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# The Effect of Preparation conditions on the Growth Rate of Films, the Yield of Precipitated Powder and the DC Conductivity of Polypyrrole

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## Abstract

Polypyrrole (PPy) was prepared by a chemical method by using oxidizing agents ferric chloride and potassium persulphate, both as films and pellets. The effect of various variables—such as aging of the films, film thickness, ratios of the reactants and type of the sample (film or disc)—on DC conductivity were investigated. The results from samples prepared with ferric chloride exhibited an increase in conductivity with increasing concentration of oxidizing agent to a certain ratio, above which a slight decrease occurs. Whereas in the case of using potassium persulphate as the oxidizing agent, a decrease in conductivity occurs with increasing its concentration. Moreover, aging of the samples caused a loss of conductivity. In addition to the DC conductivity, both the growth rate of PPy films and the yield of the powder samples were investigated and were found to be dependent on the concentration of the oxidants.

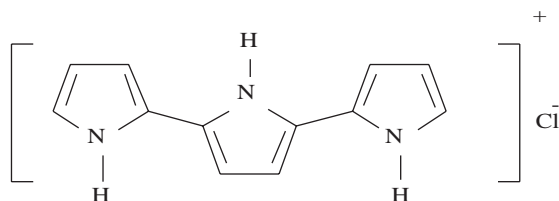
**Key Words:** DC Conductivity, Conducting Polymers, Polypyrrole, Quartz Crystal Microbalance Technique.

## 1. Introduction

Electronic conducting polymers constitute a new class of electronic materials. These organic polymers have attracted much attention because of their electronic properties [1]. There are many applications for these polymers. The first group of applications utilizes their conductivity as its main property such as electrostatic materials, conducting adhesives, printed circuit boards and switches. The second group utilizes their electroactivity such as molecular electronics, electrical displays, rechargeable batteries and solid electrolytes [2]. Moreover, at low frequencies, some conducting polymers can behave as supercapacitors, able to store significant amounts of charge.

Traditional polymers are electrically insulating. Whereas in a conducting polymer, the polymer backbone structure is conjugated (alternating single and double bonds) and the existence of an ionic dopant in the polymer results in a delocalization of the double bond electrons giving near metallic conductivity [3].

By doping with either electron acceptors or electron donors, the level of conductivity in some polymers can increase many orders of magnitude from values of conductivity of  $10^{-12} (\cdot\text{cm})^{-1}$  to values of  $10^3 (\cdot\text{cm})^{-1}$ [4]. Examples of such polymers are polyacetylene, polypyrrole, polyaniline and polythiophene. Figure 1 shows, as an example, PPy in one of its conducting states. It is described chemically as shown:



**Figure 1.** PPy in one of its conducting states.

The backbone elements consist of units of pyrrole linked together. The units are positively charged and one full charge is distributed over approximately three repeated units, giving a new periodicity of the polymer chain in terms of positively charged trimers. The positive charge on the backbone is compensated by negatively charged counterions, here for example, chlorine anion  $\text{Cl}^-$ , to maintain overall electroneutrality.

Martin et al. [5] have proposed that the size and shape of the dopant ions influence the conduction process. Also some external parameters may affect the conductivity of those polymers. In the present work, it will be shown that heating the polypyrrole samples for several days has led to an appreciable drop in its conductivity. In the literature, it has been reported before that a loss in conductivity was observed (for example, in PPy and polyaniline) during weathering, fog and humidity exposure [6, 7].

## 2. Experimental Methodology: Preparation of Polypyrrole Films

In the present work, polypyrrole (PPy) was prepared in two forms: thin films and black powder.

A chemical method was followed twice: first by using hydrous ferric chloride  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (at different concentrations) as the oxidizing agent and then by using potassium persulfate  $\text{K}_2\text{S}_2\text{O}_8$  (at only one concentration) as the oxidizing agent. In both cases the pyrrole monomer (ICN), the oxidant solutions and the solvent (carbon tetra chloride) were stirred well to ensure homogeneity and then poured into a polypropylene bottle which has a circular hole in its lid. This hole was covered by a 5 MHz AT-cut quartz crystal to monitor the deposition of the films and to calculate their thickness by the so-called quartz crystal microbalance technique [8, 9].

It should be noted that before adding the mixed solutions to the polypropylene bottle, the deposition substrates were mounted in a position parallel to the quartz crystal, so that after adding the mixed solutions, the same thickness of films will be deposited on both the substrates and the quartz crystal.

The adhesion of PPy films on smooth substrates such as glass is poor, therefore, fiber substrates were used instead of glass to obtain better adhesiveness and more homogeneous films.

### 2.1. Preparation of Polypyrrole Powder to Make Disc-Shaped Pellets

Two oxidizing agents,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{S}_2\text{O}_8$ , were used for powder preparation. Different weights of the two oxidants were dissolved in 50 ml carbon tetra chloride and then added to 0.4 g pyrrole. At various concentration of the oxidizing agents, the polymerization was made to proceed at 333 K, for two hours accompanied with constant, gentle agitation. The resulting precipitated powder was filtered, washed with 0.1 M HCl in 500 ml distilled water and dried in oven at 333 K for 7 days. The samples were then subjected to additional heating at 353 K for 4 days to enhance resistivity. Careful grinding of the powder was done using an agate mortar to obtain very fine powder.

The powder was then pressed into discs at 5000 kg/cm<sup>2</sup>. (We must mention here that the temperature of the solutions during preparation was kept at 333 K to obtain high resistance PPy, since the preparation around this temperature has been reported to give lower conductivity values in PPy [10]).

## 2.2. DC Conductivity Measurements

The resistance of the samples was checked, first at room temperature, using a Keithly 617 programmable electrometer, and was found to be above 2 kΩ for all samples. Thus the two-probe method for measuring DC conductivity is suitable since the resistance of the electrodes can be neglected. The DC conductivity is given by

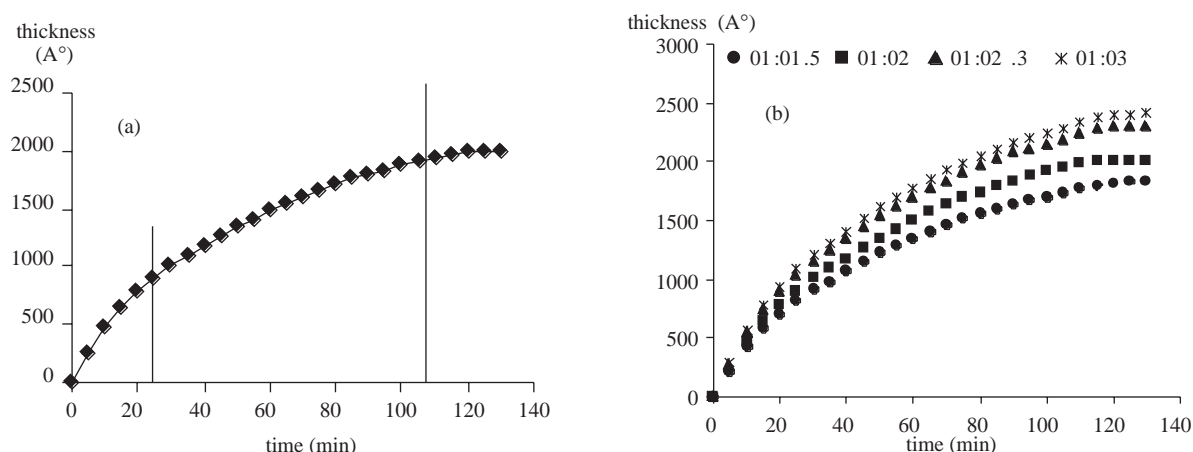
$$\sigma_{dc} = L / (R_s A),$$

where  $L$  is the distance between the two electrodes,  $A$  is the cross sectional area of the sample and  $R_s$  is the sample's resistance.

## 3. Results and Discussion

### 3.1. Effect of Both Time of Reaction and Concentration of Oxidizing Agents on the Samples

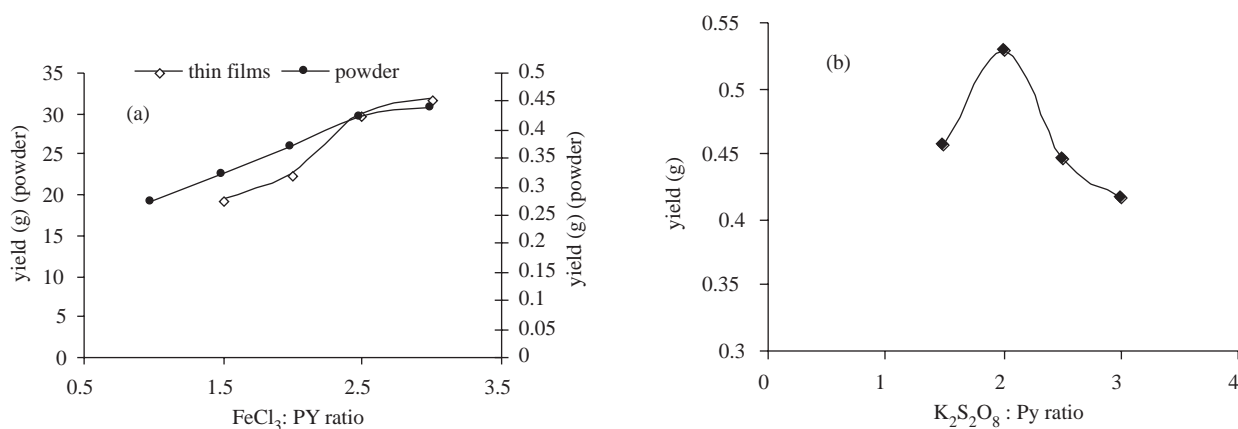
Figures 2(a, b) show the plots of the thickness of the films as a function of time of reaction for different samples. With the literature [9] in mind, three regions were expected. The first region was a nearly constant region that was due to the slow incubation for the deposition in solutions with low oxidizing agent /pyrrole ratios, but this was not observed at high ratios of oxidizing agent. The second region was expected to rise linearly with time, and is more or less present in the figures. In third region, the rate of growth was expected to slow down or decrease; note its presence in the figures. This decrease in the deposition rate can be explained by the depletion of the reactants in the solution. Finally, it was observed that after two hours the thickness of the films ceased to increase.



**Figure 2.** Film thickness as a function of time for different ratios of oxidizing agent to pyrrole: (a) prepared by using  $K_2S_2O_8$  as the oxidizing agent; (b) prepared by using  $FeCl_3$  as the oxidizing agent.

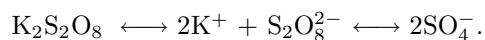
Figure 3(a) shows that, in the case of using ferric chloride as the oxidizing agent, the yield increases with increasing molar ratio  $FeCl_3$ : PY for both film and powder samples, due to the presence of the chloride counterion ( $Cl^-$ ) which catalyzes the polymerization. For molar ratios greater than 2.5:1, there is a competitive incorporation of iron-based counterions  $FeCl_4^-$  in addition to  $Cl^-$  counterions. Incorporation

of counterions heavier than chloride anions may explain the observed slowing down of the increase in yield for ratios greater than 2.5:1 [11].



**Figure 3.** The effect of oxidizing agent concentration on the yield (a) of film thickness and powder for ferric chloride, FeCl<sub>3</sub>; and (b) powder, under potassium persulfate, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

Of the polymerization of pyrrole by potassium persulfate, we can see in Figure 3(b) that the yield of polypyrrole powder increases with the concentration of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and peak at the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>:PY molar ratio equal to 2:1; after which it decreases with further increase of the molar ratio. This behaviour can be interpreted using an observation of K.C. Khulbe et al. [12], which observed that Peroxydisulfate ion is a mild oxidizing agent of many organic compounds; and that it is also a dissociative initiator for polymerization viz. the reaction



In other words, it has been suggested that the persulfate acts not only as an initiator but also as a retarder.

### 3.2. DC Conductivity Investigation

The DC conductivity of the prepared PPy samples was measured in films and disc-shaped pellets in the temperature range 293–420 K. The effect of different parameters on DC conductivity, such as aging of the films, film thickness, and concentrations of the reactants, has been studied. Also, the temperature dependence of the DC conductivity at different values of other parameters has been investigated.

#### 3.2.1. The Effect of aging of PPy film samples on the DC conductivity

The DC conductivity of PPy films was investigated for differently aged samples of PPy oxidized by ferric chloride and kept for 1–25 days inside a furnace at 353 K in air. Figure 4 shows the temperature dependence of  $\ln(\sigma_{dc})$  at some selected ages. It can be seen from the figure that conductivity decreases with the aging of the sample. Similar behaviour has been reported previously [13].

While the mechanism behind the reduction in electrical conductivity may likely involve a number of reactions, one plausible explanation is that the counterions are thermally decomposed and the products of the decomposition in turn reacts with the polymer backbone, causing a loss of conductivity through the introduction of defect structures such as cross links [4].

#### 3.2.2. The Effect of Film Thickness on the Conductance

The conductance of PPy prepared by using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> with molar ratio S<sub>2</sub>O<sub>8</sub><sup>2-</sup>:PY of 2:1 at different film thickness was investigated by the two-probe technique. Figure 5 shows a plot of  $\ln(1/R)$  versus  $1000/T$  at

three values of film thickness. It can be seen that the conductance increases with increasing film thickness. This behaviour can be explained as partially caused by the unstable nature of the film in air. Thin films react quickly and more completely with air so that thicker films would have higher conductance. The temperature dependence will be discussed at the end of this section.

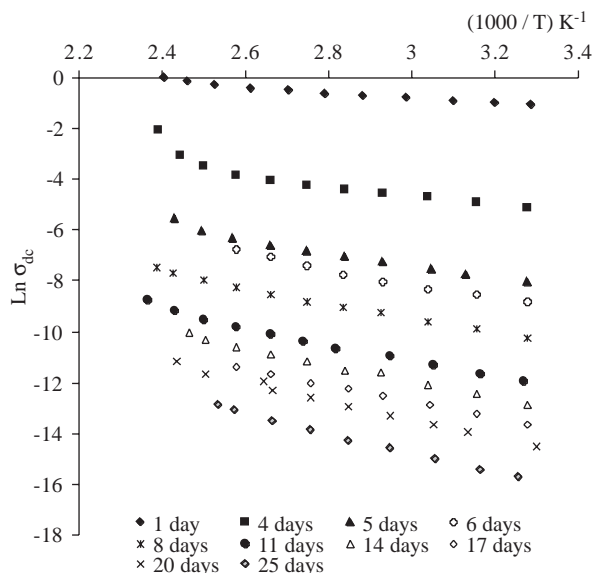


Figure 4. Temperature dependence of  $\ln(\sigma_{dc})$  at selected ages of samples.

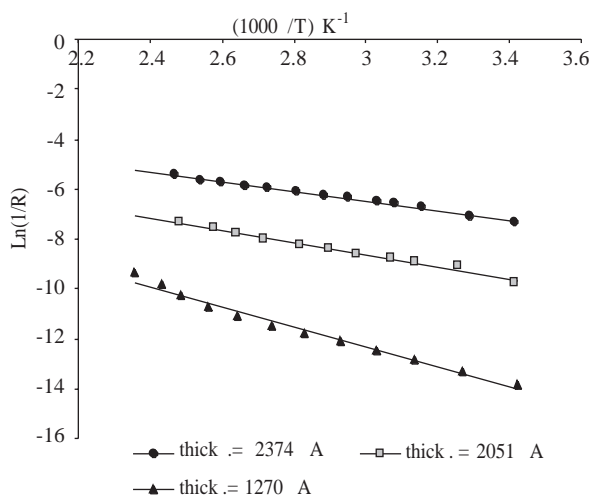
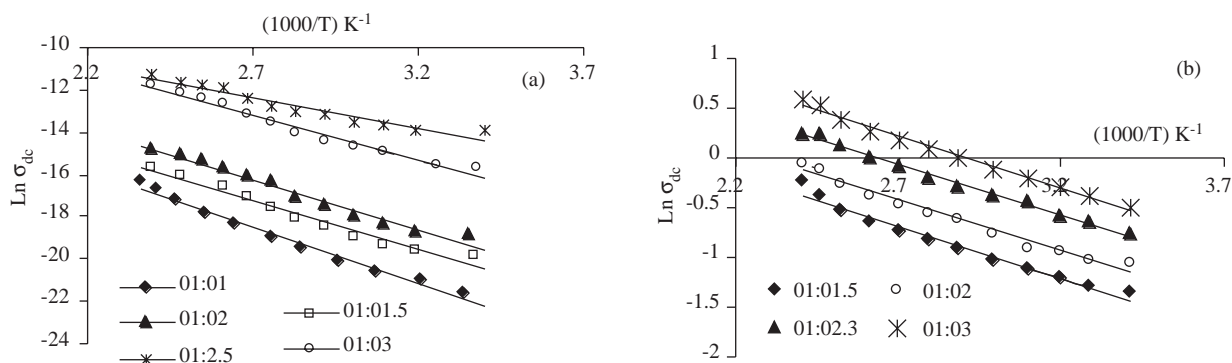


Figure 5. Temperature dependence of the conductance at three film thicknesses.

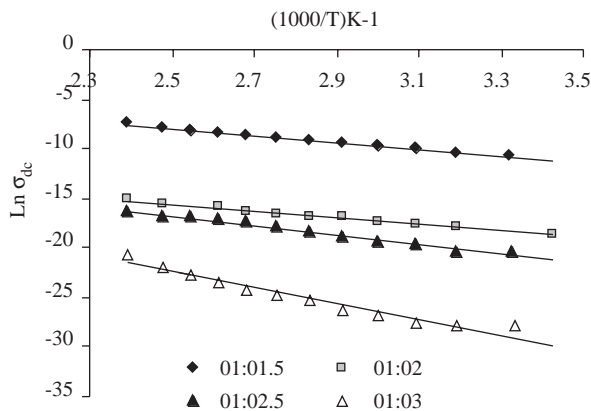
### 3.2.3. The Effect of Concentration of the Reactants on the DC Conductivity for Both Film and Powder Samples

As was mentioned above, for molar ratios of  $\text{FeCl}_3:\text{PY}$  above 2.5:1 there is the generation of  $\text{FeCl}_4^-$  counterions heavier than chloride anions; in other words, there is an excess in the heavier ions, which may present a hindrance of the motion of the charge carriers. Consequently this may be the reason for the decrease in dc conductivity with increasing  $\text{FeCl}_3$  concentration, as illustrated in Figures 6(a, b). It may be useful to mention here that S. Mashida and S. Miyata [10] invoked the same interpretation as they showed that a decrease in conductivity of conductive polyheterocycles due to overoxidation of polymers.



**Figure 6.** DC conductivity as a function of temperature at different concentrations of FeCl<sub>3</sub> (a) used in the preparation of disc-shaped samples; (b) used in the preparation of film samples.

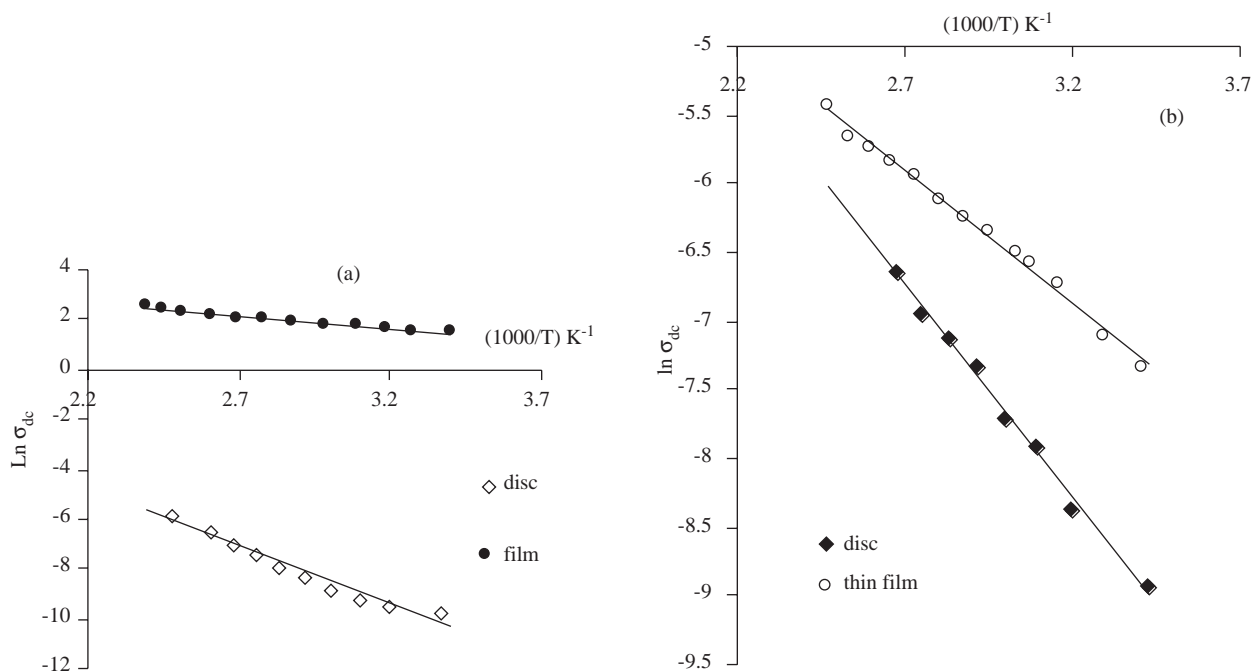
Figure 7 shows the behaviour of  $\ln(\sigma_{dc})$  as a function of  $1000/T$  for different PPy samples prepared by using potassium persulfate as the oxidizing agent. Observe that the conductivity decreases with increasing K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration. At low concentrations, small molecules of, or those of lower molecular weight, polypyrrole powders are formed. While, at high concentrations of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, possibly larger molecules of, or higher molecular weight, polymer are formed [12]. It may be suggested that small, as opposed to large, molecules may encourage the hopping of  $\pi$ -electrons, since it is known that, when the conjugation length of PPy chains decrease, the contribution of the variable range hopping becomes stronger [13], so the dc conductivity at lower concentrations of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is higher than that at higher concentrations.



**Figure 7.** DC conductivity as a function of temperature at different concentrations of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> used in preparation in disc-shaped samples.

### 3.2.4. Comparison Between the Conductivity of Film and Powder Samples

A comparison between the conductivities of film and powder samples is shown in Figures 8(a, b). It was found that the conductivity of the films is higher than that of pressed pellets. This difference in conductivity may be due to the formation of insulating air gaps between conducting powder particles in the pressed pellets [14].



**Figure 8.** A comparison of conductivity in film and powder samples when (a)  $FeCl_3$  is used as the oxidizing agent; (b) when  $K_2S_2O_8$  is used as the oxidizing agent.

### 3.2.5. The Temperature Dependence of the DC Conductivity

The temperature dependence of the DC conductivity for the present investigated polymer is clear: the conductivity increases with temperature. Several models have been proposed to describe the observed temperature dependence of polymer conductivity [3], all of the general form  $\sigma_{dc} = Ae^{-B/f(T)}$ , where  $A$ ,  $B$  and  $f(T)$  can differ from model to model [15]. The present results are seen to follow such a relation, where the increase in conductivity with temperature resembles a semiconducting behaviour. An early explanation invoked band theory, which posited that half-filled valence bands would be formed from a continuous delocalized  $\pi$ -system [2]. However, whether the charge transfer is between bands having an energy gap, or by hopping or tunnelling between localized sites—as suggested by many authors—the charge transfer or conduction in polypyrrole is, without doubt, a thermally activated process in which the  $\pi$ -electrons play the central role.

## 4. Conclusion

The growth rate of PPy films depends on the ratio of the oxidizing agent to pyrrole, or in other words, on the concentration of the reactants used in preparation. The yield of the precipitated powder and the electrical conductivity of PPy also are governed by the concentration of the reactants. Aging of the samples can introduce defect structures such as cross-links that cause a loss of conductivity.

Heating the samples with a constant temperature of 353 K for 4 days enhanced the resistivity of the samples. This heating process, which increased the resistivity, may be considered as a new method to obtain polypyrrole in a high resistance form.

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