Influence of the Dopant on the Polypyrrole Moisture Content: Effects on Conductivity and Thermal Stability

C. CASSIGNOL,¹ P. OLIVIER,² A. RICARD¹

¹ Laboratoire des Procédés de Polymérisation, Ecole Nationale Supérieure d'Ingenieurs de Génie Chimique, INPT, 18 Chemin de la Loge, 31078 Toulouse Cedex, France

² Laboratoire de Génie Mécanique, I.U.T. Paul Sabatier, 50 Chemin des maraîchers, 31077 Toulouse Cedex 4, France

Received 19 September 1997; accepted 26 April 1998

ABSTRACT: Having in mind to produce electrically conductive carbon–epoxy composite materials, we have filled an insulating epoxy resin with an electronic conducting polymer, polypyrrole (PPy). To select the PPy that best suits this process, various PPys were chemically synthesized. The syntheses were performed in water via a dispersion polymerization route using, initially, either FeCl_3 (PPy-Cl⁻) or (NH₄)₂S₂O₈ (PPy- HSO_4^-) as oxidizing agents. Then, using $(NH_4)_2S_2O_8$ as the oxidant, two other PPy doped with aromatic species were obtained due to the dissolution of paratoluenesulfonic acid $(PPy-TS^{-})$ or naphtalenesulfonic acid $(PPy-NS^{-})$ in the reaction media. The characterization of the PPy samples by conductivity measurements, together with elemental and thermal analysis, showed that PPy-TS⁻ exhibits the highest conductivity and thermal stability, with the conductivity remaining steady over 14 days. In addition, a stabilizing effect of the aromatic anions was observed. The experiments have shown that moisture in the PPy cannot be entirely removed and that, with increasing moisture content, the conductivity also increases, indicating an ionic conductivity superimposed on the electronic conductivity usually observed in PPy. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1567-1577, 1998

Key words: polypyrrole; aromatic anions; thermal stability; humidity affinity; ionic conductivity

INTRODUCTION

This study is part of our ongoing research project to develop high-performance composite materials with electrically conductive properties.

For years, the use of organic matrices for composite materials has been widespread and widely accepted by aircraft manufacturers. Composite materials consist of fibrous reinforcements within a polymeric matrix, where the interactions of the constituents give overall mechanical and physical properties satisfying stiffness, mass, and temperature requirements. However, polymeric matrices used in composite materials are, by nature, rather good electrical insulators. This property does not enable the composite materials to deal with the problem of electrostatic charge elimination usually encountered in the fuselage, wings, vertical fin, and flaps. Indeed, the problem of lightning strike protection has been solved by aircraft manufacturers for several years. In fact, various aircraft parts made of composite materials are coated with a metallic braid lightning conductor and a network of conductive aluminum straps. However, an alternative solution can be envisaged by improving the electrical conductiv-

Correspondence to: C. Cassignol.

Journal of Applied Polymer Science, Vol. 70, 1567-1577 (1998)

^{© 1998} John Wiley & Sons, Inc. CCC 0021-8995/98/081567-11

ity of the polymeric matrices. A general bibliographic study^{1,2} shows that there are several ways to make electrically conductive polymeric matrices. Two kinds of electrically conductive polymers can be distinguished. Extrinsic conductive polymers result from the combination of an insulating polymer filled with carbon black or metallic particles, which ensure the electrical conduction. These fillers can provide relatively high conductivity,^{3,4} from 10^{-4} to 0.4 S/cm for a thermosetting polymer filled with less than 2% volume of carbon black. However, such fillers induce significant increases in polymer specific mass. Indeed, for most polymers used as matrices in highperformance composites, the specific mass lies often between 1.1 and 1.4, while for carbon black or aluminum, the specific mass is, respectively, 1.8 and 2.8. Intrinsic conductive polymers are electrically conductive by themselves without any filler and may exhibit conductivity close to that of copper,⁵ that is, 10^3 S/cm. Yet, these polymers are usually very brittle and cannot carry any mechanical load. Furthermore, they are difficult to process and manufacture.¹

The solution considered here is to combine the previously mentioned approaches. An intrinsic conductive polymer, namely, polypyrrole (PPy), is used as a filler in an insulating polymeric matrix, namely, epoxy. This solution does not provide electrical conductivity as important as those obtained with metallic or carbon black fillers but they are quite sufficient to meet the specifications required for the applications. In fact, the specific masses of the epoxy matrix and the PPy particles are, respectively, 1.23 and 1.4. In addition, because of the presence of NH groups in the polymer chains, physical bonds between the epoxy matrix and the polypyrrole particles are expected. These bonds can result in an improvement of the mechanical properties of the conducting polymer. From a manufacturing point of view, PPy remains one of the easiest conductive polymers to synthesize, and the epoxy matrix can be very easily filled with the manufactured polypyrrole particles. This rather simple and rapid manufacturing process has been chosen to meet the industrial processability.

The aim of this study is to synthesize a conducting polymer (PPy) that satisfies the following requirements.

• It must be thermally stable so that the epoxy matrix curing does not induce thermal degradation.

- The particles' volume fraction must remain as low as possible in order to ensure electrical conductivity without resulting in significant modifications of the epoxy matrix's mechanical characteristics. Therefore, the PPy particles must be small in size and should exhibit a narrow distribution of particle size.
- The final composite material reinforced with carbon fibers must exhibit a sufficient electrical conductivity. Therefore, the conducting PPy must have a conductivity value as high as possible.
- The entire manufacturing process must remain as simple as possible with high synthesis yields.

BACKGROUND

During the last 20 years, several conducting polymer studies have been undertaken. One of the first conducting polymer was polyacetylene,⁶ which remains, to date, the most conductive (up to 10^5 S/cm). However, it is unstable and difficult to process. Since then, polyheterocyclic conducting polymers, such as PPy,⁷ polythiophene,⁸ and polyparaphenylene, have been developed. It has been shown that polyheterocycles, although less conductive than polyacetylene, are more thermally stable.⁹ Indeed, PPy, which is easy to synthesize, is thermally stable and remains resistant to atmospheric agents,^{10,11} was chosen for this study. For the synthesis of PPy, the dispersion polymerization technique was used. This process enables one to obtain a large quantity of conducting polymer in form of colloidal particles with a narrow distribution of particle size¹² and so this enables to obtain a homogeneous distribution of PPy in a polymeric matrix, resulting in both conductivity and physical property improvement. The polymer synthesis proceeds via an oxidation of the pyrrole monomer with a simultaneous polymerization in micelles of steric stabilizer. Among various oxidizing agents used in the literature, the metallic salt iron(III) chloride (FeCl₃) was widely investigated.¹³⁻²⁰ This oxidizing agent causes the formation of positive charges in the polymer chain, and their displacement will result in the conduction phenomena. Some milder oxidizing agents [such as $(NH_4)_2S_2O_8$], which lead to conductive and doped PPy as well, have also been studied.^{21–23} Doping anions that achieve the electrical neutrality of the polymer are present along the carbon backbone. They result from the decomposition of the oxidizing agent but they can be replaced by others anions provided by components introduced in the reaction media. Thus, the dissolution of an aromatic acid in the initial oxidative solution can provide aromatic anions, which are preferentially introduced along the carbon chain, imparting according to some authors,²³⁻²⁵ a better stability to the polymer.

This work compares the electric and thermal properties of different PPy produced under various conditions. First, PPy was obtained by using either $FeCl_3$ or $(NH_4)_2S_2O_8$ as the oxidizing agent and then, for a given oxidizing agent $((NH_4)_2S_2O_8)$, two kinds of aromatic acids (2-naphtalenesulfonic acid or *p*-toluenesulfonic acid) were added to replace the initial doping species. Conductivity measurements and thermal and elemental analyses were undertaken for the different products. The influence of the different doping species on the residual moisture content in the synthesized PPy was then examined. The effect of the drying time on the moisture content and its influence on the conductivity were also investigated. Finally, the stability of the conductivity was observed during 1 week under systematically controlled environmental and thermal atmospheric conditions.

Based on these series of experiments, a selection of a PPy, which fulfills the described requirements and which is best suited as a filler for an epoxy matrix, is presented. In addition, the nature of the conductivity of the PPy is clarified.

MATERIALS

Chemical Products

Pyrrole (Aldrich, Gillingham, UK, 98%) was vacuumdistilled and stored at 4°C in the absence of light. 2-Naphtalenesulfonic acid (HANS 70%, Aldrich), *p*toluenesulfonic acid monohydrate 98% (Janssen Chemica, Geel, Belgium), poly(vinyl alcohol) 96% hydrolyzed, (PVA 96, Janssen Chemica), ammoniumpersulfate ((NH₄)₂S₂O₈, Janssen Chemica), iron(III) chloride anhydrous 98% (FeCl₃, Janssen



Figure 1 Chemical polymerization of pyrrole with $FeCl_3$.

a)
$$Py + FeCl_3 \longrightarrow Py^{\delta_+} - FeCl_3^{\delta_-}$$

b) $Py^{\delta_{+}}-FeCl_{3}^{\delta_{-}}+FeCl_{3} \xrightarrow{k_{\bullet}} Py^{+}+FeCl_{3}+FeCl_{2}+Cl^{-}$

Figure 2 Kinetic scheme of the polymerization steps of pyrrole with $FeCl_3$ as an oxidizing agent.

Chemica), and iron(II) chloride ($FeCl_2$, Prolabo, Paris, France) were used as received.

Polymer Synthesis

As water is one of the most convenient and cheapest solvents,^{13,14} PPy was prepared via an aqueous dispersion polymerization similar to those described in previous works.^{26–28} 3.53 mL of pyrrole monomer were added to a 500-mL aqueous solution containing the steric stabilizer (PVA 96 at a PVA–pyrrole mass ratio equal to 0.12^{27}), the oxidizing agent ((NH₄)₂S₂O₈ or FeCl₃), and, in some cases, an additional aromatic acid. The reaction was allowed to proceed between 5 and 7°C^{13,17} and for a pH lower than 3,²¹ which leads to a highly conjugated polymer structure.

Synthesis with FeCl₃ as the Oxidizing Agent

The ferric ion Fe^{3+} performs the pyrrole oxidation via the reaction described in Figure 1.²⁸ The doping anion in the synthesized PPy is Cl^- (PPy-Cl⁻).

A kinetic study carried out by Thieblemont et al.²⁰ gives a better understanding of the polymerization mechanism. The reaction is acid-catalyzed. In the first step of the mechanism described by Thieblemont et al.,²⁰ there is a donor-acceptor complex formation [see Fig. 2(a)] enabling a charge transfer from the π system of pyrrole to the Lewis acid so that pyrrole oxidation is facilitated. The oxidation of the complex with FeCl₃ [see Fig. 2(b)] then leads to the formation of the pyrrole radical cation, which initiates the polymerization.

The disappearance rate of pyrrole is expressed in eq. (1), which shows that the FeCl_3 concentration has a significant influence on the polymerization rate.

$$d[Py]/dt = -K_e \cdot k_e \cdot [Py] \cdot [Fe^{3+}]^2 \qquad (1)$$

In this equation, k_e is the rate constant of the oxidation reaction, and K_e is the equilibrium constant of the complex formation.

According to the stoechiometric coefficients as seen in Figure 1 and to data in the literature, ^{15,19}

$$S_2O_8^{2-} \longrightarrow 2 SO_4^{\circ}$$
$$SO_4^{\circ} + H_2O \longrightarrow HSO_4^{\circ} + OH^{\circ}$$
$$2 OH^{\circ} \longrightarrow H_2O + 1/2 O_2$$

Figure 3 Dissociation reaction of $(NH_4)_2S_2O_8$ and generation of SO_4^{-1} radicals.

the optimal FeCl₃-pyrrole molar ratio is 2.3. In addition, to avoid a suroxidation of the PPy produced caused by a long contact time with the oxidative solution,^{14,16} FeCl₂ is added in a [FeCl₃]-to-[FeCl₂] ratio of 30 before starting the reaction. Finally, the pyrrole (Py) monomers are introduced (Py is 0.1*M*), and the polymerization takes place during 6 h. This extended reaction time is due to the added FeCl₂, which creates an induction period, necessary for the formation of a sufficient quantity of pyrrole oligomers.¹⁶

Synthesis with $(NH_4)_2S_2O_8$ as the Oxidizing Agent

 $(\mathrm{NH}_4)_2\mathrm{S}_2\mathrm{O}_8$ behaves as a dissociative initiator of the polymerization through homolytic dissociation in two sulphate radical ions. The mechanism is depicted in Figure 3.²⁹ One of the reaction products is the bisulfate anion (HSO₄⁻), which may be present along the polymer chain as a doping anion (PPy–HSO₄⁻). The reaction then occurs via a classical radical polymerization initiated by the formed SO₄⁻ radicals ions. This radical ion initiation of the polymerization follows the scheme of Figure 4, where *M* is representative of the pyrrole monomer. Several authors^{22,29} have pointed out that a chemically linked sulfur ion is present at the end of the polymer chains when (NH₄)₂S₂O₈ is used as the initiator.

In order to obtain a good conducting polymer and a reasonable yield, $(NH_4)_2S_2O_8$ is dissolved in the aqueous solution of a steric stabilizer having a molar concentration of 0.1M.²¹ The pyrrole monomer is then added with a $(NH_4)_2S_2O_8$ -to-Py molar ratio of 1. With a higher ratio, an increase of the oxygen content in the polymer may be observed. This increase can be described by the formation of carbonyl groups, which diminishes the conjugation lengths and therefore deteriorates the conductivity.²² However, a lower ratio leads to a lower yield.²² The reaction is allowed to proceed for 1 h. A longer contact time with the oxidative solution results in a suroxidation of the formed PPy. Oxygen liberated by the initiator decomposition (see Fig. 3) attacks the chain of PPy and reduces the conjugation length of the polymer.²¹ Consequently, the polymer conductivity is reduced.

As previously explained, in some cases, aromatic acids (naphtalenesulfonic or paratoluenesulfonic) may be added to this reaction media in order to replace the initial dopant. This was realized before inserting the pyrrole monomers. The dopant-to-pyrrole molar ratio should be 0.3 (according to the usual doping level, which is between 0.25-0.33).⁷ PPy doped with naphtalenesulfonate anions (PPy–NS⁻) and paratoluenesulfonate anions (PPy–TS⁻) will be obtained.

For the two PPy syntheses [with FeCl₃ or $(NH_4)_2S_2O_8$ as the oxidizing agent], it is observed that several seconds after the addition of pyrrole, the reaction media takes the characteristic black color of doped PPy (in presence of FeCl₂, several minutes are necessary). No precipitate is formed. At the end of the reaction time, the dispersion is then filtered and washed with water, ethanol, and acetone. The obtained product is dried several times under vacuum (0.09 MPa) and at ambient temperature in the presence of desiccant salts. Finally, in order to obtain a fine powder and to break the agglomerates, the crude black powder has to be crushed in a mortar. The final polypyrrole is infusible and insoluble in all solvents.

All synthesis parameters are intimately linked, and a modification of one of them results in an important variation of the characteristics of the product. Thus, the formation of nonspherical particles was observed by some authors when the correct order of addition of the reactants was not followed.²⁷ To guarantee the reproducibility of the results, all conditions have to be respected.

METHODS

The elemental analyses were carried out in the Central Analysis Service of the CNRS in Vernaison, France. The theoretical amount of polymer-

$$M + SO_4^{\circ\circ} \longrightarrow {}^{\circ}MOSO_3^{\circ}$$
$$M + {}^{\circ}MOSO_3^{\circ} \longrightarrow {}^{\circ}M_2SO_3^{\circ}$$
$$M + {}^{\circ}M_nOSO_3^{\circ} \longrightarrow {}^{\circ}M_{n+1}OSO_3^{\circ}$$

Figure 4 Initiation and propagation steps of the pyrrole polymerization initiated by $(NH_4)_2S_2O_8$.

Samples		%C	%H	%N	%S	%Cl	%Fe	%0	C/N	C/S	N/S	$m_{(\mathrm{g})}$
$PPy-HSO4^-$	Exp	44.9	4.3	10.9	7.3	_	_	29.2	4.8	16.4	3.4	3.66
	Calculated	49.3	3.4	14.4	10.9			21.9	4	12	3	2.86
$PPy-TS^-$	Exp	52.9	4.6	13	5.5			24	4.8	25.5	5	2.20
	Calculated	65.3	4.4	14.1	6.4			9.7	5.4	27	5	2.63
PPy-NS ⁻	Exp	50.3	4.2	12.9	5.04			27.5	4.5	26.6	5.8	1.76
	Calculated a	68.1	4.5	14	5.3			8.0	5.6	34	6	3.16
	Calculated b	62	4.1	16	6.25			11.6	4.5	26.6	5.9	
PPy-Cl ⁻	Exp	69.5	4.1	12.9		10.4	6.7	15.8	4.5	13.3	3	4.28
	Calculated	62.4	3.9	18.2	—	15.4	_		4	12	3	5.31

Table I Elemental Analysis of 4 Types of PPy Samples with Experimental and Calculated Values

ized pyrrole was calculated from the initial amount of pyrrole in the polymerization solution assuming that the general formula of PPy can be described as $[(C_4H_3N)^{x+}, x \text{ dop}^-]$ with x being the sulfur-to-nitrogen S/N ratio. The S/N ratio is representative of the doping level, while the Dop symbol is representative of the different dopant of the PPv. The mass fraction (%) of the different elements, present in each sort of PPy, are given in Table I. The oxygen content was calculated by subtraction of the other concentrations. The N/S molar ratio represents the doping level, which is representative of the number of pyrrole rings for one dopant. Once the experimental N/S molar ratio was determined, the theoretical percentage of each element and the theoretic mass of product were calculated for each sort of PPv. Experimental and calculated values are compared in Table I.

The conductivity was measured according to the four-points probe method. A stabilized direct current alimentation (Keithley model 224) was used to apply an intensity of 1 mA on pellets of dried PPy powder (200 to 300 mg pressed under 8 tons for 15 min). The resulting tension is measured with a precision of 0.05%, by a nanovoltmeter (Keithley 181) exhibiting an impedance of 10^9 Ω in our measurements range. Since the conductivity depends on the pellet thickness, and because the various PPy have distinct moisture contents, the amount of powder has to be adjusted so that the same pellet thickness is obtained for each of the synthesized PPy.

Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer TGA apparatus (with a sensibility of 10^{-7} g). The samples were submitted to a temperature raise from ambient temperature up to 350°C at the rate of 10°C/min. The mass fraction of the residual moisture contained in all samples, the degradation process, and the degradation temperature of PPy can be observed.

RESULTS AND DISCUSSION

Chemical Composition

For all the synthesized PPy, the analysis (Table I) shows an excess in the hydrogen and oxygen content. This was also observed by other authors.¹⁶ Although the samples were dried for 24 h at ambient temperature under 0.09 MPa, they contain a certain amount of water as shown hereafter. The difference between the experimental and the calculated data can be explained by the fact that the increase of the H and O content results in a decrease of the relative proportions of the other elements and therefore lowers their mass fraction. This means that an adequate ratio for comparing experimental and theoretical data are the C/N and C/S molar ratios, as they should remain constant.

For PPy–HSO₄⁻ and PPy–Cl⁻, the experimental C/N and C/S molar ratio are similar to those calculated. They have a doping level of one dopant for three pyrrole rings, which corresponds to the usually reported PPy doping level.⁷ In addition, the elemental analysis of PPy–Cl⁻ shows that, when FeCl₃ is used as the oxidizing agent, iron coming from FeCl₃ and FeCl₂ cannot be entirely washed out and remains in nonnegligible amounts in the synthesized PPy.

For PPy–TS⁻, the theoretical and experimental values of the C/N and C/S molar ratios are in good agreement. Consequently, it can be assumed that this PPy has a doping level of five pyrrole rings for one dopant, as calculated from experimental and theoretical data. This doping level is slightly lower than that for those generally reported in the literature. In contrast, in the case of PPy–NS⁻, the experimental C/S and C/N molar ratios are very different from the calculated ratios for a doping level of one naphtalenesulfonate an-



Figure 5 Thermogravimetric study of the $PPy-HSO_4^-$, $PPy-TS^-$, $PPy-Cl^-$, and $PPy-NS^-$ degradation.

ion for six pyrrole rings (see Table I, PPy-NS, calculated a). Since an identical N/S molar ratio is found for the experimental and theoretical calculations, and because the experimental C/S ratio is lower than expected in theory, it can be suspected that a dopant other than NS⁻ is present. The high sulfur content can be explained by the presence of the codopant HSO_4^- , which is formed through decomposition of the initiator. The calculated HSO₄⁻-to-NS⁻ molar ratio of 12/5 anions for 100 pyrrole rings agrees with the experimental data. So, PPy-NS⁻ is only slightly doped with NS⁻, and the main dopant is the bisulfate anion HSO_4^- . It can be assumed that because of their significant volume, NS⁻ anions have difficulties inserting themselves along the PPv chain. In addition, the naphtalenesulfonic acid is only slightly soluble in water. In order to reach the desired dopant-topyrrole molar ratio of 0.3, a quantity of HANS higher than the solubility limit has been added to the reaction media. The remaining crystallized HANS cannot insert along the carbon backbone and hinders the polymerization reaction. Therefore, a competitive incorporation of the codopant HSO_4^- is observed to produce the electrical neutrality of the polymer. The PPy-NS⁻ synthesis leads to a low yield and a polymer with a lower doping level than for the other synthesized PPy. In order to increase the yield and to reach the desired doping level, the synthesis of PPy-NS⁻ should be performed with a higher solvent volume

so that a dissolved dopant-to-pyrrole molar ratio of 0.3 can be obtained. This will lower concentration of the reactants in the reaction media so that the amount of produced $PPy-NS^-$ is low when compared with the involved reaction volume.

In all cases, higher experimental values of C/S or C/N can be assigned to the carbon excess caused by the residual steric stabilizer. But, even when the steric stabilizer, PVA 96, remaining in the produced PPy is taken into account, the mass of the synthesized product is relatively high for all the samples except PPy–NS⁻.

Thermal Stability

The result of TGA, which allows to study the stability of the samples of the 4 kinds of PPy, are shown in Figure 5.

Figure 5 represents the curve of mass loss versus temperature showing two significant mass losses. The first occurs at low temperatures (between 30 and 100°C) and can be ascribed to the evaporation of water and residual washing solvents (acetone, ethanol), which have low boiling points. This is in good accordance with the results of the elemental analysis, in which the four PPy samples had excessive H and O contents, which testify to the presence of residual moisture in the PPy.

For the same drying period, this first mass loss (ΔY) is not equivalent for all synthesized PPy

	Composition				
Measured Properties	$PPy-HSO_4^-$	PPy-TS ⁻	$PPy-Cl^-$	PPy-NS ⁻	
Mass loss ΔY (%) Degradation temperature (°C)	$\begin{array}{c} 16.2 \\ 251 \end{array}$	$\begin{array}{c} 12.29 \\ 254 \end{array}$	9.99 172	$\begin{array}{c} 15\\ 200 \end{array}$	

Table II Thermogravimetric Analysis, Showing the Mass Loss Due to Residual Moisture Evaporation (ΔY) and the Temperature of Degradation

dried under the same conditions. The residual moisture content depends on the kind of doping anion (Table II), it is greater for PPy doped with organic species than for the PPy doped with the anion Cl^- . Amongst all the synthesized PPy, $PPy-HSO_4^-$ undergoes the highest mass loss. So, $PPy-HSO_4^-$ is suspected to have a greater affinity for water than the three other PPy samples (PPy-TS, $PPy-Cl^-$, $PPy-NS^-$), as will be discussed in the PPy humidity affinity section.

For the PPy synthesized with $(NH_4)_2S_2O_8$ as the oxidizing agent (PPy-HSO₄⁻, PPy-TS⁻, and PPy-NS⁻), the first mass loss is followed by a large zone of thermal stability. Then the main mass loss, which corresponds to the polymer degradation, occurs at elevated temperatures (Table II and Fig. 5). Unlike PPy synthesized with $(NH_4)_2S_2O_8$, PPy-Cl⁻ does not exhibit any stability zone, and its degradation begins immediately after the solvents have been evaporated.

The degradation temperature of PPy–Cl⁻ occurs at 180°C, whereas the PPy doped with aromatic anions (NS⁻ and TS⁻) and HSO₄⁻ are stable, at least up to temperatures of 210°C. This result for the PPy doped with Cl⁻ in the presence of ferric residues, such as FeCl₃ or FeCl₂, is consistent with some reported data of previous works, which show that inorganic dopants lead to less stable PPy than those doped with aromatic anions.^{24,25} Indeed, some kinetic studies^{19,30,31} have stated that the inorganic anions decompose at low temperatures and give degradation products, which are likely to react with the carbon backbone of the polymer. However, Figure 5 shows that a plateau value in the 100-200 °C range is observed for PPy doped with HSO₄⁻.

Nevertheless, the structural stability does not mean that the temperature has no influence on the polymer conductivity.

Conductivity Measurements

The conductivity of the different PPy was measured. In order to get consistent results, the same drying period and conditions were applied to all products. The data are shown in Table III.

In spite of the use of the steric stabilizer PVA, which is an electrical insulator difficult and expensive to wash out,¹⁰ the conductivity of PPy-TS⁻, PPy-HSO₄⁻, and PPy-Cl⁻ obtained by dispersion polymerization was high (between 1 and 6 S/cm). But, as was expected, PPy–NS⁻ has a low conductivity. Indeed, since it has been argued that decreasing the doping level induces a decay of the conductivity,¹⁸ this observation is in agreement with the low doping level observed in the elemental analysis. For the other PPy samples, the conductivity values reported in literature either for PPy synthesized via a dispersion polymerization in aqueous media using FeCl₃ as the oxidizing agent^{26,27} (PPy–Cl⁻) or for PPy solution polymerization using $(NH_4)_2S_2O_8$ as the oxidizing $agent^{23}$ (Py-HSO₄⁻ or PPy-TS⁻) are similar to our data. Here, a better conductivity is observed for the PPy doped with organic anions (HSO_4^-, TS^-) when compared with the PPy doped with Cl⁻.

Table III Conductivity Values Measured After a Drying Period of 23 h

	Composition					
Conductivity	$PPy-TS^-$	$PPy-HSO_4^-$	$PPy-NS^-$	$PPy-Cl^{-}$		
σ (S/cm)	5.78	3.08	$2.1.\mathrm{E}^{-4}$	1.59		

PPy–TS⁻ has the highest conductivity amongst the four polymers (6 S/cm).

TGA has already shown that the moisture content of synthesized PPy depends on the doping anion. Therefore, in the following part, the influence of the moisture content on the conductivity is investigated. Since PPy–NS⁻ synthesis requires an important solvent volume to yield a satisfactory amount of PPy, it is obvious that PPy–NS⁻ does not fulfill the requirements of an industrial application. This is the reason why this study was only performed on PPy–TS⁻, PPy–HSO₄⁻, and PPy–Cl⁻. In addition, PPy–TS⁻ will be used to investigate the influence of an aromatic dopant on the studied phenomena.

PPy Humidity Affinity

In these experiments, different PPy were dried under vacuum (0.09 MPa) at ambient temperature in the presence of desiccating salts. At different drying times, the samples of the various PPy were removed from the vacuum bell jar and submitted to TGA in order to determine the residual moisture content. Figure 6 shows the changes in the residual humidity in the PPy depending on the drying time.

The dashed lines curves of Figure 6(a-c) show that there is a hyperbolic decrease of the moisture content with increased drying time. At short drying periods, the moisture content decreases significantly and converges on an asymptotic value, which does not change even after 168 h drying. Only the moisture content of PPy-Cl⁻ does not stabilize after 168 h. Since under these conditions (ambient temperature, 0.09 MPa) PPy-HSO₄shows the highest asymptotic value, it is clear, in accordance with TGA results, that $PPy-HSO_4^-$ is the most hydrophilic of the polymers studied here. The observed slower drying of PPy-TS⁻ can be explained by the formation of agglomerates, which hinders the solvent evaporation under vacuum.

For all the previously mentioned drying periods, each PPy sample was exposed for 168 h to a controlled atmosphere (50% relative humidity and 22°C) (solid lines of Fig. 6). The moisture content was then evaluated by TGA. Figure 6(a-c) shows that after an exposure time of 168 h, the final moisture content of the various PPy reaches an equilibrium value. This value for a given type of PPy is almost constant, it does not depend on the initial moisture content of the samples. For PPy-TS⁻ and PPy-HSO⁴, the moisture



Figure 6 Moisture content of (b) PPy–TS⁻, (c) PPy– HSO4⁻, and (a) PPy–Cl⁻ versus the drying time under vacuum of 0.09 MPa (dashed line), and after 7 days of exposure to a controlled atmosphere (50% relative humidity and 22°C) (solid line).

content after a drying period of 24 h under the previously defined drying conditions is already lower than their equilibrium values (11% RH for PPy–TS⁻ and 12% RH for PPy–HSO₄⁻, respectively), so these PPy absorb the humidity within the

air of the controlled atmosphere in order to reach their equilibrium moisture content.

Unlike PPy–HSO₄⁻ and PPy–TS⁻, the moisture content of the PPy doped with the inorganic anion Cl^- decreases continuously during the exposure and reaches a lower equilibrium value (9%).

Because all PPy exhibit a nonnil equilibrium moisture content, these experiments show that doped PPy seems to have a great affinity for humidity. This is in good accordance with the results reported in previous work,³² which notices that PPy can only be dried under vacuum at elevate temperature.

This can be explained by the disordered structure of PPy,¹¹ which has a great fraction of free volume, as well as the weakness of the polymer chain interaction and the presence of heteroatoms. Indeed, they favor the penetration of small ions and molecules, such as water. These molecules are free or linked to the PPy chains by hydrogen bonds with the NH groups. In addition, as TS^- , NS^- , and HSO_4^- dopants favor water linkage due to hydrogen bonds between water and oxygen of the doping species, PPy doped with organic anions exhibit higher equilibrium moisture content than PPy doped with the inorganic dopant Cl⁻.

As a consequence, in order to determine the real amount of dried PPy which must be incorporated in an epoxy matrix its water content must be taken into account.

Influence of the PPy Moisture Content on the Conductivity

After each drying period under conditions defined in the previous section, a conductivity measurement were performed for the various PPy. Figure 7 shows each measured value of the conductivity versus the corresponding moisture content, which was determined in the previous experiments.

Figure 7 shows that for each kind of PPy, the conductivity increases with increasing moisture content. This increase is particularly significant at a low moisture content and decreases with increasing moisture content. The general shape of these curves is the same for all kinds of PPy and is similar to those reported elsewhere.³² As was already observed in the conductivity measurements, PPy doped with HSO_4^- and TS^- anions exhibit the highest conductivity, PPy–TS⁻ being the most conductive.

In the previous part, the presence of the NH groups ionized by water molecules in the PPy



Figure 7 Conductivity versus moisture content in PPy–TS⁻, PPy–HSO4⁻, and PPy–Cl⁻.

samples was pointed out. In addition, the oxidation (which leads to a conductive polymer) and the reduction (which leads to the neutral, insulating polymer) are respectively accompanied by the acceptance and the release of doping anions along the polymer chain. These anions are therefore mobile. This means that PPy consists of ionized groups and anions, which can displace. Consequently, these ions can move under the influence of an electric field. Given that, drying decreases the content of water molecules along the polymer chain, with the content of ionized molecules therefore decreasing so that the amount of charge carriers decrease; this results in the observed decay of the conductivity.

Although PPy is usually known for the electronic nature of its conductivity, this phenomena shows that a ionic conductivity is superimposed on the electronic one. Consequently, PPy is a "mixed semiconductor."

Conductivity Stability

PPy's conductivity stability was studied during 7 days. The conductivity measurements were performed on the various PPy (PPy–TS⁻, PPy–HSO₄⁻, and PPy–Cl⁻), which were submitted to the following drying period (24, 48, 72, 168 h). Each sample was then placed for 7 days under controlled temperature (22°C) and relative humidity (50% RH) and their conductivity was measured. The results are shown in Figure 8.

The solid lines of Figure 8 show that with increasing drying time (analogous to decreasing moisture content), the conductivity of the polymer decreases. These curves have a similar shape to



Figure 8 Influence of the drying period on the PPy conductivity ($PPy-TS^-$, $PPy-HSO_4^-$, and $PPy-Cl^-$) and changes in the conductivity during 7 days.

those in Figure 6, which show the evolution of moisture content versus drying time. In both figures (6 and 8), the studied properties (moisture content and conductivity) reach an equilibrium value. This is in accordance with the observation that the moisture content and conductivity are directly related.

After 7 days of exposure (dashed line) to the controlled atmosphere, the conductivity of PPy-TS⁻ increases in the same way as the moisture content in Figure 6. However, for $PPy-HSO_4^-$, the conductivity decreases after 7 days of exposure to the controlled conditions, although its moisture content increases (Fig. 6). This decrease in conductivity is caused by oxygen, which diffuses through the polymer and reacts with the carbenium ions of the chain so that the number of positive charge carriers on the polymer chain decreases. The mechanism of diffusion of oxygen air through the polymer was also reported by other authors,^{18,30,31} who stated that the diffusion coefficient increases with the relative air humidity. TS⁻ anions, on the other hand, form a more stable complex with the polymer chains so that the attack of the chain by oxygen is hindered, and, therefore, the conductivity is constant over the period of 7 days. For all the PPy, a stabilization of the conductivity is observed after 72 h.

The results obtained for PPy–Cl⁻ are less reproducible. Nevertheless, it was observed that the decrease in the moisture content corresponds to a decrease in conductivity.

CONCLUSION

We have shown that PPy doped with paratoluenesulfonate anion TS^- and synthesized in an aqueous media via dispersion polymerization meets with each one of the specifications described in the introduction. Series of tests carried out by TGA, together with conductivity measurements, show that PPy–TS⁻ exhibits the highest electrical conductivity and thermal stability compared to other synthesized PPy. In addition, conductivity measurements have shown that unlike other PPy systems, PPy-TS⁻ conductivity remains steady over more than 14 days. Moreover, the time required to perform the PPy-TS⁻ synthesis is relatively short (an hour), which could enable PPv-TS⁻ to be industrially manufactured. Owing to their colloidal nature, PPy-TS⁻ synthesized particles have the potential to be mixed as synthesized with the epoxy matrix. We have also studied the PPy–TS⁻ humidity affinity and the nature of the electrical conductivity in order to analyze the electrical conduction mechanisms in PPy. The influence of the drying conditions on PPy moisture content has been clearly assessed, and the effects of absorbed moisture on electrical conductivity have been studied. This allowed us to show that PPy has a great affinity for air humidity and that whatever the drying conditions are, water cannot be entirely removed. Furthermore, our most important conclusion is that the PPy electrical conductivity is highly dependent on the moisture content

In fact, at low moisture contents (lower than the equilibrium value), a slight increase of this content results in a great increase of the conductivity value. At contents higher than the equilibrium moisture content defined for each kind of PPy, the influence of this residual humidity on the conductivity becomes less significant. This equilibrium value is representative of the water content sufficient to ionize some ionizing groups of the polymer chain such as NH groups and to solvate the doping anions, which participate in the conduction phenomena.

A higher moisture content would not significantly improve the conductivity and would lead to a greater volume of evolved gas when PPy mixed with the epoxy resin is submitted to the curing treatment. This would lead to a greater proportion of void content in the final material. These voids damage the mechanical³³ and electrical properties of the composite and therefore must be avoid.

Thus, these findings indicate that two kinds of conductivity occur in PPy. The first, achieved by the displacement of the positive charges on the carbon backbone, is of electronic nature. The second, of ionic nature, consists of the displacement of the doping anions and ionized water molecules along the polymer chain under an electric field.

Financial support was granted for this study by the Regional Council of Midi-Pyrénées and the aircraft manufacturer Aerospatiale. The authors thank the members of the common laboratory LRAMSA for their technical cooperation.

REFERENCES

- G. E. Wnek, Handbook of Conducting Polymer, T. A. Stockheim, Ed., Dekker, New York, 1985, Chap. 6, p. 205.
- E. Ruckenstein and L. Hong, Synth. Met., 66, 249 (1194).
- 3. T. Meraoumia, Thèse de l'Université de Bordeaux I, 1994.
- M. A. J. Michels, J. C. M. Brokken–ZIJP, W. N. Groenewoud, and A. Knoester, *Physica A*, **157**, 529 (1989).
- G. Bidan, Initiation à la Chimie et Physico-Chimie Macromoléculaire, Vol. 9, Propiétés Electriques des Polymères GFP, Dijon, 1992, pp. 137–211.
- W. J. Feast, Handbook of Conducting Polymer, T. A. Stockheim, Ed., Marcel Dekker, New York, 1985, Chap. 1, p. 1.
- A. F. Diaz and J. Bargon, Handbook of Conducting Polymer, T. A. Stockheim, Ed., Marcel Dekker, New York, 1985, Chap. 3, p. 81.
- G. Tourillon, Handbook of Conducting Polymer, T. A. Stockheim, Ed., Marcel Dekker, New York, 1985, Chap. 9, p. 293.
- 9. H. Münsted, Polymer, 29, 296 (1988).
- Y. Wang and M. F. Rubner, Synth. Met., 41-43, 1103 (1991).
- G. B. Street, Handbook of Conducting Polymer, T. A. Stockheim, Ed., Marcel Dekker, New York, 1985, p. 265.
- 12. D. H. Napper and R. H. Gilbert, *Comprehensive Polymer Science*, Vol. 4, Pergamon Press, 1989, p. 171.

- 13. R. E. Myers, J. Electron. Mater., 15, 61 (1986).
- 14. S. Machida and S. Miyata, Synth. Met., 31, 311 (1989).
- 15. S. P. Armes, Synth. Met., 20, 365 (1987).
- J. C. Thieblemont, J. L. Gabelle, and M. F. Planche, J. Chim. Phys., 92, 807 (1995).
- S. Rapi, V. Bocchi, and G. P. Gardini, Synth. Met., 24, 217 (1988).
- J. Lei, Z. Cai, and C. R. Martin, Synth. Met., 46, 53 (1992).
- J. C. Thieblemont, M. F. Planche, C. Petrescu, J. M. Bouvier, and G. Bidan, *Synth. Met.*, **59**, 81 (1993).
- J. C. Thieblemont, M. F. Planche, N. Mazars, and G. Bidan, J. Appl. Polym. Sci., 52, 1867 (1994).
- M. Morita, I. Hashida, and N. Nishimura, J. Appl. Polym. Sci., 36, 1639 (1988).
- 22. K. C. Khulbe and R. S. Mann, J. Polym. Sci., Polym. Chem. Ed., 20, 1089 (1982).
- F. Haultière-Cristofini, D. Kuffer, and L. J. Yu, C. R. Acad. Sci., Paris, 1973, t. 277.
- 24. M. Salmon, A. F. Diaz, A. J. Logan, and M. Krounbi, and J. Bargon, *Mol. Cryst. Liq.*, 83, 265 (1982).
- 25. K. G. Neoh, E. T. Kang, and T. C. Tan, *Polym. Degrad. Stab.*, **21**, 93 (1988).
- S. P. Armes, M. Aldissi, and S. F. Agnew, Synth. Met., 28, C837 (1989).
- 27. S. P. Armes and B. Vincent, J. Chem. Soc., Chem. Commun., 288 (1987).
- S. P. Armes, J. F. Miller, and B. Vincent, J. Colloid Interface Sci., 2, 410 (1987).
- F. A. Bovey, I. M. Kolthoff, A. I. Medalia, and E. J. Mechan, *Emulsion Polymerisation*, Interscience, New York, 1955, p. 10.
- L. A. Samuelson and M. A. Druy, *Macromolecules*, 19, 824 (1986).
- B. K. Moss and R. P. Burford, *Polymer*, 9, 1902 (1992).
- R. Buvet, *Chimie Macromoleculaire*, Vol. 1, Hermann, Paris, 1970, p. 469.
- P. Olivier, J. P. Cottu, and B. Ferret, *Composites*, 26, 7, 509 (1995).