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Photopolymerization of Pyrrole Initiated by the Ferrocene- and Iron-Arene Salts-Chlorinated Solvents Complexes

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PHOTOPOLYMERIZATION OF PYRROLE INITIATED BY THE FERROCENE- AND IRON-ARENE SALTS-CHLORINATED SOLVENTS COMPLEXES

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ABSTRACT

Ferrocene- and iron-arene salts can photoinitiate polymerization of pyrrole in the presence of halogenated solvents, such as $CH_2CH_2Cl_2$, $CHCl_3$, and CCl_4, when irradiated with UV light (254 nm). The polypyrroles obtained are black colloidal powders and have low conductivity in the range of 10^{-5} S cm^{-1} and rather poor electrochemical properties, which can be the result of loss of conjugation by halogenation. Polypyr-

Dedicated to Professor Otto Vogl on the occasion of his 65th birthday.

role samples contain both covalently bounded CCl_3 groups (from CCl_4) and ionic $FeCl_4^-$. A mechanism of photoinitiated polymerization of pyrrole has been proposed.

INTRODUCTION

In recent years there has been a steady growth in the studies of semiconducting polymers based on polypyrroles. Despite the extensive results obtained and published on chemical and electrochemical polymerization of pyrrole and its derivatives [1, 2], reports on the photochemical polymerization of pyrrole are relatively scarce. Even prolonged UV irradiation (24 h) of pure deoxidized pyrrole does not cause its polymerization, and free-radical polymerization of pyrrole does not occur at all. We recently reported that pyrrole can be photopolymerized in the presence of iron-arene salts [3].

The objective of this work was to examine photopolymerization of pyrrole initiated by the complex formed between ferrocene- or iron-arene salts and chlorinated solvents ($CHCl_3$, CH_2Cl_2, $CH_2CH_2Cl_2$, or CCl_4).

EXPERIMENTAL

Ferrocene (Merck, Germany) has been purified by double recrystallization from ethanol (spectral grade). Iron-arene salts cationic photoinitiators, such as: (h^5-2,4-cyclopentadien-1-yl) [(1,2,3,4,5-h-)-(1-methylethyl)-benzene]-iron(1+)-hexafluorophosphonate(1-) (Irgacure 261, CIBA-Geigy) and (h^5-2,4-cyclopentadien-1-yl) [(1,2,3,4,5-h) -naphthalene]-iron(1+)-hexafluorophosphonate(1-) (Komplex KM 1144, CIBA-Geigy), were kindly provided by Dr. G. Eugster (CIBA-Geigy). Both these photoinitiators were additionally purified by crystallization from nitromethane. Nitromethane (CH_3NO_2) (Carl Roth, GmbH, Germany) and pyrrole (Merck, Germany) have been purified by vacuum distillation. Chlorinated solvents were spectrally pure.

Measurement Instrumentation

UV/VIS and IR absorption spectra were recorded with Perkin-Elmer 575 UV/VIS and FT-IR Perkin Elmer 580B spectrometers, respectively. Mössbauer (Recoil-free Nuclear Resonance Absorption) spectra were recorded with a MS500 Oxford spectrometer, using a 50 mCi^{57} Co/Rh source. The simulation of the measured spectra was performed using the Gauss-Newton method by supposing that a single peak has a Lorentzian line shape. ESCA spectra were recorded with a VG Scientific LD spectrometer, using $AlK\alpha_{1,2}$ excitation radiation. Each spectral region was deconvoluted and the peak position were compared with known literature values [4]. SEM photomicrographs were made with the Super Mini ISI microscope. Conductivities of polypyrroles were measured using four-point resistivity probe and Solid State Electrometer Type 610C, (Keithley Instrument). Measurements were recalculated with equations published elsewhere [5]. Cyclical voltammograms were performed on an EG&G Princeton Applied Research Model 173 potentiostat/galvanostat in dry acetonitrile solutions of 0.1 *M* tetra-*n*-butyl amonium perchlorate (TBAP) at room temperature in a two-compartment cell with an Ag/AgCl reference electrode at 20 mV/s. Polymerization of pyrrole in the presence of photoinitiating systems was carried out under UV (254 nm) radiation from UV HPK 125 W (Phillips) lamp. The UV irradiance was 40 Wm^{-2} or 10^8 einstein s^{-1} cm^{-1}.

RESULTS AND DISCUSSION

Ferrocene (Cp_2Fe) (C_p = h^5-cyclopentadienyl) easily forms electron-donor acceptor (EDA) complexes with polyhalogen compounds [6–10]:

$$Cp_2Fe + CCl_4 \rightleftharpoons [Cp_2Fe]^+ [CCl_4]^- \qquad (1)$$

Formation of such EDA complexes can be easily monitored by the formation of the absorption band with maximum at 300–310 nm (Figs. 1–3).

Exposure of ferrocene in ethanol (3 h) to UV irradiation (254 nm) does not cause any detected change in its absorption spectrum (Fig. 1); however in the presence of CCl_4 (CH_3CH_2OH:CCl_4 = 10:1), ferrocene is extensively photolysed (Fig. 1). New bands at 615–617 nm and 460 nm, which belong to ferricenium ion ($Cp_2Fe^+Cl^-$) and ferricenium tetrachloroferrate ($[Cp_2Fe]^+[FeCl_4]^-$), respectively, are formed (Fig. 1). UV irradiation of ferrocene in pure CCl_4 (Fig. 2) or in pure $CHCl_3$ (Fig. 3) causes similar changes in the absorption spectra.

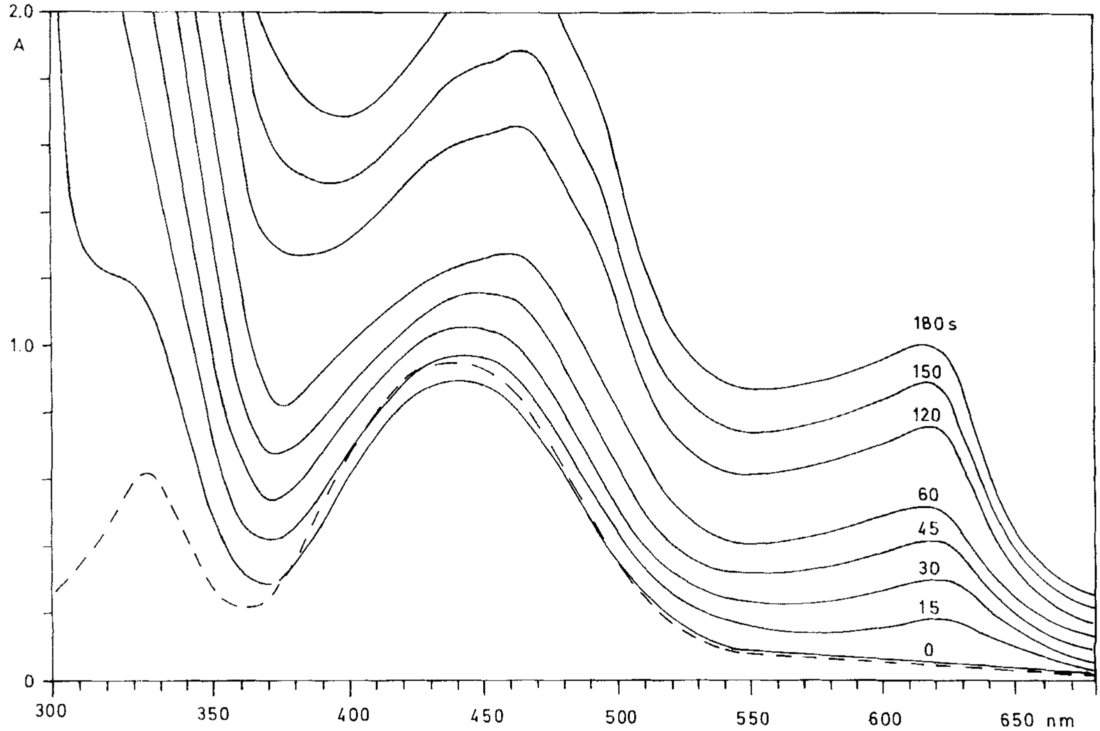


FIG. 1. Change of absorption spectra of ferrocene (Cp_2Fe) (1 × 10^{-2} M): (———) in CH_3CH_2OH:CCl_4 = 10:1, during UV (254 nm) irradiation (15, 30, 45, 60, 120, 150, 180), and (- - -) in pure CH_3CH_2OH before and after 3 h of UV irradiation.

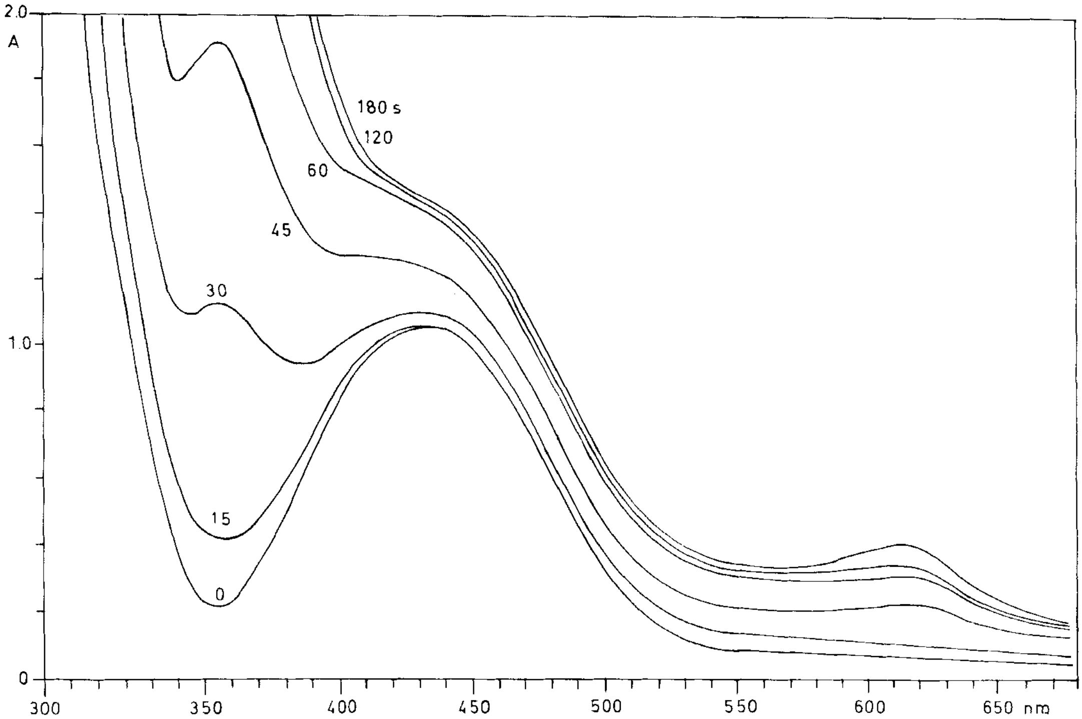


FIG. 2. Change of absorption spectra of ferrocene (Cp_2Fe) (1×10^{-2} *M*) in CCl_4, during UV (254 nm) irradiation (15, 30, 45, 60, 120, 180 s).

Ferricenium ion ($Cp_2Fe^+Cl^-$) and ferricenium tetrachloroferrate ($[Cp_2Fe]^+ [FeCl_4]^-$) are formed according to the following reactions initiated by UV irradiation [7, 11]:

$$[Cp_2Fe]^+ [CCl_4]^- \xrightarrow{+h\nu} Cp_2Fe^+Cl^- + \cdot CCl_3 \qquad (2)$$

$$Cp_2Fe^+Cl^- + 2CCl_4 \xrightarrow{+h\nu} FeCl_3 + 2\ C_pCCl_3 \qquad (3)$$

$$2\ Cp_2Fe^+Cl^- \xrightarrow{+h\nu} Cp_2Fe + FeCl_2 + 2\ Cp\cdot \qquad (4)$$

$$Cp_2Fe^+Cl^- + FeCl_2 \rightleftarrows FeCl_3 + Cp_2Fe \qquad (5)$$

$$Cp_2Fe^+Cl^- + FeCl_3 \rightleftarrows [Cp_2Fe]^+[FeCl_4]^- \qquad (6)$$

Trichloromethyl radicals ($\cdot CCl_3$) formed from UV irradiation of Cp_2Fe-CCl_4 complex initiate polymerization of vinyl monomers [12–14].

We have observed that ferrocene can also form EDA complexes with pyrrole (Py) (Fig. 4, band at 300 nm). Exposure of ferrocene in pyrrole solution to UV irradiation causes a very slow change in the absorption spectrum (Fig. 4), which evidently differs from the spectra in Figs. 1–3. No formation of bands characteristic of Cp_2Fe^+ (615–617 nm) and $[Cp_2Fe]^+[FeCl_4]^-$ (460 nm) has been observed. However, UV irradiation of three-component system Cp_2Fe:Py-CCl_4 (10:1) causes very rapid change in absorption spectra (Fig. 5), which indicates formation of ferricenium tetrachloroferrate $[Cp_2Fe]^+ [FeCl_4]^-$ (480 nm), but not ferricenium ion $Cp_2Fe^+Cl^-$ (lack of absorption at 615 nm).

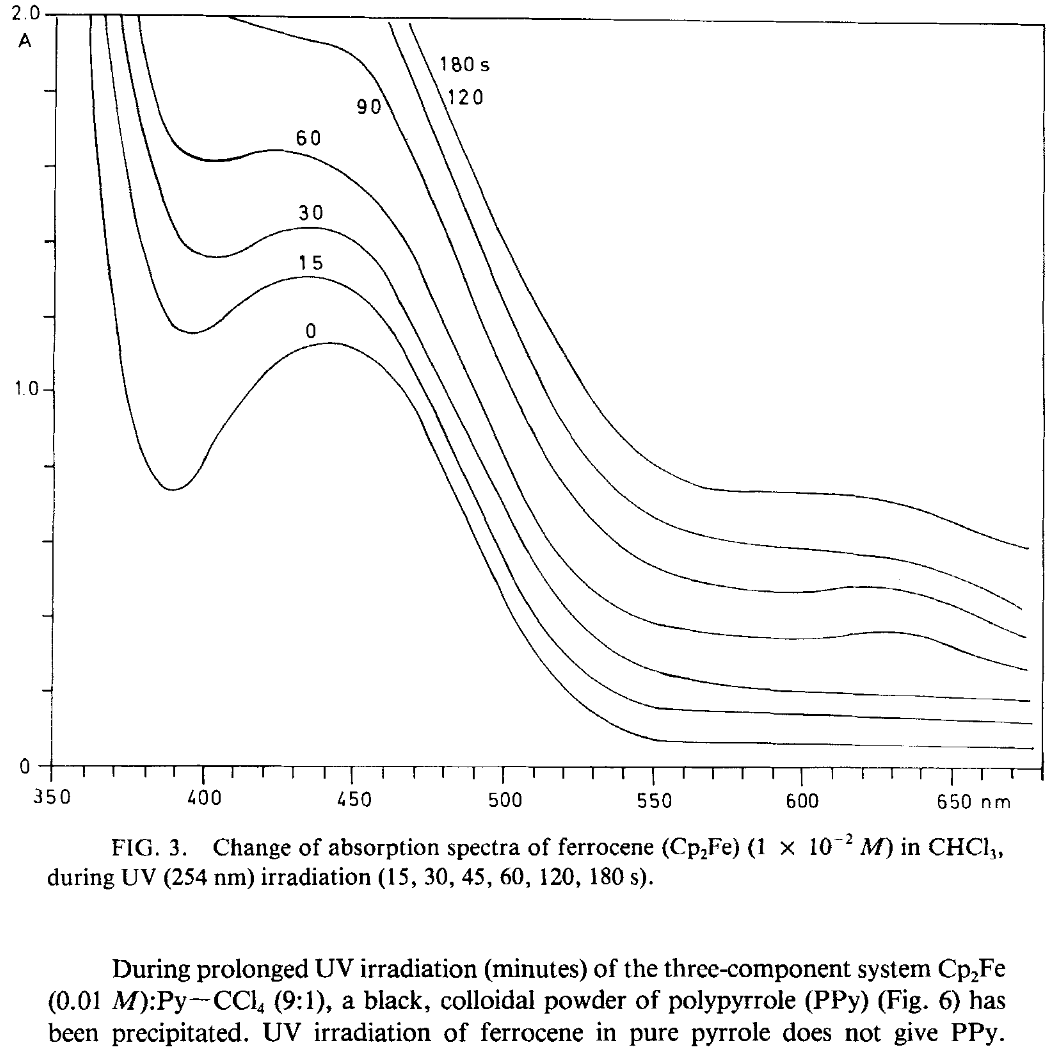


FIG. 3. Change of absorption spectra of ferrocene (Cp_2Fe) (1×10^{-2} *M*) in $CHCl_3$, during UV (254 nm) irradiation (15, 30, 45, 60, 120, 180 s).

During prolonged UV irradiation (minutes) of the three-component system Cp_2Fe (0.01 *M*):Py—CCl_4 (9:1), a black, colloidal powder of polypyrrole (PPy) (Fig. 6) has been precipitated. UV irradiation of ferrocene in pure pyrrole does not give PPy. Polymerization of pyrrole in the three-component system Cp_2Fe (0.01 *M*):Py—CCl_4 (9:1) is caused by $FeCl_3$ formed in Reactions 2-6. The mechanism for the polymerization of Py by $FeCl_3$ has been published elsewhere [15]:

$$(2 + m)nFe^{3+}mnA^{-} + nC_4H_5N \rightarrow$$
$$[(C_4H_3N)^{m+}mA^{-}]_n + 2nH^{+} + (2 + m)n\,Fe^{2+} \qquad (7)$$

The PPy obtained during UV irradiation of Cp_2Fe (0.01 *M*):Py—CCl_4 (9:1) is doped with $FeCl_4^-$ and contains covalently bonded CCl_3 groups as a result of the reaction of trichloromethyl radicals ($\cdot CCl_3$) with ene structures in PPy and probably has the composition $[(C_4H_3N)_{5-7}(CCl_3)]^{+}FeCl_4^-$ according to the elemental analysis ($C_{3.6}H_{0.3}N_{1.0}Cl_{1.2}(FeCl_4^-)_{2.35}$).

The presence of both covalently bonded and ionic chlorine in PPy is evidently seen from ESCA and Mössbauer spectra. The ESCA of PPy obtained in the presence of Cp_2Fe—CCl_4 (9:1) in a ratio 9:1 (10 wt%) shows the presence of interesting shoulders in the N_{1s} (Fig. 7A) and Cl_{2p} (Fig. 7B) spectra. The N_{1s} spectrum shows the

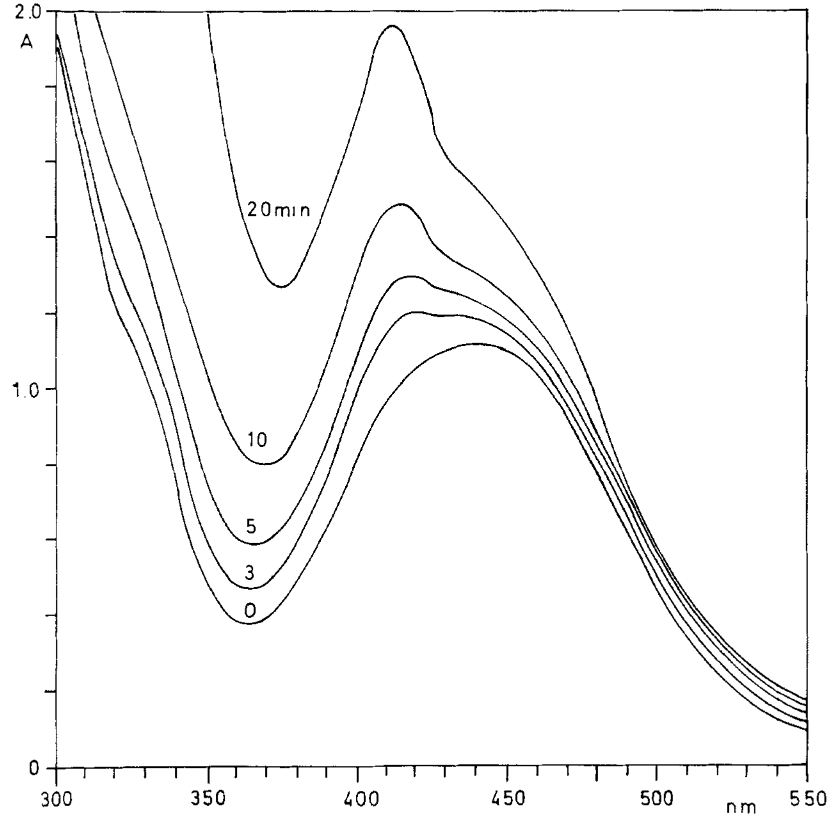


FIG. 4. Change of absorption spectra of ferrocene (Cp_2Fe) (1×10^{-2} M) in pyrrole, during UV (254 nm) irradiation (3, 5, 10, and 20 min).

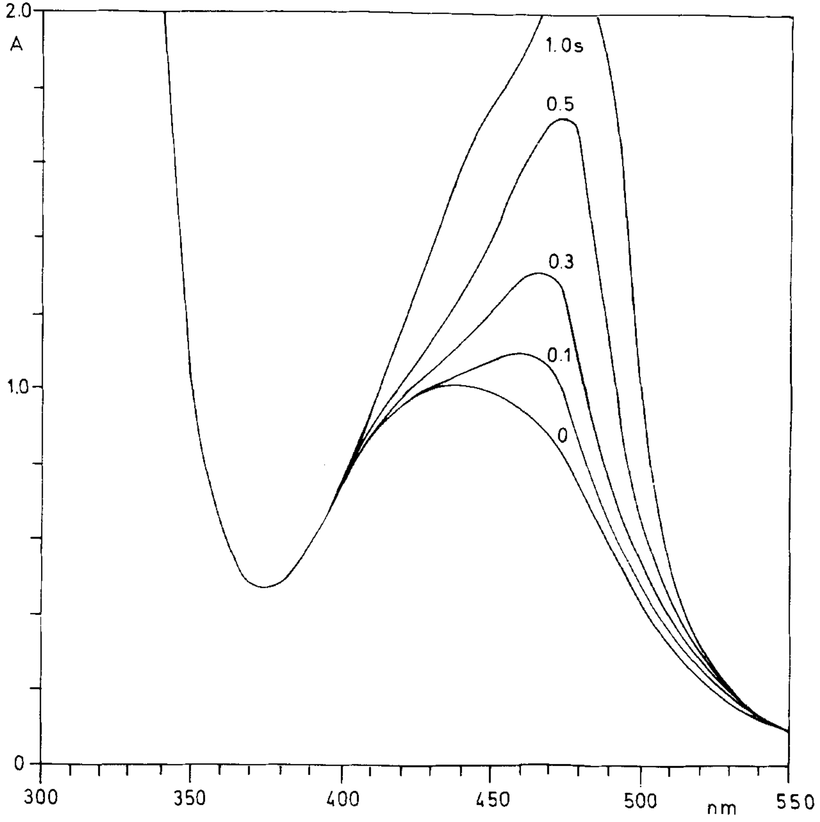


FIG. 5. Change of absorption spectra of ferrocene (Cp_2Fe) (1×10^{-2} M) in pyrrole: CCl_4 = 9:1, during UV irradiation (0.1, 0.3, 0.5, and 1.0 s).

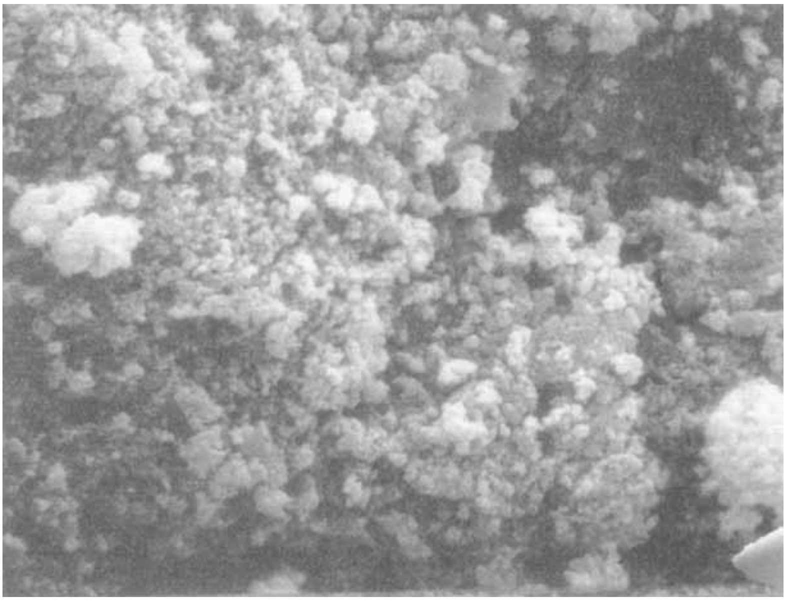


FIG. 6. SEM photomicrograph of polypyrrole (PPy) colloidal aggregates (powder) obtained in the presence of ferrocene (Cp_2Fe) (0.01 *M*) and CCl_4 (pyrrole:CCl_4 = 9:1) under UV (254 nm) irradiation (3 min).

presence of two nonequivalent high-energy component peaks, which are centered at 402.4 ± 0.2 eV and 403.0 ± 0.2 eV and probably arise from oxidized N heteroatom. A similar N_{1s} spectrum has been reported for polypyrrole perchlorate $PPy^+ClO_4^-$, where two N_{1s} peaks were centered at 401 ± 0.2 eV and 402.8 ± 0.2 eV [16]. The Cl_{2p} spectrum (Fig. 7B) shows the presence of both covalent (C—Cl, peak at 200.02 ± 0.2 eV) and ionic (Cl^-, peak at 197.2 ± 0.2 eV) species. The weak π-π^* satellite structure at 203.6 ± 0.2 eV suggests the addition of Cl to the ring by covalent bonding. Similar Cl_{2p} spectra were also reported elsewhere [16–19].

The Mössbauer spectrum of ferrocene at 77K shows a doublet (Fig. 8) (IS = 0.67 mm s^{-1}, QS = 2.36 mm s^{-1}, error limits 0.01 mm s^{-1}), which is in good agreement with the results reported previously [20–22]. The PPy obtained in the presence of Cp_2Fe—CCl_4 (9:1) shows formation of a single signal (Fig. 8). The calculated IS = 0.36 mm s^{-1} and QS = 0.46 mm s^{-1} (error limits 0.02 mm s^{-1}) are similar to $FeCl_4^-$ ion reported in the literature [15, 23–26].

The FTIR spectrum (Fig. 9A) shows the presence of very characteristic bands for PPy at about: 1540–1550, 1280, 1180–1200, 1040, and 940–900 cm^{-1} [27]. In addition, a new peak at 780 cm^{-1} arises due to the C—Cl stretch in CCl_3 groups. All of ESCA, Mössbauer, and FTIR spectra indicate that PPy contains C—CL, C—CCl_3, and Cl^- attached probably both to double bonds and to the pyrrole ring. This halogenation of PPy causes loss of conjugation along the backbone and may lead to chain segments that average from 5 to 10 pyrrole units on length, as estimated from the Cl content.

We recently reported that iron-arene salt cationic photoinitiators such as Irgacure

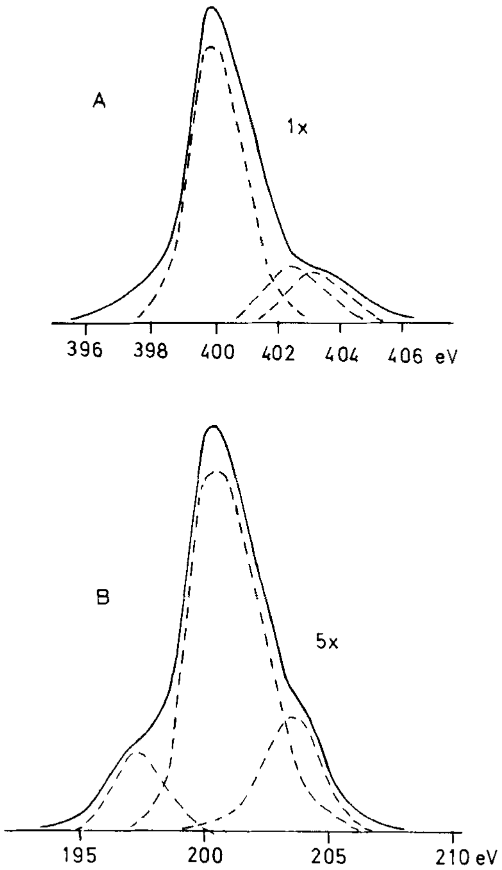


FIG. 7. ESCA spectra of polypyrrole (PPy) obtained in the presence of ferrocene (Cp_2Fe) − CCl_4 = 9:1 (10 wt%): (A) N_{1s} (1×) and (B) Cl_{2p} (5×).

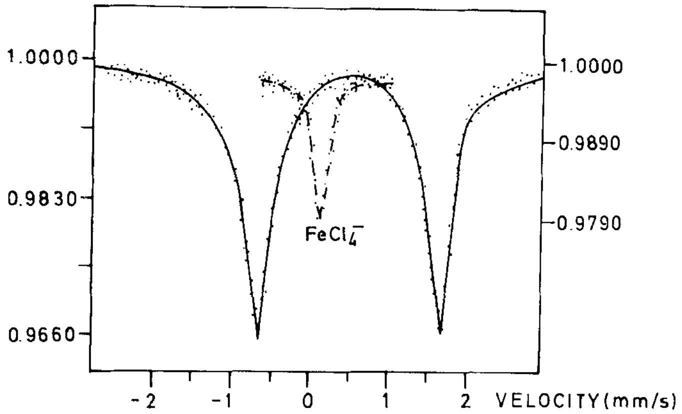


FIG. 8. Mössbauer spectra of: (———) pure ferrocene (Cp_2Fe) and (- - -) polypyrrole (PPy) obtained in the presence of Cp_2Fe (0.01 *M*) and CCl_4 (pyrrole:CCl_4 = 9:1) under UV (254 nm) irradiation (3 min).

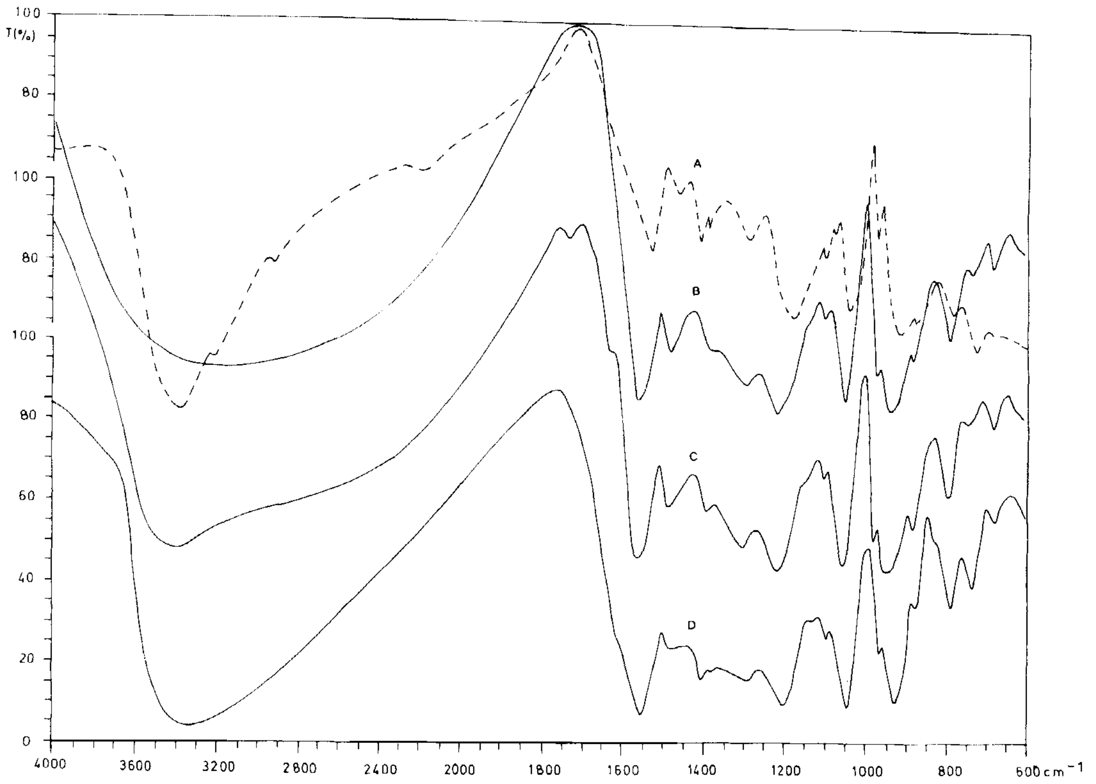


FIG. 9. IR spectra of different kinds of polypyrroles (PPy) polymerized by: (A) $FeCl_3-CH_3NO_2$ (addition complex); (B) ferrocene [(Cp_2Fe) (0.01 *M*) Py$-CCl_4$(9:1)]; (C) Irgacure 261 (0.01 *M*): Py$-CCl_4$ (9:1); and (D) Komplex 1141 (0.01 *M*): Py$-CCl_4$ (9:1), in the presence of UV (254 nm) irradiation.

261 and Komplex KM1144 initiate polymerization of pyrrole [4]. In connection with the study of the $Cp_2Fe-CCl_4$ system, we have extended our research on the iron-arene salts-polyhalogen compounds systems. We have found that addition of $CH_2CH_2Cl_2$, $CHCl_3$, or CCl_4 to the iron-arene salts-pyrrole system significantly accelerates pyrrole polymerization. This reaction occurs even in the presence of daylight in a laboratory. Polypyrroles obtained in this way are also colloidal black powders, and their FT-IR spectra (Figs. 10 and 11) differ slightly, depending on the type of iron-arene (Irgacure 261 or Komplex KM1144) and halogenated solvent ($CH_2CH_2Cl_2$, $CHCl_3$ or CCl_4) used.

IR spectra of PPy obtained in the presence of Cp_2Fe (0.01 *M*):Py$-CCl_4$ (9:1) (Fig. 9B), Irgacure 261 (0.01 *M*):Py$-CCl_4$ (9:1) (Fig. 9C), and Komplex KM1144 (0.01 *M*):Py$-CCl_4$ (Fig. 9D) are the same and differ very little from PPy polymerized in the presence of $FeCl_3-CH_3NO_2$ addition complex (Fig. 9A). These results indicate that pyrrole polymerization in the presence of iron-arene salts-CCl_4 must occur by the same mechanism as in the case of $Cp_2Fe-CCl_4$. It has been proposed that iron-arene salts are photolyzed according to the mechanism [28]:

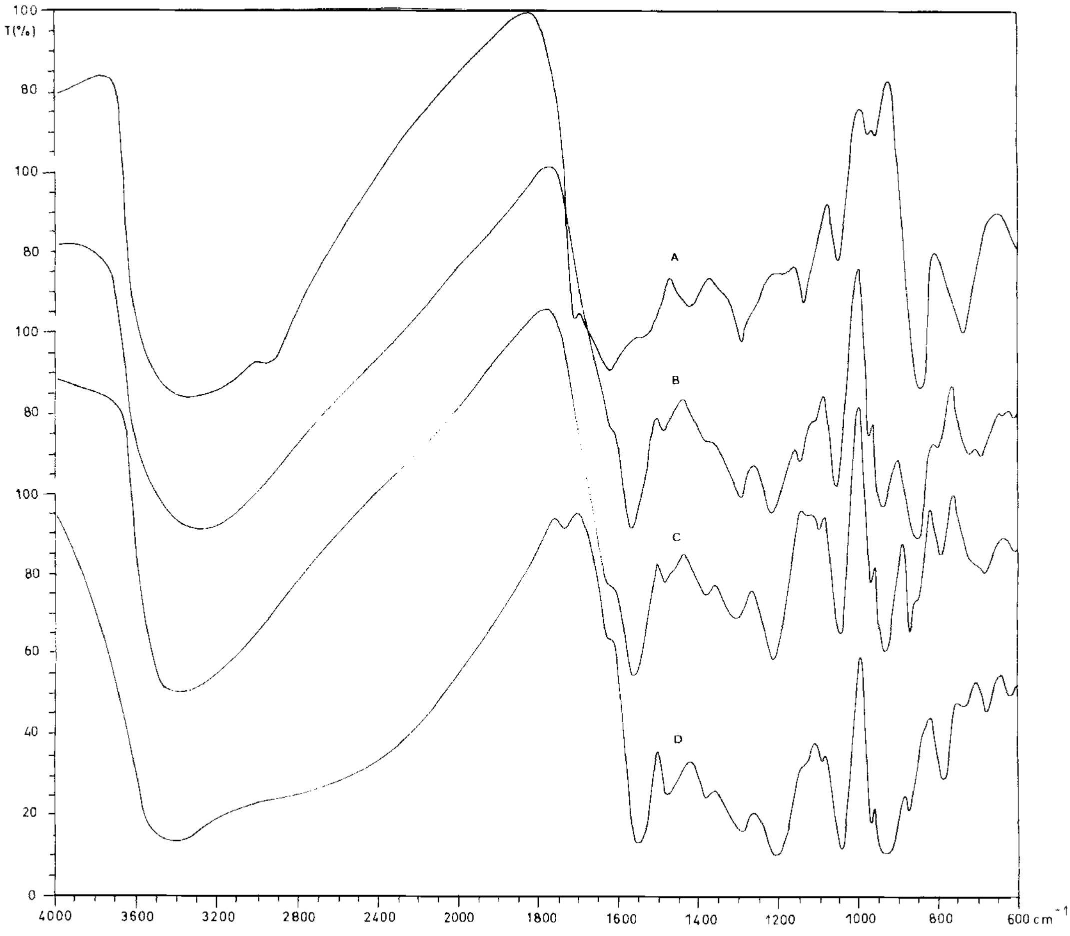
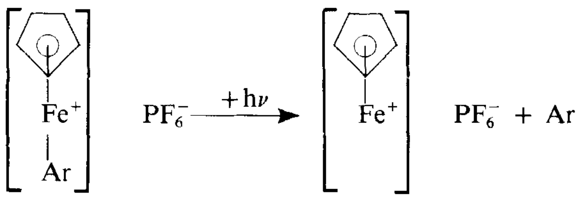


FIG. 10. IR spectra of polypyrroles polymerized by iron-arene (isopropylbenzene) (Irgacure 261) (0.01 *M*) in: (A) pure pyrrole (Py); (B) Py:$CH_2CH_2Cl_2$ (9:1); (C) Py:$CHCl_3$ (9:1); and (D) Py:CCl_4 (9:1), in the presence of UV (254 nm) irradiation.



(8)

(I)

where: Ar = iso-propylbenzene, naphthalene, pyrene, etc. On the other hand, photolysis of iron-arene salts $(\mathrm{Cp{-}Fe{-}arene})^+$ in acetonitrile solution yields Fe(II) and ferrocene (Cp_2Fe) as the Fe-containing product [29]:

$$2(\mathrm{Cp{-}Fe{-}arene})^+ \xrightarrow[\mathrm{CH_3CN}]{+h\nu} \mathrm{Fe(II)} + \mathrm{Cp_2Fe} + 2\,\mathrm{arene} \qquad (9)$$

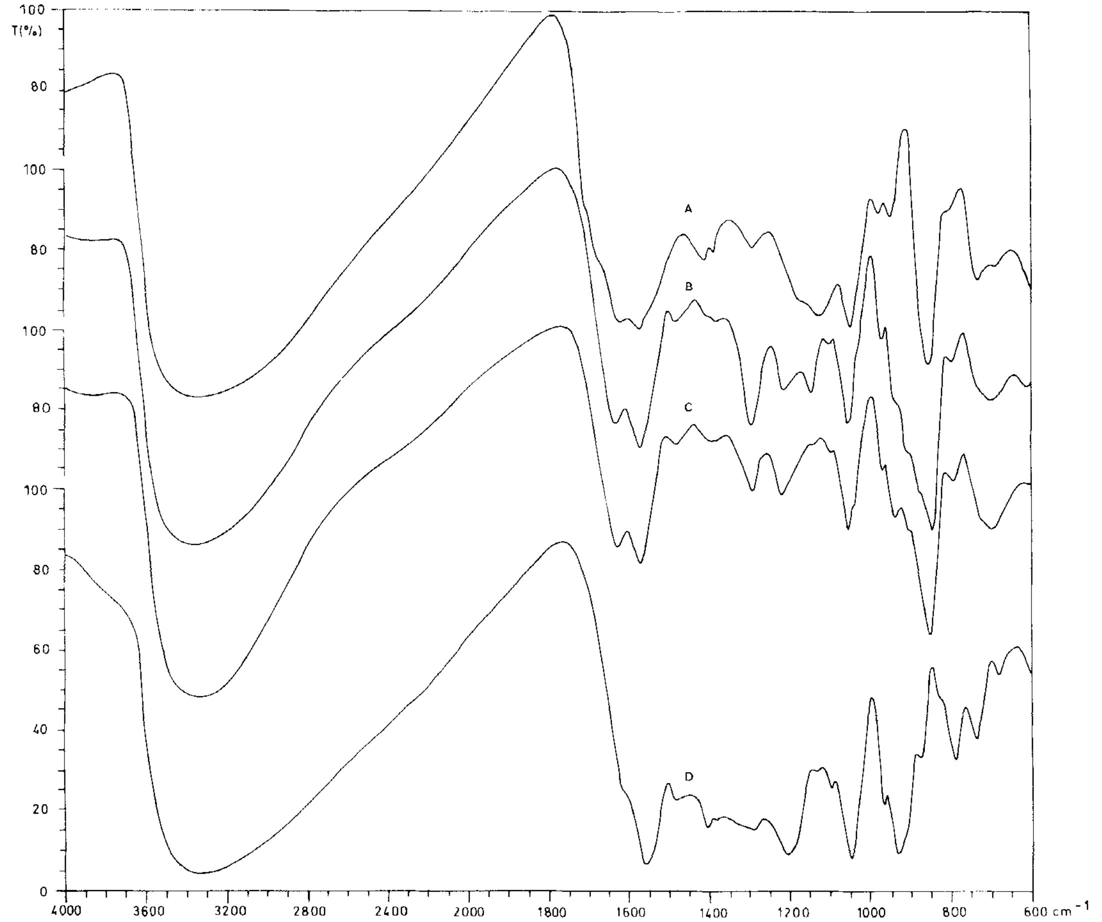


FIG. 11. IR spectra of polypyrroles polymerized by iron-arene (naphthalane) (Komplex KM1144) (0.01 *M*) in: (A) pure pyrrole (Py); (B) Py:$CH_2CH_2Cl_2$ (9:1); (C) Py:$CHCl_3$ (9:1); and (D) Py:CCl_4 (9:1) in the presence of UV (254 nm) irradiation.

Ferrocene (Cp_2Fe) and Fe(II) species formed from iron-arene salts (Cp—Fe—arene)$^+$ in acetonitrile can also result from two other independent mechanisms [30]:

Mechanism I:

$$(\mathrm{Cp{-}Fe{-}arene})^+ \xrightarrow[\mathrm{CH_3CN}]{+h\nu} (\mathrm{Cp{-}Fe{-}(CH_3CN)_3})^+ + \mathrm{arene} \tag{10}$$

$$(\mathrm{Cp{-}Fe{-}(CH_3CN)_3})^+ \overset{+\mathrm{CH_3CN}}{\rightleftharpoons} \mathrm{Fe(CH_3CN)_6^{2+}} + \mathrm{Cp}^- \tag{11}$$

$$(\mathrm{Cp{-}Fe{-}(CH_3CN)_3})^+ + \mathrm{Cp}^- \longrightarrow \mathrm{Cp_2Fe} + 3\,\mathrm{CH_3CN} \tag{12}$$

Mechanism II:

$$(\mathrm{Cp{-}Fe{-}(CH_3CN)_3})^+ + (\mathrm{Cp{-}Fe{-}(CH_3CN)_3})^+ \longrightarrow$$
$$\mathrm{Cp_2Fe} + \mathrm{Fe(II)} + 6\,\mathrm{CH_3CN} \tag{13}$$

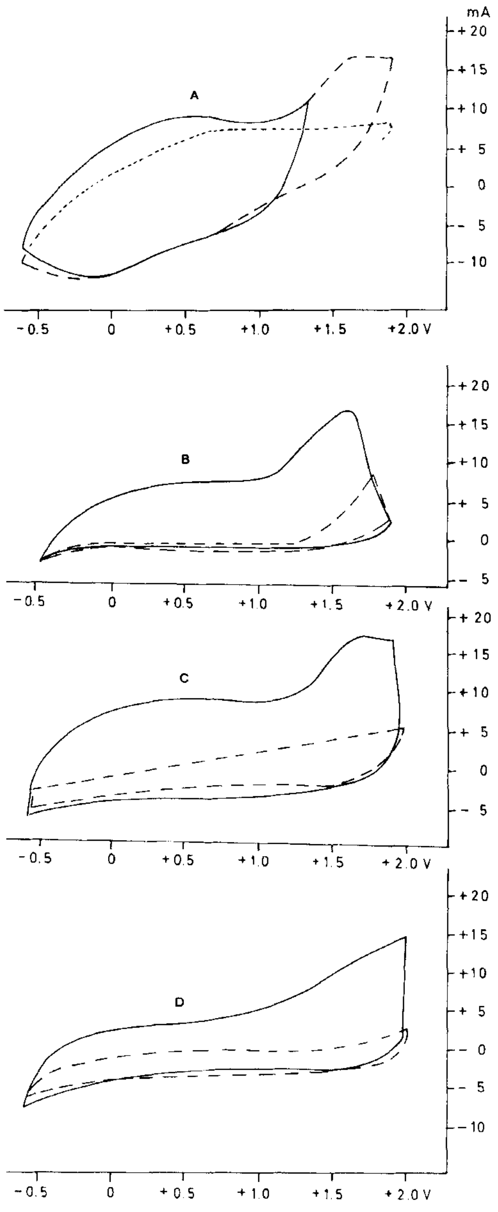


FIG. 12. Cyclical voltammograms of polypyrroles (PPy) obtained in the presence of: (A) $FeCl_3-CH_3NO_2$ (addition complex); (B) ferrocene [Cp_2Fe (0.01 *M*):Py$-CCl_4$ (9:1)]; (C) Irgacure 261 (0.01 *M*): Py$-CCl_4$ (9:1); (D) Komplex 1144 (0.01 *M*):Py$-CCl_4$ (9:1), in the presence of UV (254 nm) (B, C, D) irradiation; (———) 1st cycle, (- - -) 2nd cycle.

$$(Cp{-}Fe{-}(CH_3CN)_3)^+ + (Cp{-}Fe{-}arene)^+ \longrightarrow$$
$$Cp_2Fe + Fe(II) + arene + 3\,CH_3CN \qquad (14)$$

In the presence of oxygen (air), Fe(II) is oxidized to Fe(III). A similar mechanism for the photolysis of iron-arene salts may occur in pyrrole. If these reactions occur in the presence of CCl_4, it can be expected that Cp_2Fe formed is responsible for the initiation of pyrrole polymerization according to Reactions 2–7, and finally PPy will not differ each other (IR spectra, Fig. 9).

Conductivities of PPy obtained in the presence of Cp_2Fe (0.01 M):Py—CCl_4 (9:1) or $(Cp{-}Fe{-}arene)^+$ (0.01 M):Py—CCl_4 (9:1) are in the range of $2.0\text{–}3.0 \times 10^{-5}$ S cm^{-1}. The low conductivities can be the result of loss of conjugation by halogenation of PPy. On the other hand, the low conductivities of PPy may be due to the small colloidal particles, which are difficult to press into tablets for conductivity measurements. These are very brittle and are easily destroyed when electrodes are pressed into them. For that reason, electrodes in the measuring cell do not achieve good contact with sample colloidal grains.

The cyclical voltammograms for different PPy obtained in the presence of Cp_2Fe (0.01 M):Py—CCl_4 (9:1) (Fig. 12B), Irgacure 261 (0.01 M):Py—CCl_4 (9:1) (Fig. 12C), and Komplex KM1144 (0.01 M):Py—CCl_4 (9:1) (Fig. 12D) show low electrochemical activity of these PPy compared to PPy polymerized in the presence of $FeCl_3{-}CH_3NO_2$ addition complex (Fig. 12A). These results show the presence of nonequivalent electroactive sites in PPy(s), which may arise from the defects due to the $\beta{-}\beta$ linkages as a result of polymerization, during which reactive fragments from $Cp_2Fe{-}CCl_4$ or (Cp—Fe—arene salts)—CCl_4 [mainly trichloromethyl radicals ($\cdot CCl_3$)] react with polyene structures, disrupt the conjugation along the backbone, and lead to chain segments that average from 5 to 10 pyrrole units in length. The inverse relationship between the chain length and the anodic peak is a general feature of conjugated systems and leads to polymers with a range of formal potentials and thus to a broad peak. Somewhat conductive PPy have been obtained in the presence of $FeCl_3$ or $Fe(ClO_4)_3$ [31–33].

In conclusion, photoinitiated polymerization of pyrrole by the ferrocene and iron-arene salts-chlorinated solvents occur by the same mechanism in which Fe(III) formed from the photolysis of these initiators causes polymerization of pyrrole. The polymerization reaction is accompanied by halogenation of polypyrroles, which decrease their conductivity and electrochemical properties.

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