

OPTIMIZATION OF POLYPYRROLE CHEMICAL SYNTHESIS BY HEAT FLOW REACTION CALORIMETRY

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Abstract

Chemical polymerization of pyrrole (Py) was carried out in a reaction calorimeter by using FeCl_3 or CuCl_2 as an oxidant in an acetonitrile medium. The formation heat of polypyrrole (PPy), determined under a wide range of reactant concentrations and reaction temperatures, is directly related to the PPy yields and to the degree of polymerization. Due to the negative values of both the entropy and enthalpy of the reaction the gravimetric yield is inversely related to the temperature and directly to the Py concentration. The yields to the PPy and the related reaction heats, are close to zero when the 'ceiling temperatures' are reached ($T_{\text{ceil}}=348$ K for Fe-doped and $T_{\text{ceil}}=313$ K for Cu-doped PPys). It was observed that a 'ceiling concentration' corresponds to each 'ceiling temperature' and only light oligomers are formed if Py concentration is too low. The electric conductivity values of the products were also determined and a direct relationship to the yields was found as well. The highest electric conductivity value ($C=0.6$ S cm^{-1}) was related to the PPy fresh synthesized from a 0.017 M Py solution.

Keywords: conducting polymers, polypyrrole, pyrrole, reaction calorimetry

Introduction

Organic polymers with high conjugated π -electrons, can become conductors of electricity by an oxidation or reduction process [1, 2]. Doped polypyrrole (PPy) and its derivatives [3] seem to be some of the most promising products due to their great electric conductivity (up to 500 S cm^{-1}), their easy preparation and easy handling and manipulation [4, 5]. Different procedures [6] can be used to synthesize PPy in a wide variety of forms, although two main methods are basically used: chemical and the electrochemical oxidation [3, 7]. Electrochemical synthesis gives a more reproducible product with a higher electric conductivity, but it is often more expensive than the chemical method. However, soluble forms are chemically synthesized as graft-copolymers [8], composites [9] or in blends [10]. Many oxidants have been used to increase electric conductivity [11, 12] and to minimize the ageing produced by air exposure [13], but Fe^{+3} is still the most widely used ion [11, 13–15]. Due to the insolubility of basic Fe-doped PPy, it is quite hard to characterize fully. There-

fore, the preparation condition, structure and electrical properties of the polymers can be correlated only through indirect tests and theoretical modelling [1].

The strong dependence of both kinetics and thermodynamics on the polymerization temperature, have been extensively discussed in two previous works on the same subject [16, 17]. Other researchers found that the synthesis temperature is very important both for the performance and endurance of the product [14, 18]. The addition of water traces strongly increases the reaction rate [15]. Furthermore, as stated in the literature [16, 20], polymerization follows first-order kinetics with pyrrole and second order with FeCl_3 .

A close relationship between reaction parameters and electrical properties of the PPy can thus be found and a 'ceiling temperature', above which a long chain cannot be formed, has been hypothesized [17]. Starting from basic kinetic assumptions, the existence of a 'ceiling concentration' is also reasonable and the oxidant/Py ratio should play a role in polymerization [21]. This work aims to correlate the evolved heat, its PPy yield and its electric conductivity with the calorimetric and potentiometric data obtained in a Mettler RC1 calorimeter.

Experimental

Materials

The acetonitrile and the Py were 'Fluka pure grade' products.

Py was distilled at reduced pressure and under argon flow, immediately before use. Sublimate anhydrous ferric chloride (C. Erba RLE grade) and the copper (II) chloride (C. Erba RPE grade) were used as oxidants.

Methods

Polymerization was carried out with a Mettler RC1 reaction calorimeter, equipped with an AP01 model (2 liters) glass reactor, up flow propeller and baffles. The RC1 works according to the heat flow rate principle [22], recently resumed in literature [23, 24].

Values pertaining to the inner temperature of the reactor (T_r) to the temperature of the heating jacket (T_j), to the stirring rate and all other variables of the process of polymerization are acquired, processed and checked in real time by an IBM PS2/80 computer in the QNX environment. All the experiments were performed in a T_r control mode. The total heat evolved due to the reaction (Q) is calculated by numerical integration of the heat flow rate during the reaction (q_r), according to:

$$Q = \int_0^t q_r dt \quad (1)$$

where

$$q_r = q_{\text{flow}} + q_{\text{acc}} + q_{\text{dos}} + q_{\text{loss}} \quad (2)$$

The heat capacity of the internal fittings is summed from the individual contributions of Pt100, calibration heating, up flow stirrer and baffles. The heat loss coefficient is assumed to be, $\alpha=0.01 \text{ W K}^{-1}$, because of the adopted thermal insulation of the cover.

The polymerization and the oxidation of Py to electrically conductive forms (polarons/bipolarons) by FeCl_3 yields HCl. A 465 model 'Ingold' Pt electrode, connected to the computer, was used to monitor the variations occurring in the redox potential within the calorimetric reactor. Comparisons between the curve of the potential and that of the heat produced show that they reproduce the same reaction pattern, as the $Q=f(t)$ curve derives from the $V_{\text{redox}}=f(t)$ curve.

Preparation of the polymer

The oxidative agent (FeCl_3 or CuCl_2) was solubilized to dry acetonitrile previously deoxygenated by bubbling $300 \text{ cm}^3 \text{ min}^{-1}$ of Ar. Such a flow kept bubbling for about half an hour before the test was started. After calibration, a prearranged volume of Py would be added to the solution.

The formation of the oxidized polymer, highlighted by the black colour of the product occurs together with the development of heat and variation in the redox potential of the solution.

After one hour of reaction at constant temperature, the slurry was filtered by means of a vacuum Buckner funnel; the precipitate was repeatedly washed in acetonitrile, dried for about one hour at reduced pressure in an electrical stove, ($T=353 \text{ K}$) and then weighed. The final dry mass of PPy reported to the initial mass of Py represents the yield of the polymerization reaction.

All tests, unless otherwise specified, were carried out at room temperature ($T_r=303 \text{ K}$) and stirred at a speed of 500 rpm. The initial concentration of the solution was 0.017 M in Py and 0.042 M in oxidant so that their ratio (oxidant/Py) was 2.5 mol mol^{-1} . Most of the tests were performed using 600 mL of acetonitrile. These base-line reaction conditions were prearranged starting from the previous studies on the same subject [16, 17].

Chemico-physical characterization of the products

As detailed in a previous work [17], 30–40 mg of PPy were reduced into pellets by means of a hydraulic cold press (Specac P/N 15.011 model). The pressure was made to increase slowly up to a value of 5 tons for a pellet with a diameter of 8 mm. A micrometer supplied with a vernier able to make measurements from 0 to $25 \pm 0.01 \text{ mm}$, was used to measure the thickness of the pellets. The pellets were then introduced into an appropriate cylinder made of teflon with a hole along its length and were interposed between two golden brass electrodes. The electrical resistance of the pellets was measured with an S17071 model 'Schlumberger' digital multimeter able to record resistance values of $10^{-4} \pm 10^{-6} \text{ Ohm}$.

The metal content was determined by TG analysis as the combustion residue at $T=1173 \text{ K}$.

Results

Influence of temperature and concentration

The yield, metal (Fe and Cu) content, electric conductivity and enthalpy of PPy formation are very important factors needed to optimize both the process and the product. In order to correlate such properties and to point out the influence that every variable of the process produces on each of them, we programmed a series of tests in which the Fe/N ratio, concentration and temperature vary. In previous studies [16, 17] we measured the heat produced by polymerization with FeCl_3 according to the reaction time to three different temperatures (288, 303 and 323 K). By assuming that the polymerization degree depends on the first power of the concentration of Py, as per ref. [20], the specific reaction rate was likewise evaluated at the three temperatures and, in accordance with the Arrhenius equation, apparent activation energy of 32 kJ mol^{-1} was evaluated.

The Fig. 1 reports synthesis temperature and yield as a function of the evolved heat. The tests, conducted in a large range of temperatures, point out a linear reduction of the yield as the temperature increases. The yield drops to zero and no heat is developed by the reaction for $T=348\pm 5 \text{ K}$ for FeCl_3 as oxidant, whereas when CuCl_2 is used it can be assumed that yields and polymerization cancel each other out when a lower temperature is reached ($T=313\pm 10 \text{ K}$). The pattern of the reaction yield also depends on the evolved heat (Fig. 1). Yield increases linearly along with the evolved heat both for the tests that use FeCl_3 as an oxidant agent and for those which use CuCl_2 . In any case the yield of PPy produced by oxidation with FeCl_3 , proves to be much higher than that obtained with CuCl_2 .

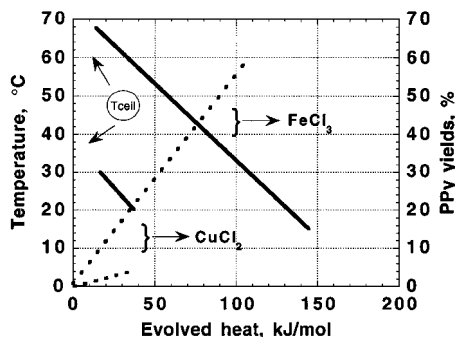


Fig. 1 Synthesis temperature (—) and related yields (---) vs. the evolved heat

The reaction yield and the residue derived from the TG analysis for a series of micro-tests performed with FeCl_3 are reported in Fig. 2. Independently of any other variable, both the yield and the TG residue, rise when the concentration of Py increases, while only yield increases by increasing the Fe/N molar ratio. It must be noted that, in accordance with what has been reported in literature [25], this is true only for a Fe/N ratio near to the stoichiometric ($\text{Fe/N}=2.5$) and too high ($100\leq\text{Fe/N}\leq 200$) or too low ($\text{Fe/N}\leq 1$) molar ratios, given null yields.

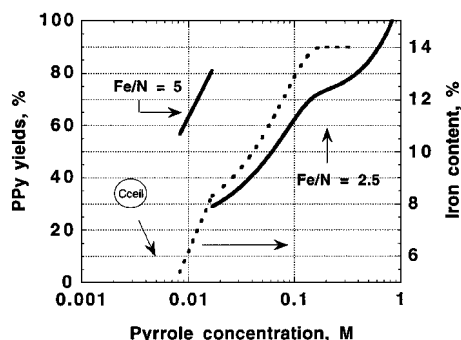


Fig. 2 Yields (—) and related iron content determined by TG analysis (---) vs. the initial pyrrole concentration. Two oxidant/pyrrole ratios ($\text{Fe}/\text{N}=2.5$ and $\text{Fe}/\text{N}=5$) were examined, but an univocal behaviour was found for the Fe content

Influence of H_2O and HCl

The redox potential of solutions such as FeCl_3 in acetonitrile is not stable in the ambient air. In fact, a series of tests, showed that redox potential of a solution of 0.042 M decreases notably when the solution is kept in an open container and that the colour of the solution, initially reddish-brown, changes into yellow with a similar pattern. This slow variation was attributed to the environment moisture. As shown in Fig. 3, in fact, the bubbling of moist air ($50 \text{ cm}^3 \text{ min}^{-1}$) causes an evident change in the colour and a related diminution of the redox potential. The latter effect immediately occurs if a corresponding amount of H_2O is directly added to the starting solution, so that both the potential and the colour happen to be very similar to the ones obtained at the end of the bubbling. To evaluate the contemporaneous influence of H_2O and HCl , produced by the polymerization-oxidation reaction [26], we added subsequent small volumes of concentrated HCl to a base-line ferric solution and to a solution twice more concentrated ($[\text{FeCl}_3]=0.084 \text{ M}$). As shown in Fig. 3b, the obtained plots represent typical titration curves ($[\text{FeCl}_3]=0.042 \text{ M}$) with a toning point from red (anhydrous solution) into yellow (aqueous acid solution) which corre-

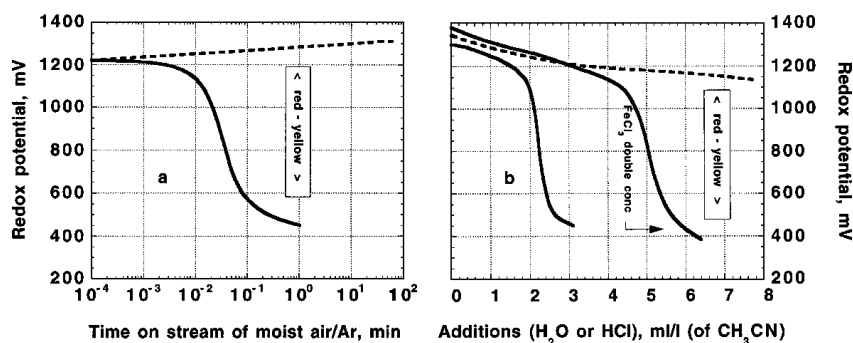


Fig. 3 Redox potential of $\text{FeCl}_3/\text{CH}_3\text{CN}$ solutions and related colours, as a function: a) of the time on stream of moist air (—) or Ar (---); b) of addition of water (---) or concentrated HCl (—) at $[\text{FeCl}_3]=0.042 \text{ M}$ and 0.084 M

sponds to the addition of an amount of HCl equivalent to the ferric chloride present in the starting solution. Two different redox potentials, 1400 and 600 mV (referred to the standard calomelan electrode), respectively correspond to the anhydrous and aqueous acid solutions.

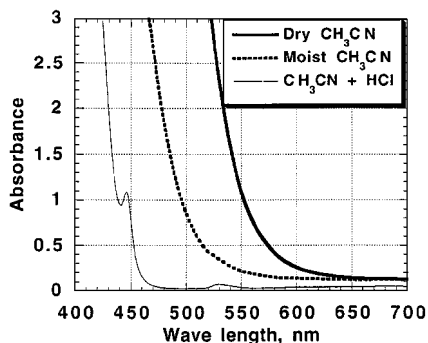


Fig. 4 Iron chloride spectra in acetonitrile solutions

UV-visible spectra of the solutions treated with H₂O and HCl with reference to an anhydrous solution with equal concentration are shown in Fig. 4.

Electric conductivity tests

As reported in a previous study [17], the electric conductivity of PPy, quite unchanged for temperatures lower than 320 K drops quickly if the synthesis is carried out at higher temperatures. The initial conductivity values measured soon after the pellet was prepared ranges from 0.61 S cm⁻¹ (for $T_r=303$ K) to 0.045 S cm⁻¹ (for $T_r=343$ K – near to the boiling point of acetonitrile). The conductivity of PPy decreases markedly when the sample is exposed to air and the synthesis temperature of the polymer does not seem to have any influence on the rate of decay. For almost all checked samples we recorded after three days a decrease of the conductivity close to 90% of the initial value.

Discussion

If an exothermic and exoentropic polymerization follows a polyaddition process at any concentration of the starting monomer, it is matched by a limit temperature known as ceiling temperature above which long polymeric chains cannot be formed.

In line with the basic polymerization [26] concepts and by appropriate approximations, we can draw the equation that correlates T_{ceil} to the reaction thermodynamic parameters and to the concentration of the starting monomer:

$$T_{\text{ceil}} = \frac{\Delta H}{\Delta S + R \log C_{\text{ceil}}} \quad (3)$$

From the experimental point of view, T_{ceil} can be evaluated by extrapolating to zero the yields, the rate or the degree of polymerization if reported *vs.* temperature for a prefixed C_{ceil} . As reported in Fig. 1 for $[\text{Py}]=0.017\text{ M}$, the gravimetric yields and the evolved heat are inversely related to the temperature and both drop to zero when T_{ceil} is reached. The extrapolations, give $T_{\text{ceil}}=348\pm 5\text{ K}$ and $T_{\text{ceil}}=313\pm 10\text{ K}$ respectively for Fe and Cu doped PPys.

These ceiling temperature values are relatively high if compared to those reported in literature [27] for a wide variety of polyaddition reactions, therefore we have to conclude that the entropic increase is quite smaller. On the other hand, it is to be emphasized that the Py polymerization is to be considered a polycondensation, because of the HCl losses, and no ceiling temperature can be detected for an irreversible polycondensation reaction. A kinetic approach assumes that the HCl losses and the PPy precipitation are two very slow reaction steps with respect to the chain growth so that the reaction proceeds like a polyaddition. Unfortunately, no investigation has been carried out to confirm this assumption.

In any case, according to the above, each 'ceiling concentration' should correspond to each 'ceiling temperature' and the formation of the highest mean molecular mass polymers is impossible below a prefixed Py concentration. Our tests (Fig. 2), aimed to C_{ceil} determination, point out the initial Py concentration must be higher than $[\text{Py}]_{\text{ceil}}\approx 8\cdot 10^{-3}\text{ M}$ if FeCl_3 is used as oxidant and a corresponding $T_{\text{ceil}}\approx 350\text{ K}$ is found. According to Eq. (3), we will find a direct relationship between the T_{ceil} and the C_{ceil} , so that a $C_{\text{ceil}}< 8\cdot 10^{-3}\text{ M}$ corresponds to a $T_{\text{ceil}}=303\text{ K}$ ('base line' condition). Unfortunately, due to the experimental errors, no precise evaluation can be made of ΔH and ΔS from Eq. (3) and we can account only for the extrapolated (too high) values of $\Delta H_{[\text{at yield}=100\%]}=-200\pm 40\text{ kJ mol}^{-1}$ and $\Delta S_{[\text{at yield}=100\%]}=-580\pm 120\text{ J mol}^{-1}\text{ K}^{-1}$. All efforts addressed to the error minimization were useless because of undetermined factors affecting the PPy nucleation and the logarithmic influence of C_{ceil} (a slight variation in the logarithm leads to a big difference in the absolute value).

The molar oxidant/Py ratio and the solvent effect also play a very important role in the non-determination of C_{ceil} . In fact, according to the literature [25], the highest yield was obtained at a molar ratio close to 2.5 mol mol^{-1} and polymerization is very slow if there are traces of water ($\geq 0.4\text{ mL L}^{-1}$) in acetonitrile. This result seems to be in contrast with that obtained by Stanke *et al.* [15] in nitromethane, where traces of water increase the reaction rate up to ten times. We have to stress, that in nitromethane the polymerization process is much slower than in CH_3CN and the rate determining step can be different (i.e. the chain growth). Figure 3 shows the tests we carried out on the influence that concentration and Fe/N ratio have on the yield and the quality of the products. The Fe content of the polymer and the yield of the reaction show a direct trend, thus it seems reasonable to hypothesize that to high yields correspond products with higher Fe content. Moreover, as pointed out above, at high yields we have high electric conductivity, thus we can summarise that also the Fe content and the electric conductivity reflect a similar trend. According to these observations, Myers *et al.* [25], starting from FeCl_3 in ethyl ether, obtained polypyrroles with a high electric conductivity ($C\geq 45\text{ S cm}^{-1}$) and they hypothesize that PPys

with the highest Fe content, show the highest electric conductivity thanks to the formation of a greater amount of bipolarons.

The optimum ratio oxidant/Py (Fe/N) allowing the yield and electric conductivity maximization was shown not to be very far from stoichiometry, i.e. Fe/N=2.5. Probably below that ratio there occurs a prevailing formation of polaronic species, which do not give much contribution to electric conductivity, whereas for high values an excessive action of the oxidant agent gives degradation products.

The polymerization of Py in acetonitrile, in which the percentage of the mass of the total impurities is lower than 1 wt%, progresses more quickly if compared to the polymerization in presence of traces of H₂O ($\geq 2.5 \cdot 10^{-2}$ M). As seen in Fig. 3, the redox potential of anhydrous ferric solutions (1200–1400 mV) is higher when compared to that of isotonic solutions pre-treated with small amounts of H₂O or concentrated HCl (400–700 mV). Such a potential, while constant or even slowly increasing, if the solution is kept under Ar, decreases rapidly when exposed to air. At last, dyeing of the anhydrous ferric solution (dark red), changes markedly with the addition of little amounts of H₂O (orange) and/or HCl (yellow-greenish). Visible absorption spectra (wave length $\lambda=400-700$ nm) of the anhydrous solution, of which one is at 0.5 wt% of H₂O and the other at 0.5 wt% of concentrated HCl are very different (Fig. 4) and the solution does not follow Lambert & Beer's law in every spectrum zone. Just as was observed for the redox potential, the change in the colour occurs also when the anhydrous solution is exposed for a long time to the air, whereas the dark red colour is stable under Ar.

Based on all these observations it is highlighted that the thermodynamic stability and the inertia of the solvated ferric ion have a peculiar importance for the definition of the reaction rate, the quality of the product and, consequently, the C_{ceil} value.

The relationship between kinetics of the reaction and quality of the product, is not deeply understood, even though several authors get good yields and high electric conductivity values only from polypyrroles reached after a sufficiently long polymerization time. Higher mean values ($C \approx 190$ S cm⁻¹), close to those obtained by the electrochemical syntheses can be obtained controlling the redox potential. Machida *et al.* [28], for example observe that the addition of Fe(II) to the starting ferric solution, reducing the redox potential and therefore the reaction rate, gives products with higher electric conductivity. Protic solvents (H₂O, methanol, ethanol, etc.) play the same effect on kinetics, even if, in diluted aqueous solutions, yields are extremely low. At last, to a further confirmation, the use of CuCl₂, AgNO₃, Fe[BF₄]₃, (NH₄)₂S₂O₈ and of other oxidant agents with lower redox potential [29], brings about slower kinetics and products with higher electric conductivity.

Table 1 reports, either the behaviour of electric conductivity of the products obtained in function of the synthesis temperature and its quick decay due to the exposure to air. High synthesis temperatures bring to polypyrroles with lower electric conductivity and to lower reaction yields.

Furthermore, the synthesis temperature is not significant in slowing the unwanted ageing phenomena [18, 19]. Whatever the temperature is, the electric conductivity of the product always decreases at the same unwanted speed when exposed to air.

Conclusions

A comparison between the ΔH values, the reaction yield evaluated by gravimetry and the Fe content of 'doped' polymer, allowed us to point out the presence of a 'ceiling concentration' related to each 'ceiling temperature'. This temperature, that matches a reaction ΔG close to zero, varies according to the oxidant agent used, e.g. 348 ± 5 K or 313 ± 10 K, depending on whether it relates to FeCl_3 or CuCl_2 and the corresponding starting Py concentrations should never fall below 10^{-2} M.

The presence of traces of water in the solvent (CH_3CN), greatly affects the reaction path, because a stable bond is formed with the oxidant. In effect, H_2O acts as an iron ion getter and in a diluted solution can significantly modify the oxidant/Py ratio.

The above findings are further confirmed if one considers that the amount of polymer obtained by filtration of the compound resulting from the reaction carried out at a lower temperature and higher concentration, is greater than that produced at a higher temperature and lower concentration. In fact oligomers with a low molecular mass, form in ever increasing percentages as they approach the 'ceiling temperature', thus leading to a greater solubility in the filtrate. Finally, we should mention that electric conductivity is directly correlated to the 'doping' percentage. Conversely an inverted proportion is observed in the synthesis temperature. The experimental data lead us to believe that a better electric conductivity should be attributed to a higher value of the mean molecular mass. This leads to a higher degree of conjugation of the chains as well as easier electronic 'hopping', related to a higher mean molecular mass and to a higher amount of the polaron/bipolaron counter ions $[\text{FeCl}_4]^-$. On the other hand, the temperature of synthesis does not show any influence on the initial electric conductivity of PPy and on its stability to the air oxidation as well.

In conclusion, the maximization on the yields and on the electric conductivity seems to be reached when the reaction temperature is the lowest possible (the farthest from the ceiling value), the Py concentration is ≥ 0.1 M and the Fe/N molar ratio is close to 2.5 mol mol^{-1} .

List of symbols:

C	specific conductivity, S cm^{-1}
C_{ceil}	ceiling concentration, M
Fe/N	iron/nitrogen (Py) molar ratio, dimensionless
q_r	heat flow rate due to chemical reaction, W
q_{flow}	heat flow rate through the reactor wall, W
q_{acc}	heat accumulation rate by reaction mass and internal fittings, W
q_{dos}	heat flow rate due to manual dosing, W
q_{loss}	heat flow rate through the reactor cover, W
R	ideal gas constant
t	reaction time, h
T_{ceil}	ceiling temperature, K
T_j	jacket reactor temperature, K
T_r	reacting mixture temperature, K

V_{redox} redox potential measured by a Pt/SCE electrode, mV
 α heat loss coefficient = 0.01 W K^{-1}

Abbreviations

Py Pyrrole
 PPy Polypyrrole

* * *

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