

Kinetic Study of Pyrrole Polymerization with Iron(III) Chloride in Water

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SYNOPSIS

The chemical synthesis of polypyrrole in water, with FeCl₃ as an oxidant of pyrrole, was investigated. During these experiments in ambient air, a large evaporation of pyrrole was observed. Moreover, a kinetic study of pyrrole disappearance by high-performance liquid chromatography (HPLC), with various FeCl₃ concentrations, proved that the polymerization is first order with respect to the pyrrole and second order with respect to the FeCl₃. These kinetics can be explained by the formation of an intermediary FeCl₃-pyrrole complex as the first step of the polymerization. The second step, which is rate-determining, is the pyrrole oxidation by FeCl₃. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polypyrrole is probably one of the most promising conducting polymers for industrial developments, due to its good conductivity and relatively good stability. Therefore, it is one of the most investigated conducting polymers. Polypyrrole is generally synthesized by simultaneous polymerization and oxidation of pyrrole by electrochemistry¹ or by chemistry.² The electrochemical synthesis gives a polymer film deposited on an electrode surface. On the other hand, the chemical synthesis easily gives a large quantity of powder or a deposit.³ Therefore, this chemical synthesis seems better for industrial applications. We are studying the optimization of the polypyrrole chemical synthesis to obtain, with a good yield, a stable polymer with high conductivity.

There are, in the literature, many examples of polypyrrole chemical syntheses. As a matter of fact, "pyrrole blacks," whose synthesis includes an oxidation, have been known since 1916,⁴ but these materials have a poor conductivity. Practically, the search of an efficient oxidizing species is limited by

some necessary conditions: The oxidant redox potential must be close to that of pyrrole; there must be no interfering reactions; and the reduced form of the oxidant must be easily taken out of the polymer. Some metallic ions seem to fulfill these conditions, particularly Fe³⁺ and Cu²⁺. Some authors have used Cu²⁺,^{2,5-7} but most of them have chosen Fe³⁺,^{2,5,8-15} which gives a better polymer conductivity² and a higher rate of synthesis.⁴ The most commonly used ferric salt is FeCl₃,^{2,5,6,8,9,12} which is easily handled and dissolved. A highly conductive polymer, with a good yield, can be thus rapidly obtained. Generally, in almost all the publications mentioned, the iron counterion is also the polypyrrole doping species.

Several electrochemical synthesis studies have shown that mineral doping species (Cl⁻, ClO₄⁻, NO₃⁻, etc.) give an unstable polypyrrole, which rapidly loses its conductivity.^{16,17} The stability, as well as the conductivity, is improved by using arylsulfonate ions¹⁸⁻²⁰ as doping species. The same results have been obtained for chemical synthesis by using aromatic sulfonate iron salts¹⁰ or by adding an aromatic sulfonate to the FeCl₃ solution.²¹

The solvent used for the polypyrrole chemical synthesis depends on the choice of the oxidizing species. The best solvents allow one to obtain a high conductivity polymer, by a rapid synthesis. For iron

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salts, they are water,^{5,6,8,15} alcohols,^{9-11,14,15} and ether.² Water is the most practical when considering industrialization of the process.

Therefore, for us, the best existing process for polypyrrole chemical synthesis seems to be the pyrrole oxidation by FeCl₃ in water, with an aromatic sulfonate as the doping species. This easy and inexpensive way of synthesis allows one to obtain polypyrrole of good quality and high stability. Furthermore, an easy industrial development seems possible. We chose this method of synthesis.

This work is a kinetic study of the pyrrole concentration in the reaction solution during this chemical synthesis. For this purpose, a method was developed to titrate pyrrole in solution by the use of high-performance liquid chromatography (HPLC). This allowed, on the one hand, the optimization of the recovery of polypyrrole and, on the other hand, the explanation of the mechanisms of the first steps of the reaction, which are rate-determining. Moreover, some preliminary results on the polymer conductivity are presented for different concentrations of FeCl₃.

EXPERIMENTAL

Chemical Products

Pyrrole (Prolabo) was vacuum-distilled and stored at 3°C in the absence of light. 1-Naphthalene sulfonic acid (HANS) (Aldrich 70–75%, containing 11% H₂O and 16% H₂SO₄) and FeCl₃ (Prolabo, 41% aqueous solution) were used as received.

Polymer Synthesis

Polypyrrole was synthesized in water by FeCl₃-oxidizing polymerization of pyrrole, adding an aromatic sulfonate doping species. Our previous studies²¹ showed that naphthalene sulfonates are very good polypyrrole-doping species, better than the *p*-toluene sulfonate usually used. The naphthalene sulfonates are easily inserted in the polymer and allow one to obtain a polymer of good conductivity and high stability. In this study, we used 1-naphthalene sulfonate. The synthesis was performed by mixing three aqueous solutions of pyrrole, HANS, and FeCl₃.

The pyrrole concentration in the synthesis solution was 0.033 M or 0.044 M, the FeCl₃ concentration was variable, and the HANS/pyrrole ratio was always 0.3 (according to the usually obtained doping

levels, between 0.25 and 0.33 [Ref. 22]). This pyrrole concentration in the reaction solution is not high because it is limited by the poor HANS solubility in water (to have a good ANS⁻ anion-doped polymer, the pyrrole/HANS molar ratio must be lower than 3).

These syntheses were performed under atmospheric pressure in ambient air (or sometimes in argon). At the end of the synthesis, the polypyrrole powder was filtered, washed with water (until no iron remained), and dried in vacuum at ambient temperature for 16 h.

Analysis Methods

The recovery of polypyrrole (in percent) is defined as the quantity of polymerized pyrrole, normalized by the initial amount of pyrrole in the polymerization solution. The amount of polymerized pyrrole was calculated from the quantity of synthesized polypyrrole (evaluated by weighing), assuming that the polypyrrole formula is [(C₄H₃N)^{0.3+}, 0.3 ANS⁻]_n. This formula was confirmed by previous results²¹ showing that the polypyrrole doping species is preferentially the ANS⁻ anion.

The conductivity was measured by the four-point probe method (Alessi four-point head, Keithley current generator, DANA Electronics voltmeter) on pellets of dried polypyrrole powder (100 mg pressed under 7 tons for 5 min).

Pyrrole was dosed in the solution by liquid chromatography (HPLC) using a UV detection. The following processing conditions were determined: Chrompack Zorbax C18 "inverse-phase" column (5 μm phase, length 25 cm, diameter 4.6 mm); mobile phase 30% acetonitrile (Prolabo, for HPLC)/70% "Millipore" water (18 MΩcm); mobile phase rate 1 mL/min; and injection 20 μL. The UV detection is made at 220 nm.

The measured signal is the pyrrole peak area, which is proportional to its concentration. This signal rises linearly in the 0–60 mg/L concentration range (this range was chosen for the standard curve).

Samples were taken during the synthesis and immediately diluted to 1/100th in water. This dilution allows one to have pyrrole concentrations in the range chosen for the standard curve. Moreover, it allows one to lower the rate of the polymerization (after 24 h, the pyrrole concentration is nearly the same). The diluted sample was analyzed as fast as possible, generally less than 1 h after the sample had been taken.

RESULTS AND DISCUSSION

Optimization of the Recovery of Polypyrrole

The recovery and the conductivity of the polypyrrole, made by pyrrole oxidation by FeCl_3 with HANS, were previously systematically studied considering several processing parameters: length of reaction, temperature, atmosphere (ambient air or argon), and stirring.²³ This study was performed for a stoichiometric FeCl_3 concentration ($\text{FeCl}_3/\text{pyrrole}$ molar ratio was 2.3 [Ref. 8]), and pyrrole concentration was 0.044 M.

As shown in Figure 1 (for a synthesis made in ambient air and at ambient temperature [close to 22°C], without stirring), the recovery of polypyrrole first rises regularly with the length of synthesis, then seems to become stable, at about 50%, after 4 h of reaction. Therefore, a large quantity of pyrrole does not polymerize. Modifying the processing conditions (lowering or increasing the temperature, stirring and/or working in inert atmosphere) does not really change this result, the best recovery of polypyrrole always being around 50%.²³

Variable recoveries of polypyrrole (from some % to 100%) can be found in the literature, but few authors have wondered why and have searched to optimize the amount of synthesized polymer. For some authors,^{8,24} the recovery of polypyrrole becomes constant after a certain length of reaction.

But this optimal length of reaction is variable: 12 and 24 h,⁸ 1 h,²⁴ or 4 h for us. We used HPLC to understand and optimize, for this reaction, the recovery of polypyrrole. This study gave kinetic results on pyrrole disappearance during the synthesis and allowed us to compare the quantity of polypyrrole obtained with the quantity of pyrrole consumed.

The disappearance of pyrrole vs. time (t) was studied for the previous syntheses (in ambient air) at different temperatures or stirring rates.²³ The obtained results (e.g., in Fig. 2) show that pyrrole always disappeared with first-order kinetics with respect to the pyrrole:

$$[\text{Py}] = [\text{Py}]_0 e^{-kt} \quad \text{or} \quad \ln[\text{Py}] = \ln[\text{Py}]_0 - kt$$

with $[\text{Py}]$ the pyrrole concentration at time t , $[\text{Py}]_0$ the initial pyrrole concentration, and k the rate constant.

Tables I and II show the different k (min^{-1}) values obtained, which allow one to calculate the quantities of pyrrole consumed for a 4 h reaction. These values are compared to the quantities of polypyrrole obtained. A large part of the pyrrole used does not polymerize and is thus consumed in an interfering process. This parasite process, under certain conditions, may be dominant. For example, at 280 rpm, 59% of the pyrrole is used in this process and only 25% polymerizes. The parasite process is favored

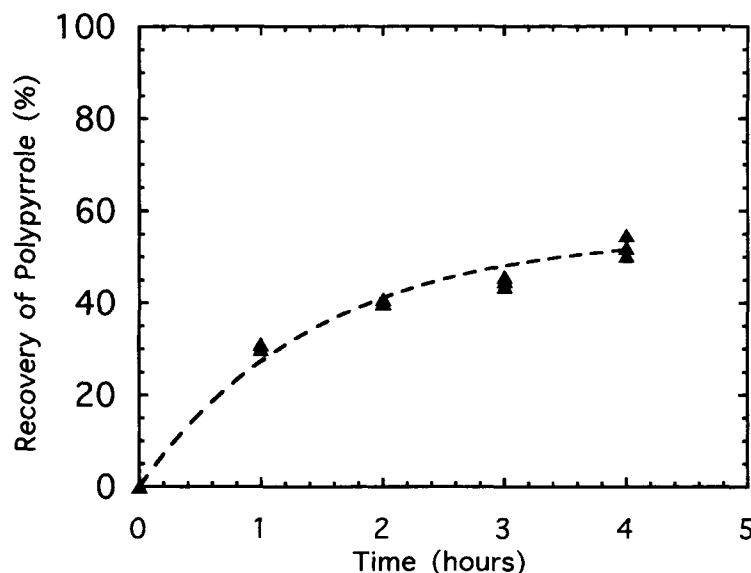


Figure 1 Time dependence of the recovery of polypyrrole for a synthesis performed in ambient conditions without stirring (pyrrole concentration = 0.044 M, molar ratio of $\text{FeCl}_3/\text{pyrrole}$ = 2.3, molar ratio of HANS/pyrrole = 0.3).

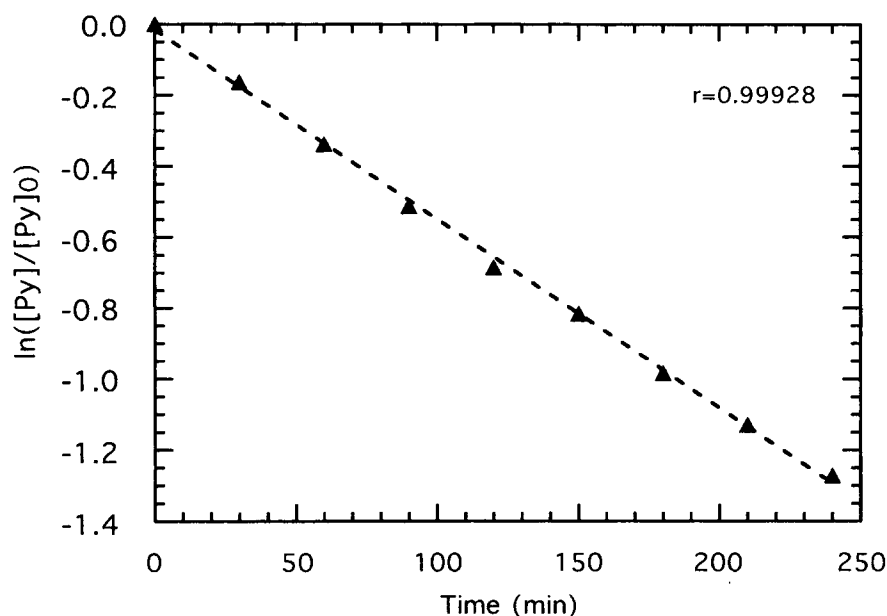


Figure 2 Typical decay of pyrrole concentration ($[Py]$) in the polymerization medium (initial molar ratio of $FeCl_3$ /pyrrole = 2.3, initial molar ratio of HANS/pyrrole = 0.3, initial pyrrole concentration ($[Py]_0$) = 0.044 M).

(with respect to the polymerization) by stirring and by a low synthesis temperature.

According to Lei et al.,²⁴ the small recovery of polypyrrole obtained may be explained by the formation of soluble polypyrrole oligomers. Nevertheless, we cannot find quantitative quantities of these soluble products by HPLC analytical investigation of the synthesis solution.

To determine what this interfering process is, some simple aqueous solutions of pyrrole (without

$FeCl_3$ and HANS), with the same concentrations as in the previous studies, were stirred in open containers and analyzed by HPLC. In these conditions, pyrrole disappeared with the same first-order kinetics. The values of k obtained for experiments performed in air, at ambient temperature (close to 22°C), under atmospheric pressure, and with various stirring rates are presented in Table III. A pyrrole disappearance is also observed if the same solution is stirred in an open container but in an inert at-

Table I Values of the Rate Constant (k) of the Pyrrole Disappearance and of the Quantity of Pyrrole Used (to Produce or Not Produce Polypyrrole [PPy]) and the Quantity of Pyrrole Left

Stirring (rpm)	k (min^{-1})	% of Pyrrole Used		
		Producing PPy	Not Producing PPy	% of Pyrrole Left
0	1.7×10^{-3}	42	0	58
150	4.7×10^{-3}	37	29	34
200	5.8×10^{-3}	31	42	27
280	7.6×10^{-3}	25	59	16

The length of reaction was 4 h, for experiments made at different stirring rates, in ambient atmosphere and at ambient temperature (close to 22°C).

Table II Values of the Rate Constant (k) of the Pyrrole Disappearance and of the Quantity of Pyrrole Used (to Produce or Not Produce Polypyrrole [PPy]) and the Quantity of Pyrrole Left

T (°C)	k (min^{-1})	% of Pyrrole Used		
		Producing PPy	Not Producing PPy	% of Pyrrole Left
11	2.6×10^{-3}	13	35	52
25	6.8×10^{-3}	35	45	20
38	1.7×10^{-2}	47	52	1
50	2.8×10^{-2}	55	45	0

The length of reaction was 4 h, for tests made at different temperatures (T), in ambient atmosphere and with a stirring rate of 200 rpm.

Table III Values of the Rate Constant (k) of the Pyrrole Evaporation in Pure Water, for Experiments Made at Different Stirring Rates, in Air, Under Atmospheric Pressure, and at Ambient Temperature (Close to 22°C)

Stirring (rpm)	k (min ⁻¹)
0	0
150	1.3×10^{-3}
200	1.6×10^{-3}
280	5.0×10^{-3}

mosphere (argon in a glove box). Moreover, the quantity of pyrrole remains constant if the same solution is stirred 24 h in a hermetically sealed container. Therefore, this pyrrole disappearance is not a reaction with oxygen, nor an hydrolysis of pyrrole. We believe that it is due to pyrrole evaporation because of stirring. As the pyrrole boiling point is 130°C, this could indicate the existence of a pyrrole/water azeotrope, as was found for water with other aromatic amines.²⁵ It must be emphasized that this evaporation phenomenon is very sensitive to the geometrical characteristics of the polymerization reactor, but also to the amount of solution in this reactor: For example, decreasing 10 times this quantity leads to a large increase of k , from $1.3 \times 10^{-3} \text{ min}^{-1}$ to $2.1 \times 10^{-2} \text{ min}^{-1}$ (for a stirring rate of 150 rpm). Therefore, this pyrrole evaporation should be evaluated for each processing condition.

This pyrrole evaporation is likely a prime reason for the poor recoveries of polypyrrole obtained in chemical syntheses by different authors. For example, the maximum recoveries of polypyrrole, obtained by Lei et al.,²⁴ for syntheses made with weak concentrations but with an iron excess (FeCl_3 /pyrrole molar ratio is 50), with stirring, in ambient conditions, are low. This is explained by these authors by the formation of soluble polypyrrole oligomers. We made the same syntheses in sealed containers. Contrary to Lei et al.'s results,²⁴ the quan-

tities of polypyrrole obtained increase with the length of the synthesis, even after 1 h. The corresponding recoveries of polypyrrole, after pyrrole has totally disappeared (the length of synthesis should be 1 week), are presented in Table IV, together with the results of the above authors. The conductivities of the synthesized products are also compared. The recoveries of polypyrrole that we obtained are distinctly higher than those of the above authors. They are nearly quantitative, though the conductivities of the polymers are in the same range as those of Lei et al.²⁴ Therefore, the low optimum recoveries obtained by Lei et al.²⁴ must be attributed more to the pyrrole evaporation than to the formation of soluble polypyrrole oligomers.

In addition, the effect of the stirring rate on the polymerization kinetic constant was evaluated for syntheses performed in air, in closed containers, and at ambient temperature (close to 22°C). The k values obtained, presented in Table V, seem to indicate that the polymerization kinetic constant does not depend on stirring. Moreover, these values are in perfect agreement with those that can be calculated from Table I, taking into account the amounts of polypyrrole obtained.[†] Nevertheless, they are a little smaller than those evaluated, by subtraction, from Tables I and III, which can suggest that pyrrole evaporation is a little faster in water containing FeCl_3 and HANS than in pure water.

Finally, pyrrole oxidation by FeCl_3 in water, with ANS^- as the doping species, gives a polypyrrole of good quality,²¹ which can be obtained with an optimum recovery if the synthesis is performed in a sealed container. However, provided that pyrrole evaporation is prevented, obtaining a complete polymerization of pyrrole will need, in practice, a long reaction time when stoichiometric quantities of FeCl_3 are used (Tables I, II, and V). Therefore, it is important to increase the rate of polymerization,

[†] This calculation is made assuming that the ratio (% of pyrrole producing polypyrrole)/(% of pyrrole used) is equal to the ratio (rate constant for pyrrole polymerization)/(rate constant for pyrrole disappearance).

Table IV Recoveries and Conductivities of Polypyrrole, When Synthesizing in Sealed Containers, with Low FeCl_3 ([Fe]) and Pyrrole ([Py]) Concentrations; the Results are Compared with Those of Lei et al.²⁴

[Fe] (mol/L)	[Py] (mol/L)	Recovery (%)		Conductivity (S/cm)	
		Lei et al.	This Study	Lei et al.	This Study
0.13	0.0025	51	98	1.1×10^{-4}	1.2×10^{-4}
0.06	0.0013	40	87	2.7×10^{-5}	8.3×10^{-6}

Table V Values of the Rate Constant (k) of the Pyrrole Polymerization, for Experiments Made at Different Stirring Rates, in Closed Containers and at Ambient Temperature (close to 22°C), These Values (1) Are Compared to Those Calculated from Table I (2) and to Those Evaluated from Table I and III (3) (See Text)

Stirring (rpm)	(1) k (min^{-1})	(2) k (min^{-1})	(3) k (min^{-1})
150	2.0×10^{-3}	2.6×10^{-3}	3.4×10^{-3}
200	2.5×10^{-3}	2.5×10^{-3}	4.2×10^{-3}
280	2.8×10^{-3}	2.3×10^{-3}	2.6×10^{-3}

without lessening the conductivity of the obtained polymer.

Influence of the FeCl_3 Concentration on Pyrrole Polymerization

Many authors have studied the influence of the FeCl_3 concentration on the recovery and conductivity of polypyrrole. Generally, they studied the influence of the FeCl_3 /pyrrole molar ratio, lower, higher, or equal to the stoichiometry of the polymerization reaction (2.3). They work with a constant pyrrole concentration, varying the FeCl_3 concentration.^{2,6,8,9,15,26} For

FeCl_3 /pyrrole molar ratios lower than 2.3, the rate of polymerization and the recovery of polypyrrole decrease rapidly; the reaction cannot go to completion.^{2,6,8,15,26} On the other hand, the FeCl_3 /pyrrole molar ratio has nearly no influence on the conductivity of the synthesized polypyrrole.^{2,6,8,9,15} For ratios higher or equal to 1 (and sometimes 0.1 [Ref. 8]), the conductivities are all in the same range. According to Slama,¹⁵ this is because the doping reaction has a higher rate than that of the polymerization reaction. This result is consistent with the last work of Lei et al.,²⁴ where they showed that the quality of the obtained polypyrrole is not determined by the FeCl_3 /pyrrole ratio, but, essentially, by the concentrations of pyrrole and FeCl_3 . The higher the concentrations, the faster the kinetics and the better the quality of polypyrrole.

As mentioned previously, our pyrrole concentration, close to 0.04 M, is an optimum because of the doping species that we have chosen. Thus, the most obvious way to try to optimize the recovery and the conductivity of polypyrrole (within a reasonable length of reaction) is by varying the FeCl_3 concentration ($[\text{Fe}]$). This study of the influence of the FeCl_3 concentration, on the pyrrole polymerization, was performed with a pyrrole concentration of 0.033 M, with HANS (molar ratio HANS/pyrrole = 0.3). The experiments were done stirring (160 rpm), in ambient air and at ambient temperature (close to 22°C) and in an open container (under

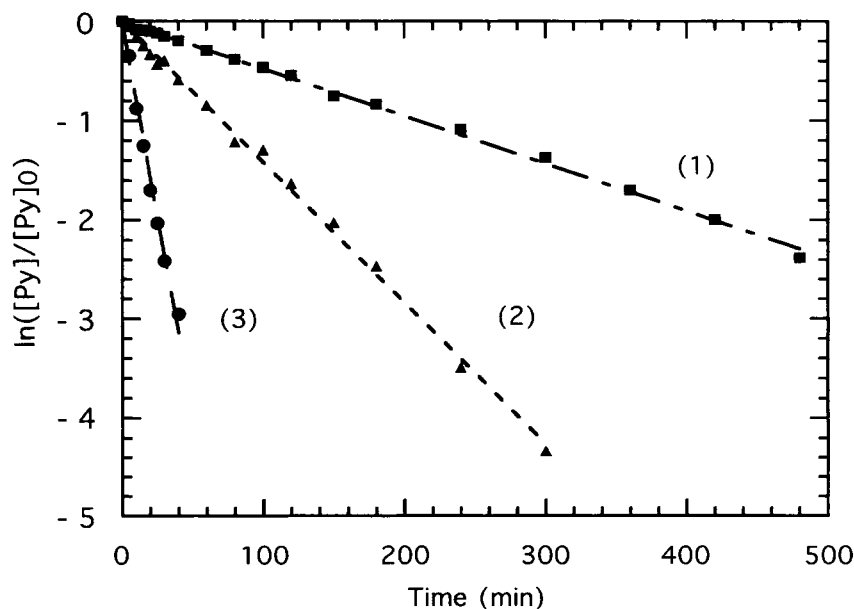


Figure 3 Decay of pyrrole concentration ($[\text{Py}]$) in the polymerization medium for various FeCl_3 concentrations: (1) 0.002 M; (2) 0.16 M; (3) 0.78 M (initial molar ratio of HANS/pyrrole = 0.3, initial pyrrole concentration ($[\text{Py}]_0$) = 0.033 M).

atmospheric pressure). We were first interested in the pyrrole disappearance kinetics. This allowed us to understand the pyrrole polymerization kinetics and mechanisms, with FeCl_3 as an oxidant.

Pyrrole Disappearance Kinetics

For FeCl_3 concentrations between $4 \times 10^{-4} \text{ M}$ and 1.8 M (the FeCl_3 /pyrrole molar ratio is between 0.012 and 55), the pyrrole disappearance kinetics are always first order with respect to the pyrrole (Fig. 3). The rate constants k are plotted (Fig. 4), vs. the FeCl_3 concentrations.

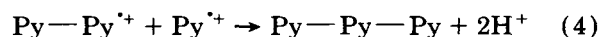
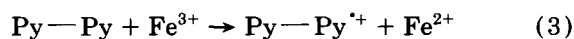
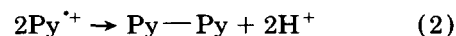
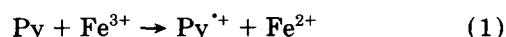
For low FeCl_3 concentrations ($4 \times 10^{-4} \text{ M} < [\text{Fe}] < 0.03 \text{ M}$ or $0.012 < [\text{Fe}]/[\text{Py}] < 1$), the k values are nearly constant (k is around $5 \times 10^{-3} \text{ min}^{-1}$) and close to the pyrrole evaporation rate constant evaluated (in pure water) for the processing conditions of this study (volume of solution, reactor geometrical characteristics, see above). On the other hand, for high FeCl_3 concentrations ($0.3 \text{ M} < [\text{Fe}] < 1.8 \text{ M}$ or $10 < [\text{Fe}]/[\text{Py}] < 55$), the pyrrole disappearance rate constant rapidly rises with the FeCl_3 concentration. Thus, for low FeCl_3 concentrations, the pyrrole disappearance seems essentially determined by the pyrrole evaporation, the polymerization probably being slow. But for high FeCl_3 concentrations, the pyrrole disappearance is most likely determined by the polymerization, which appears to be very fast, the pyrrole evaporation being negligible

(for $[\text{Fe}]/[\text{Py}] = 15$, $k = 0.045 \text{ min}^{-1}$, which is about 10 times the value of the evaporation rate constant). For medium FeCl_3 concentrations, particularly for the stoichiometric reaction ($[\text{Fe}]/[\text{Py}] = 2.3$ or $[\text{Fe}] = 0.075 \text{ M}$), the evaporation and polymerization rate constants seem in the same range (k is around 10^{-2} min^{-1}).

Pyrrole Polymerization Kinetics and Mechanisms with FeCl_3

The kinetics of the pyrrole polymerization by FeCl_3 were studied by Bjorklund.²⁷ He measured the polypyrrole concentration during the reaction by UV spectroscopy at 800 nm (his polypyrrole was a colloidal suspension). Some authors also tried Raman spectroscopy or potentiometry.^{28,29}

Similarly to the process proposed by Geniès et al.³⁰ (lately confirmed by Andrieux et al.³¹) for the pyrrole (Py) electropolymerization, the reaction of pyrrole with FeCl_3 is likely the following:



The first step [eq. (1)] is a pyrrole oxidation leading to a radical cation ($\text{Py}^{\cdot+}$). This radical can

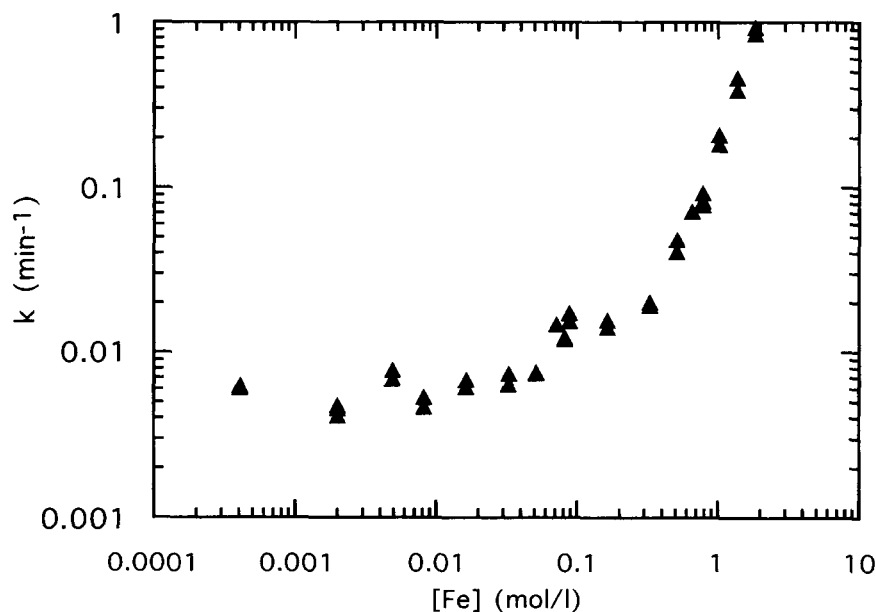
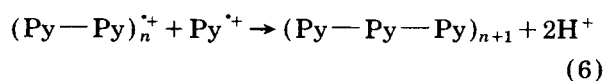
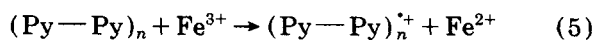


Figure 4 Variation vs. FeCl_3 initial concentration ($[\text{Fe}]$) of the rate parameter (k) of pyrrole concentration decay in the polymerization medium (initial molar ratio of HANS/pyrrole = 0.3).

dimerize to make bipyrrrole (Py—Py) [eq. (2), condensation] by setting two protons free. As indicated by eqs. (3) and (5) and (4) and (6), the polycondensation proceeds similarly. At the same time, the polypyrrole chain is doped (oxidized):



The formation of bipyrrrole by dimerization of pyrrole [eqs. (1) and (2)] was shown to be the slowest process, which was confirmed by Wei et al.,³² by adding this dimer to the reaction solution. According to Geniès et al.,³⁰ the kinetically determining step of the electropolymerization of pyrrole appears to be the condensation of the cation radical (Py^{*+}) [eq. (2)], but the chemical synthesis of polypyrrole, with FeCl_3 as an oxidant, might be kinetically limited by the pyrrole oxidation [eq. (1)].²⁷

The results of the study of the polypyrrole recovery, discussed above, seem to indicate that the polypyrrole formation is determined by the pyrrole reaction. As a matter of fact, the rates of these two phenomena are found to be of the same order of magnitude (Tables I, II, and V), showing that the pyrrole likely participates in the rate-determining step of the polymerization process, in agreement with Bjorklund's hypothesis.²⁷

The influence of the pyrrole concentration on the kinetics of the polymerization process can be quantitatively specified using the results obtained for high FeCl_3 concentrations ($[\text{Fe}]/[\text{Py}] > 10$). As a matter of fact, with the pyrrole evaporation being slow, and negligible in these conditions, the pyrrole disappearance can be attributed here solely to its polymerization. Consequently, with the FeCl_3 concentrations being high, and remaining nearly constant during the reaction, the variation of the pyrrole concentration, during the polymerization process, is kinetically pseudo-first order with respect to the pyrrole:

$$d[\text{Py}]/dt = -k[\text{Py}]$$

As shown in Figure 4, the rate constant, k , of this phenomenon depends on the FeCl_3 concentration. It allows one to evaluate the order (n) of the pyrrole disappearance, with respect to the FeCl_3 . As a matter of fact, for high FeCl_3 concentrations ($[\text{Fe}]$), $[\text{Fe}]$ is nearly constant and we can write

$$k = \beta[\text{Fe}]^n \quad \text{and} \quad \ln k = \ln \beta + n \ln [\text{Fe}]$$

where β is a constant.

Figure 5 shows the variation of $\ln k$ vs. $\ln [\text{Fe}]$ for the values of the above paragraph. In addition, we have reported the values obtained for two tests made in sealed containers in the conditions of Lei

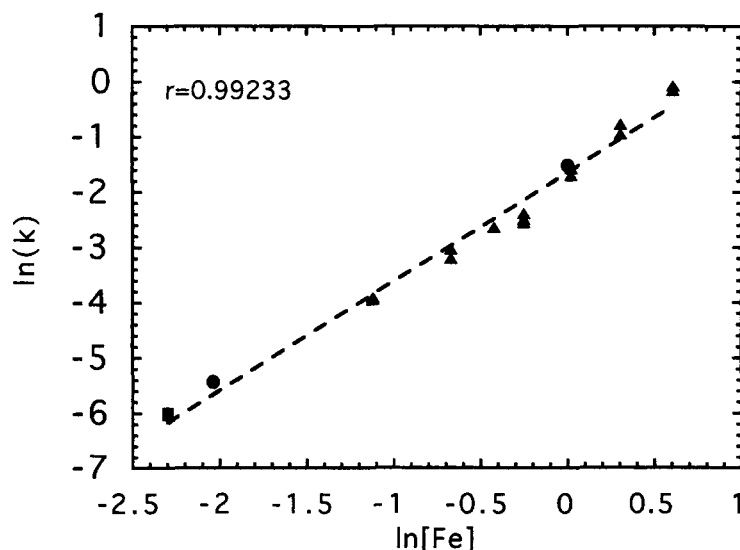


Figure 5 Variation vs. FeCl_3 initial concentration ($[\text{Fe}]$) of the rate parameter (k) of pyrrole polymerization: (●) molar ratio of FeCl_3 /pyrrole = 50, without HANS, closed reactor; (▲) pyrrole concentration = 0.033 M, molar ratio of HANS/pyrrole = 0.3, open reactor; (■) pyrrole concentration = 0.044 M, molar ratio of HANS/pyrrole = 0.3, closed reactor.

et al.²⁴ (without HANS and with $[Fe] = 1$ and $0.13M$, $[Fe]/[Py] = 50$) and the values previously obtained in closed containers in our synthesis conditions for $[Fe] = 0.1M$ (see the previous section). This variation of $\ln k$ vs. $\ln [Fe]$ is nearly linear. Its slope n , which is the order of the reaction with respect to the $FeCl_3$, is 2. Thus, the rate of the pyrrole disappearance, determining the kinetics of the polymerization process, can be written as follows:

$$d[Py]/dt = -0.195[Py][Fe]^2$$

with $d[Py]/dt$ in mol/(L min) and $[Py]$ and $[Fe]$ in mol/L, for our processing conditions: synthesis in ambient air, under atmospheric pressure, at ambient temperature ($22 \pm 2^\circ C$).

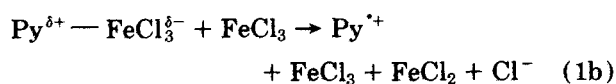
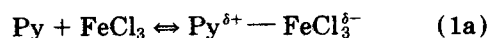
This result emphasizes that the rate and the length of the polymerization are extremely sensitive to the $FeCl_3$ concentration. For example, the length of reaction, for a 95% recovery of the polypyrrole, is shortened from 25 h to 15 min, when changing this concentration from $0.1M$ (polymerization stoichiometry for $[Py] = 0.044M$) to $1M$. However, this relation, for the pyrrole disappearance rate during polymerization, does not agree with the simple mechanism of the pyrrole oxidation presented above [eq. (1)] and proposed by Geniès et al.³⁰ for the electropolymerization of pyrrole. Thus, the chemical oxidation of pyrrole with $FeCl_3$ should follow a more complicated mechanism.

In fact, the chemical or electrochemical pyrrole oxidation is suspected, according to different authors, to be catalyzed. The acid catalysis of the electrochemical pyrrole oxidation was described by Qian et al.,³³ who completely inhibited the polymerization by using a proton trap: di-*tert*-butylpyridine. This sort of acid catalysis was also noted for the polypyrrole chemical synthesis (pyrrole oxidation by $FeCl_3$)^{4,27,34} and attributed by Bjorklund²⁷ to the acid hydrolysis of Fe^{3+} , which might lead to an increase of its reactivity with pyrrole.

According to Myers,² $FeCl_3$ can also react with pyrrole, in a first-step reaction involving the Lewis acid properties of $FeCl_3$ and the base properties of pyrrole. Such a reaction leads to an intermediary complex, pyrrole— $FeCl_3$, whose presence was underlined by calorimetric measurements. This complex is then easily oxidized, leading to the polypyrrole formation. This mechanism is consistent with the hindrance of the polymerization, observed by this author and others,³⁵ in good electron-donor solvents (which are good $FeCl_3$ solvents), where such a complex formation should be inhibited. This sort of Lewis acid catalysis of the pyrrole polymerization

was also noticed by Yoshino et al.¹² and more spectacularly by Chao and March.⁵ Indeed, these authors induced a rapid pyrrole polymerization by Cu^{2+} (which very slowly reacts with pyrrole), by adding $AlCl_3$ in the reaction solution. Consequently, Chao and March⁵ explained this phenomenon by the formation, during the oxidation, of an intermediary species, whose redox potential is less than $0.15V$ (value of the redox potential of Cu^{2+}). Additionally, it must be noted that some coordination complexes, between iron and pyrrole, were already described in the literature.³⁶

Thus, taking into account all these statements, a mechanism of the pyrrole oxidation by $FeCl_3$ might be



The first step is an equilibrium producing a donor/acceptor complex between the π -pyrrole system and the Lewis acid (here, $FeCl_3$). This step allows a charge transfer from the pyrrole ring to the Lewis acid, so that the pyrrole oxidation is facilitated. The second step, which is kinetically determining, is the oxidation of this complex by $FeCl_3$. So, as suggested by Myers,² with respect to the pyrrole, $FeCl_3$ might be a Lewis acid catalyzer and an oxidant.

With this sort of mechanism, the pyrrole disappearance rate can be written as the standard kinetic expression, obtained for an equilibrium followed by a kinetically determining reaction³⁷:

$$d[Py]/dt = -k_e K_e [Py][Fe]^2$$

with k_e the rate constant of reaction (1b) and K_e the equilibrium constant of the complex $Py - FeCl_3$. This expression agrees perfectly with our experimental results.

Therefore, the kinetically determining step of the pyrrole oxidation by $FeCl_3$, in an aqueous solution is the pyrrole oxidation step. This oxidation is catalyzed, possibly by a Lewis acid-base complex between pyrrole and $FeCl_3$. This mechanism leads to first-order polymerization kinetics with respect to the pyrrole and second-order with respect to the $FeCl_3$.

Influence of the $FeCl_3$ Concentration on the Obtained Polypyrrole

All the above results show that the pyrrole polymerization kinetics with $FeCl_3$ can be controlled and,

if needed, considerably increased by the addition of an excess of FeCl_3 . In these conditions, it seems possible to obtain a quantitative pyrrole polymerization within a short reaction length (15 min when using FeCl_3 1M) and, additionally, without any need for working in a sealed container. Furthermore, according to Lei et al.,²⁴ this modification of the polymerization rate should induce a better conductivity of the obtained polymer. In fact, this result, obtained in a reaction medium containing only Cl^- anion,²⁴ must be confirmed for our synthesis with HANS. Because it is essentially here the way in which the ANS^- doping species will be incorporated into the polymer (instead of Cl^-) that will determine its good conductivity and stability.²¹

Table VI presents some results of the preliminary tests made by stirring (160 rpm), in an open container, under atmospheric pressure, in ambient air and at ambient temperature (close to 22°C). These experiments were performed with a pyrrole concentration of 0.033M, with HANS (molar ratio HANS/pyrrole = 0.3), and variable concentrations of FeCl_3 until no pyrrole remained in the solution. This study confirms some of the literature results presented above. As a matter of fact, the decrease of the $[\text{Fe}]/[\text{Py}]$ molar ratio to 0.25 induces a sharp loss of the recovery of polypyrrole but has no drastic consequence on the conductivity of the obtained polymer. Particularly, a loss of several decades, as found by Myers² in ether, is not observed. For the stoichiometric reaction, the pyrrole evaporation is the major phenomenon, and the recovery of polypyrrole is consistent with the ratio of the calculated rate constant of pyrrole polymerization ($1.3 \times 10^{-3} \text{ w}^{-3} \text{ min}^{-1}$, see above) to the rate constant of pyrrole evaporation ($5 \times 10^{-3} \text{ min}^{-1}$, see above). Surprisingly, with an excess of FeCl_3 , the recovery of polypyrrole is high, but not quantitative. Therefore, with all the

Table VI Evolution of the Polymer Recovery and of the Obtained Polypyrrole Conductivity vs. the FeCl_3 Concentrations ($[\text{Fe}]$)

[Fe] (mol/L)	[Fe]/[Py]	Length of Synthesis (h)	Recovery (%)	Conductivity (S/cm)
0.008	0.25	7	5	12
0.08	2.5	5	21	16
0.8	25	1	72	30

Syntheses were made in ambient conditions, stirring (160 rpm) in an open container. The pyrrole concentration ($[\text{Py}]$) was 0.033 M; the HANS/pyrrole ratio was 0.3. The syntheses were made until no pyrrole was left in the solution.

pyrrole being polymerized, this result can only be explained by an erroneous calculation of the recovery of polypyrrole. In fact, in these conditions of a large excess of FeCl_3 , an important incorporation of the Cl^- anion in the polymer may be expected. Complementary experiments are in progress.

CONCLUSION

For an industrial development of conducting polymers, it is necessary to find a process that allows one to obtain easily a stable polymer with a high conductivity and a high yield. Accordingly, we examined the polypyrrole chemical synthesis, by a pyrrole oxidation with FeCl_3 , in an aqueous solution and with an aromatic sulfonate. The main conclusions of this study are the following:

- The pyrrole evaporates during the synthesis, probably through a pyrrole/water azeotrope. This phenomenon was quantified. It was determined that the evaporation is amplified by stirring and can be detrimental to obtaining a good polypyrrole yield. This involves working in a sealed container.
- The quantity of polypyrrole obtained is related to the FeCl_3 concentration. To obtain a good recovery of polypyrrole, it is better to use an excess of FeCl_3 .

Moreover, we determined that the kinetics of the pyrrole polymerization with FeCl_3 are first order with respect to the pyrrole and second order with respect to the FeCl_3 . The rate-determining step of this process was identified: It is the pyrrole oxidation. This oxidation is likely catalyzed by producing a Lewis acid-base complex between pyrrole and FeCl_3 .

In the stoichiometric conditions, the obtained polypyrrole conductivity is about 15 S/cm. The characteristics of the polymer synthesized with an excess of FeCl_3 are being evaluated and optimized.

The authors thank E. M. Geniès, R. Jolly, C. Pétrescu, and N. Mermilliod for constructive and informative discussions and M. J. Chamel and J. L. Gabelle for a part of the HPLC analysis.

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Received September 27, 1993

Accepted January 8, 1994