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# Thermal analysis of polypyrrole oxidation in air

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The oxidation of chemically synthesized polypyrrole powders, doped with arylsulfonates, was investigated by thermal analysis. At high temperatures (typically $T > 230°C$) oxidation appears to be a bulk phenomenon, which leads to the decomposition and complete combustion of the polymer. At moderate temperatures (typically $T < 230°C$) oxidation is a slow gradual process, most likely limited by $O_2$ diffusion in the oxidized material. The kinetics of this oxidation process was determined and its activation energy was evaluated to be about $110\,kJ\,mol^{-1}$. At its early stage, this oxidation was shown to induce a proportional, but enhanced, decrease in the conductivity of the material.

**(Keywords: polypyrrole; oxidation; thermal analysis; conductivity; stability)**

## INTRODUCTION

Polypyrrole (PPy) is one of the most investigated conducting polymers, due to its easy synthesis and good conductivity. Moreover, this polymer shows good stability and undergoes only slow degradation in ambient atmosphere. The observed decreases of conductivity, for the best materials, are typically 80% in 2 years at ambient temperature[1], 40% in 1 year at 30°C (ref. 2) and 50% in 120 days at 60°C (ref. 3). Although these decreases are not dramatic, the stability of polypyrrole is obviously not sufficient for many practical applications and further improvements of this property are needed.

The most stable polypyrroles are synthesized using arylsulfonate anions (generally *p*-toluenesulfonate) as doping species[3–8]. In view of the almost perfect stability of these materials in inert atmosphere at moderate temperatures ($T < 200°C$), the ambient degradation of these polypyrroles has been attributed to oxidation by air[4–8], with a synergistic effect of ambient humidity[5,8]. This relation between oxidation by air and conductivity decrease has been confirmed by some analytical characterizations (X-ray photoelectron spectroscopy)[9], but neither quantitative nor qualitative data have yet been established between these two phenomena. This is probably due to serious analytical difficulties[8], resulting from two main reasons: rather large variations of conductivity can be induced by only subtle chemical or structural modifications[7,10] and freshly prepared polypyrroles generally already contain large amounts of oxygen[11]. Therefore, it seems of paramount importance to get a better understanding of the relation between oxidation in air and the conductivity decay of polypyrrole, especially with respect to practical developments of this material, to slow down or prevent such degradation.

This study is a detailed investigation of polypyrrole oxidation in air. It is performed by thermal analysis (differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.)), using various chemically synthesized polypyrrole powders. Two major oxidation regimes are considered, quantitative data are obtained and the results are discussed with reference to the conductivity decays previously reported for these polypyrroles[3,12].

## EXPERIMENTAL

### *Materials*

Pyrrole obtained from Prolabo as a clear liquid product was generally used on receipt or after distilling under vacuum to remove brown aged products. 1-Naphthalenesulfonic acid (1-ANS, Aldrich), 2-naphthalenesulfonic acid (2-ANS, Aldrich) and *p*-toluenesulfonic acid monohydrate (ATS, Aldrich) were used without additional purification. We used either $FeCl_3 \cdot 6H_2O$ (Prolabo) or an aqueous solution of $FeCl_3$ (41%, Prolabo).

### *Powder synthesis*

Polypyrrole is generally prepared electrochemically as a thin film[13], but chemical synthesis is a more convenient and simple procedure for the bulk production of powder[14–17].

Polypyrrole was synthesized in water, by chemical

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*To whom correspondence should be addressed. Present address: DCC/DESD/SEP/SETED, BAT. 326, Centre d'Etudes Nucléaires de Cadarache, BP 1, 13108 Saint-Paul-Lez-Durance, France oxidation and by polymerization of pyrrole by $FeCl_3$, according to the procedure previously described[3]. In most cases, an extra doping agent (ATS, 2-ANS or 1-ANS) was added to the polymerization bath. The precipitates were collected by filtration and thoroughly rinsed and dried[3]. Based on neutronic activation determinations[3] or elemental analyses, the doping contents (molar ratios of anion to pyrrole ring) of these various powders are, for the *p*-toluenesulfonate ($TS^-$) doping: 0.12 $TS^-$, 0.02 $FeCl_4^-$, 0.18 $Cl^-$; for the 2-naphthalenesulfonate (2-$NS^-$) doping: 0.27 2-$NS^-$, 0.01 $FeCl_4^-$, 0.04 $Cl^-$; and for the 1-naphthalenesulfonate (1-$NS^-$) doping: 0.25 1-$NS^-$, 0.07 $Cl^-$. The total doping levels (~0.32) are in good agreement with the values determined by Salmon *et al.*[18].

### *Thermal analysis*

D.s.c. experiments were performed either on a Setaram C80 calorimeter or on a Du Pont 990 thermal analyser. T.g.a. experiments were performed on a Du Pont 951 thermogravimetric analyser. The samples were heated either under a gas flow (air, $O_2$ or $N_2$) or in a closed cell (15 ml) filled with gas (air, $O_2$ or $N_2$ under atmospheric pressure). The quantity of polypyrrole analysed was in the range 10–500 mg. We used ambient air, or $O_2$ ($H_2O$ < 3 ppm) and $N_2$ ($H_2O$ < 5 ppm) from Prodair. The polymer samples were generally weighed before and after d.s.c. experiments to determine the corresponding weight losses.

## RESULTS AND DISCUSSION

### *Oxidizing decomposition of polypyrrole at high temperatures*

T.g.a. experiments were performed on various arylsulfonate-doped polypyrroles, under an air or $N_2$ flow, with about 10 mg of polymer. The results obtained for the 2-ANS doped polypyrrole are presented in *Figure 1* and are qualitatively similar to these obtained for the other polypyrroles. Under air or $N_2$ at moderate temperatures ($T < 275°C$ for the 2-ANS polypyrrole), the polymer initially undergoes a small weight decrease of between 6 and 12%. Such behaviour has been noticed by many authors[1,19–21] and is attributed to water evaporation; however, in our case, it must also be related to the removal of the chlorine species previously pointed out[3]. In $N_2$, a second, more pronounced weight loss step is observed for $T > 300°C$. Such a weight loss has also been noticed by many authors[1,6,19,20] and can be attributed, according to Truong *et al.*[6], to the decomposition of the doping species. In air, the t.g.a. curves of these arylsulfonate-doped polypyrroles indicate a rapid weight loss at high temperatures ($T > 275°C$ for the 2-ANS polypyrrole). This phenomenon is exothermic in nature (see below), and can be attributed to the oxidizing decomposition of the material. This intense oxidation occurs in two major steps, and is complete at 650°C, leading to the formation of a few per cent of $Fe_2O_3$. The characteristics of this two-step reaction are reported in *Table 1* for the 2-ANS and ATS doped polypyrroles. This behaviour in air is a little different from that described by Arca *et al.*[19] for $BF_4^-$ doped polypyrroles prepared electrochemically, who observed a one-step oxidation process and a partial loss of weight (about 60%) at 650°C. However, our arylsulfonate-doped polypyrroles appear, from these results, to be thermally stable materials, showing both good intrinsic stability and good resistance against oxidation until $T = 240–270°C$. Based on these t.g.a. experiments, the resistance against oxidation of these various polypyrrole samples is in the following order:

PPy synthesized without an extra doping agent < ATS doped PPy < 1-ANS doped PPy ⩽ 2-ANS doped PPy

Nevertheless, oxidative stability of these materials, at moderate temperatures, will be best studied by d.s.c.

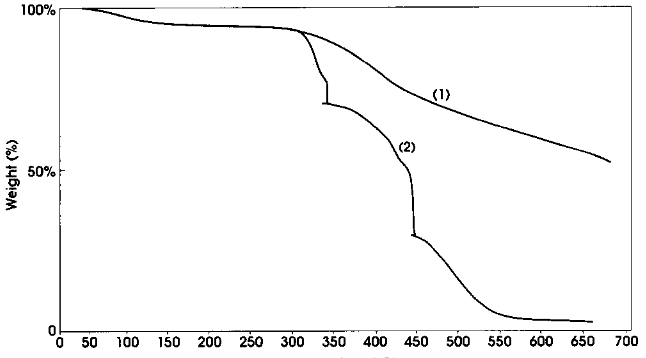

**Figure 1** T.g.a. curves at 10°C min$^{-1}$: (1) 10 mg of 2-ANS doped polypyrrole in $N_2$ flow; (2) 10 mg of 2-ANS doped polypyrrole in air flow

**Table 1** Characterization of the two-step oxidizing decomposition of polypyrrole. 2-ANS and ATS doped polymers, t.g.a. under an air flow, 10°C min$^{-1}$

| | Starting temperature (°C) | Critical temperature (°C) | Weight loss (%) |
|---|---|---|---|
| 2-ANS/1st step | 275 | 330 | 24 |
| 2-ANS/2nd step | 330 | 435 | 41 |
| ATS/1st step | 240 | 300 | 46 |
| ATS/2nd step | 295 | 385 | 32 |

### *Polypyrrole oxidation at moderate temperatures*

*Evidence for oxidation at moderate temperatures.* The d.s.c. experiments were first performed in a closed cell (15 ml) filled with air and containing 500 mg of polypyrrole. In such conditions, all the samples studied underwent exothermic reaction at low temperatures (in the range 120–140°C) (*Figure 2*). This exothermic reaction is unambiguously an oxidation of the polypyrrole, as proved by various experiments carried out in air, $N_2$ or $O_2$, on 200 mg of the 2-ANS doped polypyrrole (*Figure 3*), while measuring reaction enthalpy ($\Delta H$):

- in $N_2$, no reaction, $\Delta H = 0$;
- in air, $\Delta H = 22.4$ J;
- in $O_2$, $\Delta H = 70.5$ J*.

This oxidation starts at very low temperatures ($T < 100°C$), and leads only to a slight weight loss (a few per cent), in

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* Polypyrrole oxidation is, in these experimental conditions, a partial reaction limited by the available oxygen and is thus enhanced with increasing quantities of $O_2$

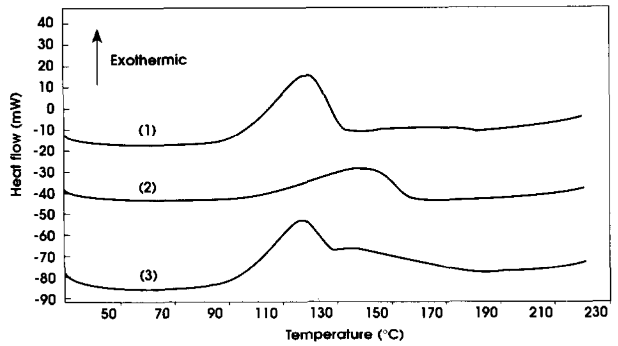

**Figure 2** D.s.c. curves at 1°C $min^{-1}$ in a closed cell filled with air: (1) 441 mg of ATS doped polypyrrole; (2) 481 mg of 2-ANS doped polypyrrole; (3) 542 mg of polypyrrole synthesized without an additional arylsulfonate doping species

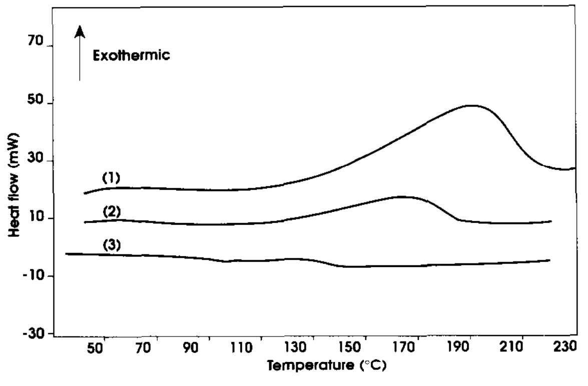

**Figure 3** D.s.c. curves at 1°C $min^{-1}$ of 200 mg of 2-ANS doped polypyrrole: (1) $O_2$ in a closed cell; (2) air in a closed cell; (3) $N_2$ in a closed cell

agreement with the t.g.a. determinations. Indeed, this oxidation concerns the polymer backbone instead of the doping species, which are not oxidized until at least 140°C (d.s.c. results not shown).

*Quantitative aspect.* The quantitative aspect of polypyrrole oxidation at moderate temperatures was studied by d.s.c. in the isothermal mode. These experiments were performed under an $O_2$ flow, on 50 mg of the 1-ANS doped polypyrrole, generally for 4 h. The samples were first heated to the experimental temperature in $N_2$, then $O_2$ flow was admitted to the d.s.c. cell.

The strong oxidation enhancement, previously observed at high temperatures for t.g.a. experiments, is clearly revealed by d.s.c. in the isothermal mode. As shown in *Figure 4*, heating the sample at 240°C gives rise to a very sharp signal, with a corresponding weight loss of 40%. Such a result indicates a fast and intense oxidizing decomposition of the material, in accordance with the t.g.a. data. This behaviour is much more pronounced than that observed in heating the sample at 230°C. In this case, the exothermic signal is rather smooth and weak, with a weight loss of only 10% in 3 h. In such conditions, oxidation is therefore a gradual, rather slow phenomenon. Decreasing the experimental temperature leads to a similar but weaker response (*Figure 5*).

These d.s.c. results at moderate temperatures can be related to the oxidation reaction rate. Assuming a unique oxidation reaction, heat flow ($\Phi$) is proportional to oxidation rate ($dn/dt$), where $n$ is the molar quantity of oxidized pyrrole ring and $t$ the time. Thus:

$$\Phi = \Delta H_s \, dn/dt \tag{1}$$

where $\Delta H_s$ is the specific enthalpy of this oxidation reaction with respect to the molar amount of pyrrole ring involved.

This specific enthalpy was measured for a d.s.c. run at 225°C, performed on 50 mg of the 1-ANS doped polypyrrole, under an $O_2$ flow. In such conditions, complete oxidation, achieved when $\Phi = 0$, is obtained in 8 h. Thus:

$$\Delta H_s = \int_0^{8h} \Phi \, dt/n_0$$

where $n_0$ is the initial molar quantity of pyrrole ring. This evaluation leads to $\Delta H_s = 600\,kJ\,mol^{-1}$ pyrrole ring, which is rather a high value. Thus, polypyrrole oxidation at moderate temperatures is a strong exothermic reaction.

Consequently, the proportion of oxidized polypyrrole ($n/n_0$) can be evaluated by integrating the above relation (1) for each time and temperature:

$$n/n_0 = \int_0^t \Phi \, dt/(n_0 \Delta H_s)$$

The results deduced from *Figure 5*, for 50 mg of the 1-ANS doped polypyrrole, are presented in *Figure 6*.

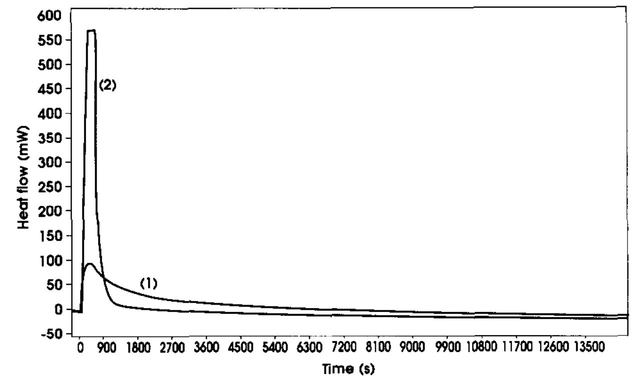

**Figure 4** D.s.c. curves in the isothermal mode for 50 mg of 1-ANS doped polypyrrole under an $O_2$ flow: (1) 230°C; (2) 240°C

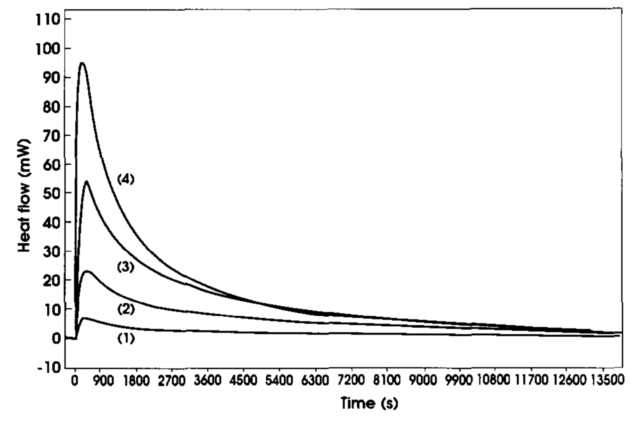

**Figure 5** D.s.c. curves in the isothermal mode for 50 mg of 1-ANS doped polypyrrole under an $O_2$ flow: (1) 180°C; (2) 200°C; (3) 220°C; (4) 230°C

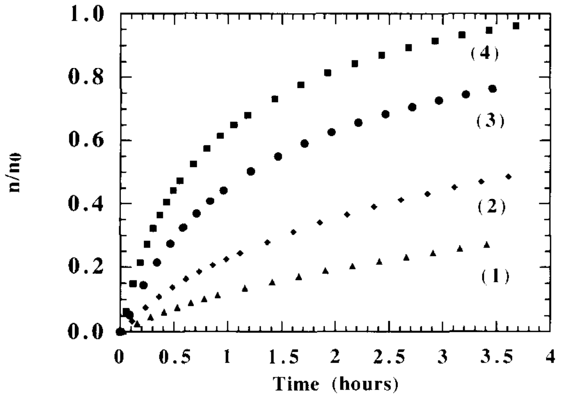

**Figure 6** Variation *versus* time of the proportion of oxidized polypyrrole ($n/n_0$) at different temperatures: (1) 180°C; (2) 200°C; (3) 220°C; (4) 230°C

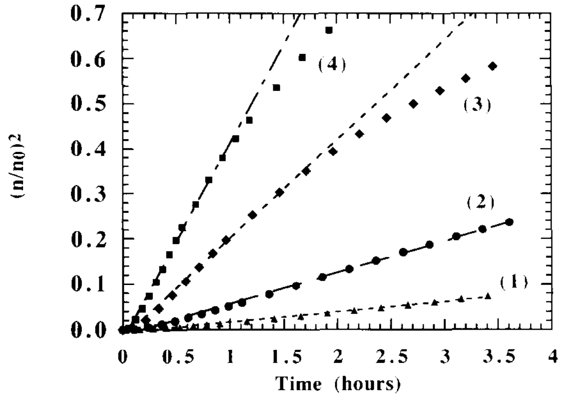

**Figure 7** Variation *versus* time of the square of the proportion of oxidized polypyrrole ($(n/n_0)^2$) at different temperatures: (1) 180°C; (2) 200°C; (3) 220°C; (4) 230°C

*Kinetic aspect.* The oxidation kinetics of polypyrrole at moderate temperatures can be obtained from the d.s.c. results in the isothermal mode, i.e. the $n/n_0$ variations *versus t*. In agreement with Truong *et al.*[6], we found that the oxidation kinetics in the 120–230°C temperature range was better described by a parabolic relationship between $n/n_0$ and time $t$, rather than by simple first- or second-order kinetics. The results, deduced from *Figure 6*, are presented in *Figure 7*. Until $n/n_0 = 0.5$, the plots of $(n/n_0)^2$ *versus t* are linear, passing through the origin. Thus, during a first period until $n/n_0 = 0.5$, the extent of oxidation can be described by the simple law:

$$(n/n_0)^2 = At \qquad \text{or} \qquad n/n_0 = (At)^{1/2} \qquad (2)$$

with $A$ being a function of temperature.

The values of $A$ obtained in the temperature range 120–230°C are listed in *Table 2*. The plot of $\ln A$ *versus* $1/T$ gives rise to a perfectly straight line (*Figure 8*), which is in agreement with a temperature dependence described by an Arrhenius law. The slope of this straight line can be related to the activation energy ($E_a$) of this oxidation phenomenon as:

$$\ln A = \ln A_0 - E_a/RT \qquad \text{or} \qquad A = A_0 \exp(-E_a/RT)$$

where $A_0$ is a constant. Therefore:

$$A(\mathrm{h}^{-1}) = 31.4 \times 10^{10} \exp[-13\,783/T(\mathrm{K})]$$

and

$$E_a = 110\,\mathrm{kJ\,mol^{-1}}$$

*Phenomenological aspect.* As is generally done, the linear relationship between the amount of oxidized polypyrrole, $n/n_0$, and $t^{1/2}$ can be attributed to diffusion kinetics*. This assumption is in agreement with that of the preliminary study of Truong *et al.*[6]. Moreover, this statement is consistent with the results of the atom-probe study of Nishikawa and Kato[22], which indicate that polypyrrole oxidation progresses from the surface to the core of the material. This aspect can be underlined by working with a constant amount of $O_2$, while using various quantities of polypyrrole in excess with respect to oxygen (i.e. partial oxidation of the polymer). The results obtained, for experiments carried out in a closed cell filled with air on the 2-ANS doped polypyrrole, are presented in *Figure 9*. They show a considerable shift of the oxidation signal with the analysed mass, which can be explained in the following manner. For the higher pyrrole ring/$O_2$ ratios, oxidation is a superficial phenomenon which can be observed at moderate temperatures. For the lower ratios, oxidation can be effective until the core of the material, but needs high temperatures for $O_2$ diffusion.

As proposed by Truong *et al.*[6], the feature that underlies polypyrrole oxidation might be the amount of oxygen absorbed in the polymer, which can be governed by typical Fickian sorption kinetics. Nevertheless, Nishikawa and Kato's analyses[22] suggest a rather different mechanism.

**Table 2** Oxidation kinetic parameter ($A$) of the 1-ANS doped polypyrrole at various temperatures. The oxidations were performed under an $O_2$ flow, on different weights of polymer

| Oxidation temperature (°C) | $A$ ($\mathrm{h}^{-1}$) |
|---|---|
| 120[a] | 0.00024 |
| 140[a] | 0.00081 |
| 160[a] | 0.0037 |
| 180[a] | 0.022 |
| 200[b] | 0.069 |
| 220[b] | 0.22 |
| 230[b] | 0.43 |

[a] Weight of polymer = 500 mg
[b] Weight of polymer = 50 mg

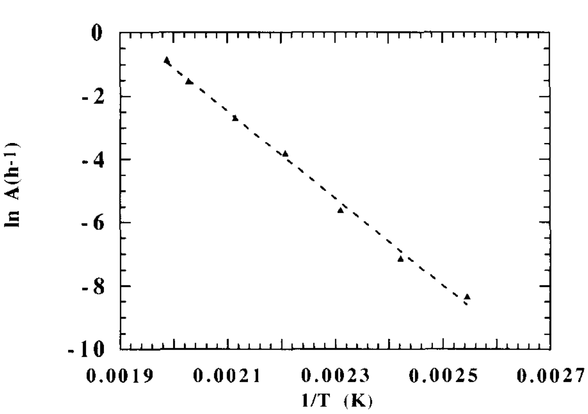

**Figure 8** Variation of the logarithm of the oxidation kinetic parameter ($A$) as a function of the inverse of temperature ($T$)

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* As a matter of fact, relation (2) leads to −1 order reaction kinetics with respect to $n/n_0$ ($\mathrm{d}(n/n_0)/\mathrm{d}t = A/2(n/n_0)^{-1}$), which is unlikely to be related to chemical reaction kinetics

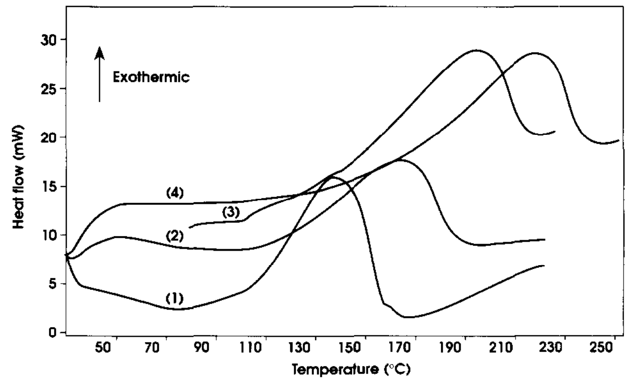

**Figure 9** D.s.c. curves at 1°C $min^{-1}$ in a closed cell filled with air: (1) 481 mg of 2-ANS doped polypyrrole; (2) 202 mg of 2-ANS doped polypyrrole; (3) 100 mg of 2-ANS doped polypyrrole; (4) 50 mg of 2-ANS doped polypyrrole

Like oxidized metals, the oxidized polypyrrole appears to be composed of two phases: a fully oxidized surface layer and an unoxidized material section, with a rather abrupt boundary between them. Therefore, polypyrrole oxidation might occur according to a metal-like corrosion mechanism[23]. In both cases (Fickian sorption or corrosion kinetics), parabolic variations of the quantity of oxidized polymer *versus* time can be expected for a significant time, with a further increase at a slower rate due to the finite dimensions of the sample particles.

Therefore, the oxidation of arylsulfonate-doped polypyrroles is an exothermic reaction, which occurs even at low temperatures ($T < 100$°C). Nevertheless, the extent of oxidation seems in practice to be limited by $O_2$ diffusion in the oxidized material, which appears to be the rate-determining step of the process until at least 230°C (for the 1-ANS doped polypyrrole). Beyond this temperature, oxidation appears to be a bulk phenomenon.

Finally, it must be noted that the activation energy ($E_a = 110\,kJ\,mol^{-1}$) of this limiting diffusion phenomenon is rather high, and thus suggests strong bonding interactions between $O_2$ and the oxidized polymer, rather than weak Van der Waals' interactions (about $5\,kJ\,mol^{-1}$). Such a statement was also emphasized by Nishikawa and Kato[22].

*Relation between polypyrrole oxidation at moderate temperatures and its conductivity degradation.* We have previously reported[3,12] the conductivity decays of some of the above-mentioned arylsulfonate-doped polypyrroles, in the form of films deposited on various fabrics. These measurements were performed *in situ*, in ambient air at different temperatures (in the range 60–140°C). Various arylsulfonate doping species, especially ATS and 2-ANS, were used.

A typical variation of the square of the relative decrease in conductivity, $[(\sigma_0 - \sigma)/\sigma_0]^2$ (where $\sigma_0$ and $\sigma$ are the conductivities at the initial time and at time $t$, respectively), *versus* time is reported in *Figure 10*. In this figure, an experiment performed at 140°C on the most stable of these polypyrrole films (2-ANS doped material) is presented together with the above-mentioned variation of $(n/n_0)^2$ *versus* time, observed at the same temperature in $O_2$ for the 1-ANS doped polymer in the form of powder. These variations show a marked similarity and present, after about 1 h, good linearity. More generally, the variations of $[(\sigma_0 - \sigma)/\sigma_0]^2$ *versus* time, observed for all these films, were shown to be linear up to $\sigma/\sigma_0 = 0.5$. Moreover, the activation energy of the conductivity decay of these films was shown to be almost constant for all the samples and equal to about $85\,kJ\,mol^{-1}$, a value quite close to that which governs the oxidation of these materials (about $110\,kJ\,mol^{-1}$).

Therefore, a proportionality between the amount of oxidized polypyrrole, at the early stage of oxidation, and the corresponding decrease of conductivity of the polymer film (until $\sigma/\sigma_0 = 0.5$), can be reasonably assumed:

$$[(\sigma_0 - \sigma)/\sigma_0](t, T) = B[n/n_0](t, T)$$

with $B$ a constant. Moreover, as suggested by *Figure 10*, the decrease in conductivity is most likely enhanced with respect to polymer oxidation. An evaluation of $B$ can be made, taking into account the fact that the stabilities of the 1-ANS doped and 2-ANS doped polymers are not very different, and that the polymer is more easily oxidized in the form of powder than in the form of film, and in $O_2$ than in air. Therefore, according to *Figure 10, $B \geqslant 10$;* i.e. 1% of oxidized polymer gives rise to a decrease of > 10% in conductivity.

For powders, conductivity is classically measured on pressed pellets[3]; dramatic decreases of measured conductivity can thus be expected for slight oxidations of the material. For example, the oxidation of about 5% of the 1-ANS doped polypyrrole leads to a corresponding conductivity decrease of 95% (from 50 to 2 $S\,cm^{-1}$, measured on pressed pellets of the oxidized and unoxidized samples).

## CONCLUSION

Polypyrrole is oxidized in the presence of $O_2$, inducing a degradation of its conductivity. At high temperatures (typically, $T > 230$°C), this oxidation is a bulk phenomenon which leads to the decomposition and complete combustion of the polymer. At moderate temperatures ($T < 230$°C), this oxidation is a gradual, rather slow phenomenon, which seems to be limited by the diffusion of $O_2$ in the oxidized material. Consequently, the amount of oxidized polypyrrole is a linear function of the square root of time, $t^{1/2}$. This diffusion process is very slow at

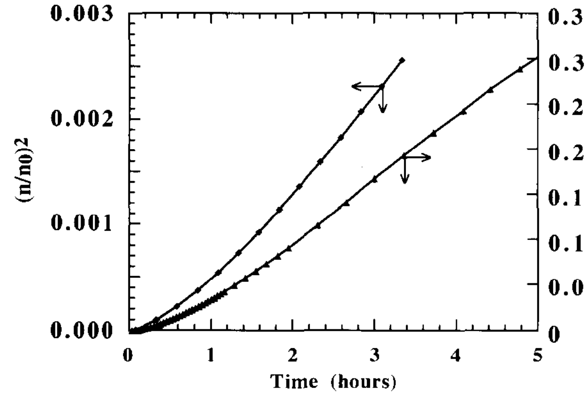

**Figure 10** Comparison, at 140°C, of the proportion of oxidized polypyrrole ($n/n_0$) and of the conductivity decrease of polypyrrole ($(\sigma_0 - \sigma)/\sigma_0$) as square functions of time. $n/n_0$ is measured for a powder of 1-ANS doped polypyrrole under $O_2$, $(\sigma_0 - \sigma)/\sigma_0$ is measured for a film of 2-ANS doped polypyrrole under air

moderate temperatures, most likely due to strong bonding interactions between $O_2$ and the material, but is strongly thermally activated. At its early stage, this oxidation is suspected to induce a proportional, but enhanced, decrease of the conductivity of the material. Further experiments are in progress to better define this relation between oxidation and conductivity decrease, and to improve the resistance of polypyrrole against oxidation.

## ACKNOWLEDGEMENTS

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