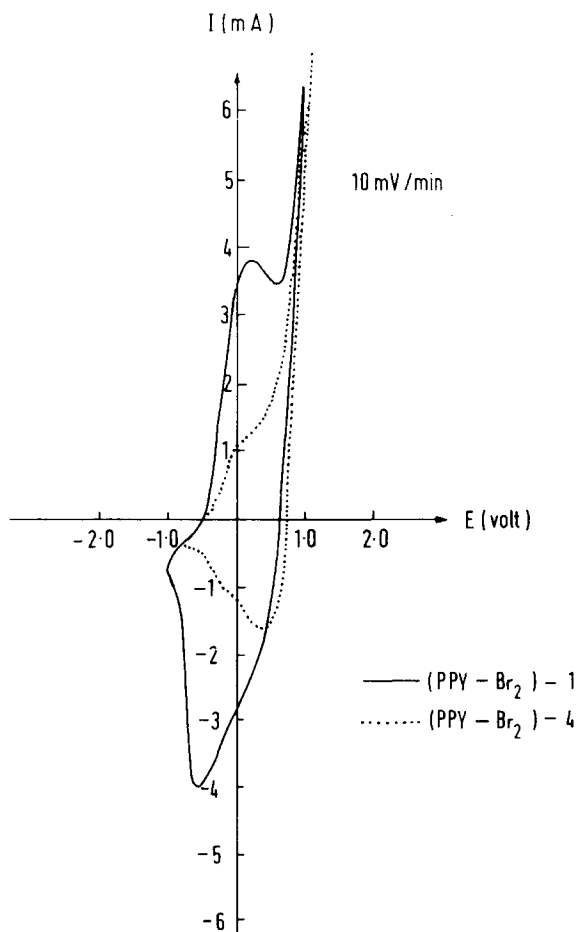


Fig. 4. Cyclic voltammogram of (PPY-Br₂)-1 (—) and (PPY-Br₂)-4 (·····) samples in 0.5-M aqueous NaBr at 10 mV/min.

avoided, however, since PPY has been known to undergo structural changes under strongly oxidizing conditions.¹⁵ The voltammogram for PPY-Cl₂ complex also shows a significantly more positive redox potential and poorer resolution than that of the PPY-I₂ complexes. Of the four polyhalopyrroles tested by Audebert and Bidan, poly(3,4-dichloropyrrole) shows the largest positive shift in redox potential from that of PPY.⁹ Since the PPY-Cl₂ complexes have a high degree of covalent chloride, an explanation of the voltammogram similar to that given for (PPY-Br₂)-4 would apply. On the other hand, the PPY-I₂ complexes having almost exclusively ionic iodide show well defined oxidation and reduction peaks with a redox potential of about -0.4 V.

CONCLUSION

We have shown that a large variation in the acceptor level of the PPY-Br₂ complexes can occur with changing bromine concentration during simultaneous chemical polymerization and oxidation of pyrrole by the acceptor. However, using the same chemical synthesis method, the acceptor level in PPY-I₂ and PPY-Cl₂ complexes do not vary substantially with changes in I₂ or Cl₂ concentration in the reaction medium. The reactivity of the halogen acceptor will affect its nature in the resulting PPY-halogen complex. Of the three halogens tested, Cl₂ being the most reactive will substitute at the β position of the pyrrole ring while I₂ being the least reactive will be present mainly as ionic iodide regardless of the amount of acceptor used. With Br₂, the degree of C-Br bond formation and percentage of Br₂ in the complex increase strongly with Br₂ concentration. The presence of covalent halide species decreases σ and also the thermal stability of the complex. Cyclic voltammetry results are consistent with the postulate that C_β-halide bonds are formed when either Cl₂ or large amounts of Br₂ is used as acceptor.

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