Polymer 51 (2010) 1716–1722

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Conducting polyaniline composite: From syntheses in waterborne systems to chemical sensor devices

Mathieu Joubert[a], Myriam Bouhadid[a,c], Didier Bégué[b], Pierre Iratçabal[a], Nathalie Redon[c], Jacques Desbrières[a], Stéphanie Reynaud[a,*]

[a] IPREM-EPCP, UMR 5254 (CNRS/UPPA), Hélioparc, 2 avenue du président Angot, 64053 Pau Cedex 9, France
[b] IPREM-ECP, UMR 5254 (CNRS/UPPA), Hélioparc, 2 avenue du président Angot, 64053 Pau Cedex 9, France
[c] Ecole des Mines de Douai, 941 rue Charles Bourseul, B.P. 10838 Douai Cedex, France

ARTICLE INFO

Article history:
Received 8 June 2009
Received in revised form
14 January 2010
Accepted 25 January 2010
Available online 2 February 2010

Keywords:
Sensor
Polyaniline
Dispersion

ABSTRACT

The development of a conducting composite from its one-step synthesis in aqueous dispersed medium to the characterization of its chemical sensor performance is detailed. Composite films of polyaniline and polyacrylate were processed from the crude dispersion with no need for post-formulation. The synthesis has been optimized to be as simple, cheap and transferable as possible. The composite composition is tunable, *i.e.* the nature of the dopant was varied and its effect on kinetic parameters was observed. *Ab initio* calculations have been performed on a series of six ionic systems to gain a deeper insight into the contribution of both the stability of the anilinium salts in the composite polymerization. The conductivities of all composites were recorded from room temperature to 150 °C and the thermal stability *versus* dopant highlighted. The conducting films were then studied as active layers in a chemical sensor. The results showed that these composites, easily synthesized and processed, are ammonia sensitive and exhibit a fast response when exposed to air pollution.

1. Introduction

Among intrinsically conducting polymers (ICPs), polyaniline (PAni) has attracted particular attention because of its ease of doping, its various chemical forms available depending on acid/base treatment and its good stability in air. All these characteristics explain why PAni is considered as a relatively easily prepared and processed ICP for a wide range of applications. Nevertheless, to overcome the lack of processability inherent to ICPs, related to their rigid π-conjugated backbone, and widen their application fields, different strategies have been used such as preparing ring-substituted polyanilines [1,2], particular dopants [3,4], polymer composites [5–7], and mixed networks [8,9]. In the latter case, the syntheses of composite particles may also be mentioned where the core is made up of an inorganic polymer [10–12] or a vinyl polymer [5,13,14] giving the system mechanical properties while the shell contains a conducting polymer. It has been demonstrated that the resulting conductivity depends on many parameters: the nature of the core composition [15,16], the surfactant [17,18] and the method of synthesis of the conducting polymer [5,19]. Even with this wide range of routes and modifications, it remains a challenge to develop a facile route to obtain processable composites that exhibit high conductivities. In addition, it is worth remembering that the ability of a material to respond to an external stimulus with a change in one of its properties can define it as an intelligent or smart material. PAni is a good candidate in the development of these types of material. Indeed, PAni is pH sensitive and may fulfil the requirements for the development of chemical sensors [20–22]. Previous works confirmed that PAni is a good choice for the detection of some chemicals. However, the processes used to prepare such devices were multi-step and involved toxic and/or corrosive solvents, and the active layers exhibited poor mechanical properties. This combination meant that the device was difficult to prepare, manipulate, and transfer to industry [23–25].

Our objectives were to develop new ammonia sensors in line with the market needs in terms of cost, ease of preparation and assembly, and performances. A low cost synthesis in a water dispersed medium is adopted so as to respect as much as possible environmental and safety requirements. Film forming properties were targeted to easily obtain the device active layer and the sensor sensitivity was measured at low concentration of ammonia in accordance with the permissible exposure limit (PEL, 50 ppm) and the immediately dangerous to life or health concentration (IDLH, 300 ppm).

In the present study, conducting composites are obtained *via* the synthesis of core-shell particles in an aqueous dispersed medium. The sensitive film is obtained by the evaporation of the continuous

---

* Corresponding author.
E-mail address: stephanie.reynaud@univ-pau.fr (S. Reynaud).

0032-3861/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2010.01.052

phase, *i.e.* water with no need of post-formulation treatment. The film forming properties were obtained by preparing strawberry-like core-shell particles with a low-T_g polymer core and a PAni shell [26]. Low-T_g polymer such as polyacrylate-based latexes is widely used in industry. Butyl acrylate was chosen based on previous studies describing the synthesis of poly(butyl acrylate) particles stabilized by non-ionic surfactants [27]. A prior article reported the synthesis of composite core-shell containing conducting HCl-doped PAni [28] and the ability of the resulting composite film to detect ammonia has been demonstrated [26]. The present work shows that the chemical nature of the PAni dopant may be varied by using the same simple process and compares the chemical formulation on both kinetics and sensor performance. PAni was obtained from various anilinium salts each differing by way of their counter-ions. The chemical nature of the counter-ions was chosen based on their ability to properly dope the PAni and specific properties as thermal stability. The kinetic of the synthesis was observed and *ab initio* calculations were performed to assess the influence of the dopant nature on the polymerization process and the resulting composite properties. The conducting properties were characterized at room and elevated temperatures to estimate the thermal properties *versus* composite formulation. Finally, three of the composites, *i.e.* containing 10 *wt%* HCl-, H_2SO_4- or H_3PO_4-doped PAni were successfully tested as sensor materials to detect ammonia.

2. Experimental

2.1. Material and reagents

Surfactants were commercially obtained, *i.e.* nonylphenol-ethoxylate (NP40, 70% in water) from Rhodia (France) and non-ionic surfactant (Surfamid, a lauramideethoxylate with six units of ethoxylate) bearing an amide group from Stepan (France). Ammonium persulfate (APS) (Aldrich; 248614, >98%), aniline (Ani) (Aldrich; 3293-4, 99%), aniline hydrochloride (AniCl) (Aldrich; 13,331-0, 97%), aniline sulfate (AniS) (Aldrich; 285153, 98%), methanesulfonic acid (MSo) (Aldrich; 47.135–6, 99+%), ethanesulfonic acid (ESo) (Aldrich; 471550, 70 *wt%* in water), phosphoric acid (P) (Aldrich; 21,510-4, 85 *wt%* in water) and ethylphosphonic acid (EPo) (Aldrich; 289876, 98%) were used as received. Butyl acrylate (BuA) monomer (Aldrich; 234923, >99%) inhibited with 10–55 ppm of monomethyl ether hydroquinone was passed through an activated aluminum oxide to remove inhibitor.

2.2. Preparation of the anilinium salts: AniMSo, AniESo, AniP, AniEPo (AniCl and AniS are commercially available)

In a typical procedure, the acid (0.060 mol) was added to 100 mL of acetonitrile and then cooled with an ice bath. Aniline (5 g, 0.054 mol) was then poured dropwise to the above mixture. The white precipitate was filtered, washed with cooled acetonitrile and dried under dynamic vacuum at room temperature till reaching a constant weight.

The chemical structures of the anilinium salts synthesized as described above are reported in Fig. 1 and were determined by ^{1}H NMR and ^{31}P NMR on a Bruker AVANCE 400 spectrometer at room temperature. The chemical shifts (δ) in ppm are referred to internal standard: tetramethylsilane. AniMSo: ^{1}H NMR (DMSO-d_6): $\delta = 7.5$ (t, 2H, benzenic CH *meta* to NH_3^+), $\delta = 7.4$ (t, 1H, benzenic CH *para* to NH_3^+), $\delta = 7.3$ (d, 2H, benzenic CH *ortho* to NH_3^+), $\delta = 2.3$ (s, 1H, CH_3). AniESo: ^{1}H NMR (DMSO-d_6): $\delta = 7.5$ (t, 2H, benzenic CH *meta* to NH_3^+), $\delta = 7.4$ (t, 1H, benzenic CH *para* to NH_3^+), $\delta = 7.3$ (d, 2H, benzenic CH *ortho* to NH_3^+), $\delta = 2.3$ (q, 2H, CH_2), 1.1 (t, 3H, CH_3). AniEPo ^{1}H NMR (DMSO-d_6): $\delta = 7.0$ (t, 2H, benzenic CH *meta* to NH_3^+), $\delta = 6.5$ (d, 2H, benzenic CH *ortho* to NH_3^+), $\delta = 6.4$ (t, 1H, benzenic CH *para* to NH_3^+), $\delta = 1.5$ (m, 2H, CH_2), $\delta = 1.0$ (m, 3H, CH_3). AniP ^{31}P NMR (DMSO-d_6): $\delta = 29.4$. Elemental analysis, AniP salt: theory: %C = 37.6, %H = 5.23, %N = 7.32, %O = 33.49, %P = 16.22; exp.: %C = 38.24, %H = 5.04, %N = 7.98, %O = 32.09, %P = 15.18.

2.3. Polymerization procedures [29]: synthesis of composite particles

The core particles were synthesized according to the procedure described by El-Aasser et al. [27]. The reaction vessel was purged with nitrogen to remove all traces of oxygen. A 500 mL three-necked round-bottom flask was charged under nitrogen atmosphere with a mixture of NP40 (2.374 g) and Surfamid (1.175 g) in 200 mL of distilled water. (NP40 ensures good emulsion stability while surfamide helps conducting properties due to the occurrence of H bonds with the PAni backbone). The purified monomer (BuA, 86 g) was added to the aqueous solution and emulsified under vigorous stirring. The emulsion was purged from oxygen by nitrogen bubbling. The reaction vessel was then heated under mechanical stirring up to 70 °C. The aqueous solution of APS (0.3 g in 5 mL of distilled water) was then added drop by drop. The polymerization was then allowed to proceed for 24 h under mechanical stirring at 70 °C. A solid content of 30 *wt%* has been calculated by gravimetric method. The diameter of the core particles has been evaluated to 320 nm by dynamic light scattering.

Anilinium salt was then added to the PBuA latex dispersion to generate core-shell particles. The concentration of anilinium ions was kept constant (0.157 mol L^{-1}) and the solid content of the PBuA latex was adjusted with respect to the targeted core-shell mass ratio expressed with equation (1). It is worth noticing that the PAni *wt%* does not take in account the weight contribution of the dopant.

$$\text{PAni \%wt} = \frac{m_{\text{Ani}}}{m_{\text{PBuA latex dispersion}} \times wt_{\text{core solution}}} \qquad (1)$$

with m_{Ani}: the mass of aniline within the reactive medium, with the respect of [Ani] = 0.157 mol L^{-1}, $m_{\text{PBuA latex dispersion}}$: the mass of the seed dispersion and $wt_{\text{core solution}}$: the solid content of the PBuA latex dispersion in weight percent.

The mixture was left 30 min under stirring prior to be purged by nitrogen and then cooled down to 0 °C. The oxidant solution (APS in water, [oxidant]/[anilinium salt] = 1)) was then added dropwise to

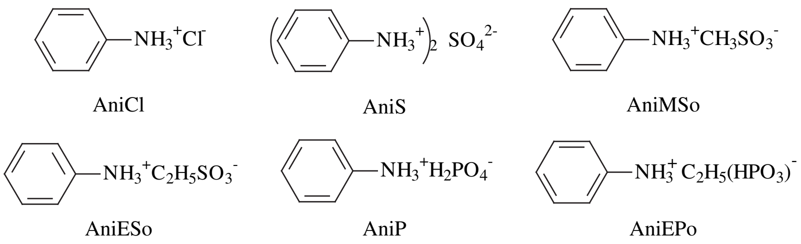


Fig. 1. Chemical structure of the anilinium salts.

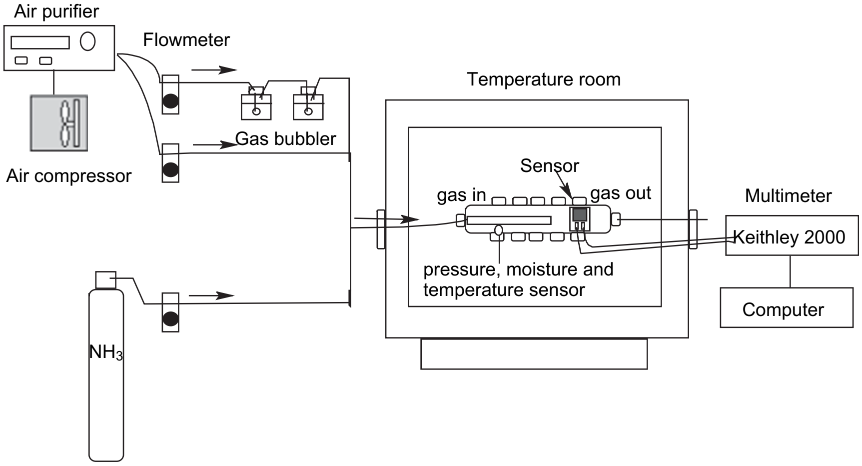


Fig. 2. Scheme of the exposure chamber system used to test the ammonia sensor.

the above dispersion. Polymerization was carried out under nitrogen and stirring; the temperature was maintained at 0 °C for 5 h. The reaction mixture was then left at room temperature overnight.

2.4. Characterization techniques

For conductivity measurements, each PAni sample was oven-dried at 60 °C under vacuum overnight. The conductivity was measured using the standard four-point probe technique.

UV spectra were recorded on a Shimadzu UV 2101 from 900 to 190 nm. The solvent was distilled water.

The particle size was measured on a DL 135-45 dynamic light scattering apparatus developed by the IFP (French Petroleum Institute) and working on very thin suspension layer in order to avoid multi-scattering phenomenon. It is equipped with a laser (wavelength 633 nm). The results were confirmed by classical dynamic light scattering (Sematech) operating on very diluted latex solutions (solvent: water, wavelength 514.5 nm) after checking the stability of latex solutions even at low concentration.

The pH of the reaction mixture was recorded during the polymerization with a pH meter 744 from Metrohm using a glass pH electrode with a calomel reference and Pt 1000 temperature sensor.

2.5. Gas sensor

For sensing properties, the polymer composite in aqueous dispersion was initially subject to sonification for 5–10 min. Then, the reactive medium was spread with a film applicator on a substrate and the water was evaporated (the sample was heated up at 40 °C for several hours). A thin conducting film was then formed (from 50 to 80 μm) and incorporated into sensor system as an active layer. Its resistance was measured. The sensor devices were exposed in a dynamic exposure chamber where the ammonia concentration, the temperature and the relative humidity were monitored (see Fig. 2).

Before any measurement, the sensor device is exposed to controlled atmospheric conditions: temperature and relative humidity (rh%). The initial resistance R_0 is determined at 25 °C and 50 rh% for 120 s. The device is then exposed to air polluted by 100 ppm of ammonia for 30 min and the sensor resistance was recorded throughout. The chemical sensor performance is evaluated by several parameters reported in Fig. 3 as R/R_0, the ratio of the sensor response to the relative resistance of the sensor active layer and $\Delta(R/R_0) = R_{\mathrm{texpo}}/R_0 - 1$ also called the response gap with t_{expo}, the time of exposure to ammonia. Finally, $S = \Delta(R/R_0)/[NH_3]$ is defined as the sensor sensitivity in ppm^{-1}.

2.6. Computational details

Calculations were carried out by using Dunning correlation consistent pVTZ ($X = T$ or Q) cartesian basis set [30]. Additional diffuse functions (aug-) were added in order to well describe the anionic character of each counterion. The method used in the present study was the density functional theory (DFT) namely

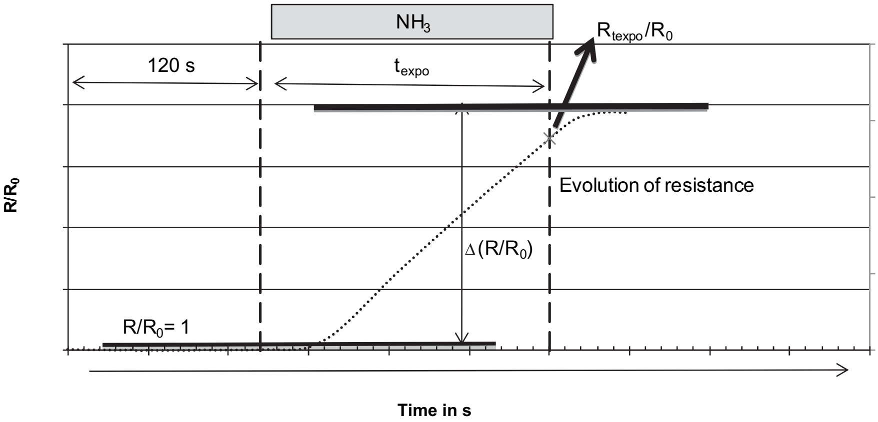


Fig. 3. Curve of evaluation for the chemical sensor performance.

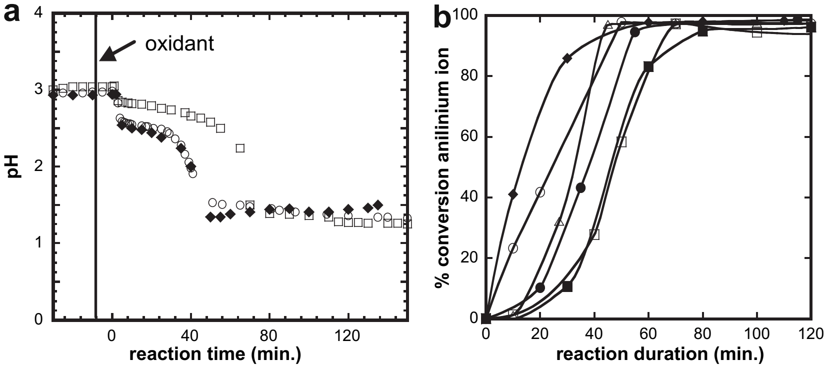


Fig. 4. a) Evolution of the pH during the polymerization of AniCl (◆), AniS (○), and AniP (□). b) Polymerization yields for PAni synthesized from AniCl (◆), AniS(○), AniMSo (●), AniESo (△), AniP (□) and AniEPo (■).

B3LYP [31] *i.e.* three-parameter exchange functional (B3) in combination with the Lee, Yang and Parr (LYP) [32] correlation functional. Optimized geometries, energies, and analytical first derivatives were obtained with the GAUSSIAN 03 package [33]. Zero-point energy, (an)harmonic frequencies [34], dipole moment, static mean polarizability, molar volume and non-bonding orbital (NBO) atomic charges were also calculated. Dissociation energies of both "tight" (TC) and "loose" (LC) clusters [35] of the anilinium salts were determined at the B3LYP/6-31G* theoretical level. The terms "tight" and "loose" ion pairs, as defined by Szwrac [35], are only valid in the case of monovalent anions. The role of the solvent was taken into account by using a cluster-(CPCM) model [36,37]. The basis set superposition error was also corrected with the use of the counterpoise method.

3. Results and discussion

3.1. Synthesis and characterization of the PAni composites

The goal was to obtain a composite exhibiting *both* good conducting and film forming properties. We also targeted a process with the aim of being as simple, low cost and safe as possible. PBuA particles prepared in the presence of a mixture of non-ionic surfactants in aqueous dispersion polymerization exhibit a diameter of 320 nm. Based on previous results obtained by our group [7,28,38], this latex was then used as seed particles to prepare composite colloids. Here, various anilinium salts (corresponding to aniline monomer doped by various dopants) were used and the kinetics of the aniline polymerization, the conductivity and the chemical performance of the final composites were studied. Finally, these composites were tested as chemical sensors to detect ammonia in atmosphere.

Poly(butyl acrylate) latex particles were first synthesized in classical emulsion process followed by the addition of the anilinium salt at the end of the acrylate polymerization. Initially, the anilinium salt is soluble in the continuous phase (water), oligo-aniline chains then become insoluble [39] and adsorbed onto the latex seed particle surface. This mechanism was confirmed by the particle size enhancement (as measured by light scattering) during the aniline polymerization. The particle size distribution is monomodal and confirms that there is no secondary nucleation of pure PAni particles. This process remains a facile route to poly(BuA-PAni) particles with architectural control using few commercially available reagents under environmental-friendly conditions.

For all the syntheses, the content of PAni was kept close to 17 *wt%* to allow sample comparisons. The UV–visible spectroscopy and pH-measurements were used to follow the progress of the aniline polymerization. Before the addition of APS, three samples were withdrawn from the reaction mixture. For UV–visible analysis, the PBuA particles were separated from the solution by centrifugation and the clear supernatant was diluted with distilled water. The intensity (I_0) obtained at 254 nm, was attributed to the initial concentration in anilinium salt. Then, samples of the mixture were withdrawn at periodic intervals. The conversion was determined with respect to equation (2).

$$\%\,\text{conversion} = \frac{I_0 - I_t}{I_0} \times 100 \tag{2}$$

Since dispersion polymerizations were carried out in water at 0 °C, the variation of temperature (exothermic process) was considered as negligible. Kinetic results for the polymerization of aniline in the presence of various dopants are presented in Fig. 4.

At the beginning of the process, regardless of the anilinium salt used, the pH was close to 3 (Fig. 4a). With respect to the pKa of aniline (4.6) and if we consider the relation for the pH of aqueous solutions of weak bases ($x_{\text{prot}} = [1 + 10^{(\text{pH}-\text{pKa})}]^{-1}$), about 97% of aniline monomer are kept as anilinium cations [40]. Protonated aniline is much more difficult to oxidize than their non-protonated homologues due to the localization of a positive charge leading to higher oxidation potential. During the polymerization process, aniline monomer looses hydrogen atoms to be incorporated in an oligomer and then in polymer chains. This results to a decrease of the pH of the polymerization reaction mixture. In this study, the oxidation starts at pH = 3. As soon as APS is added to the polymerization mixture, the pH slowly decreases to reach pH = 2.5, referred as the critical value at which the polymer chain growth starts. In each case, the monomer conversion exceeds 96% and is reached within the first hour of the reaction (Fig. 4b). Nevertheless, the time required to obtain complete conversion depends on the

Table 1
Interaction energy as obtained using B3LYP/aug-cc-pVTZ for the clusters $((\phi - NH_3^+)_n - X^{n-})$ with $X = Cl^-$, SO_4^{2-}, $CH_3SO_3^-$, $C_2H_5SO_3^-$, $H_2PO_4^-$ and $C_2H_5HPO_3^-$ respectively noted Cl, S, MSo, ESo, P and EPo.

Counter ions	Interaction energy (kJ mol^{-1})
charge$^-$	
Cl	4.74
S	11.4–11.2[a]
MSo	14.9
ESo	12.3
H bound	
EPo	110.7
P	125.3

[a] This energy corresponds to the removal of AniH$^+$ from the [AniS]$^-$ cluster.

Table 2
Conductivity at room temperature of the composites poly(BuA/doped PAni).

Dopant	*wt%* PAni[a]	σ S cm^{-1} $\times$ 10^2
Cl	17.2	10.9
S	17.4	6.5
Mso	17.3	7.2
Eso	17.3	6.0
P	17.3	4.2
Epo	19.1	4.1

[a] PAni mass loading into the composite Poly(BuA/PAni), the dopant weight is not taken into account.

nature of the anilinium salt. The polymerization rates are classified as follows: AniCl > AniS > AniMSo ≈ AniESo>AniP ≈ AniEPo and these results are in accordance with previous data [41] reported in the literature. This feature may be partially explained by the pH effect of the by-product released during the oxidative polymerization. Nevertheless, many other factors could be involved at the same time (H-bond, ionic strength, hindrance effects…).

Previous studies [41,42] suggested that the difference observed in the induction time and the rate of oxidative polymerization of aniline may be related to the stability of the ion pairs [41] *i.e.* dopant/anilinium which are related to hydrophobic effects. The more lipophilic the dopant is, more stable the ion pairs are. However, during the course of the polymerization, the dissociation of the ion pair precedes the formation of the radical anilinium or nitrenium cation. Thus kinetics of polymerizations that involves hydrophobic acids is expected to be the slowest ones. The pH curves (Fig. 4a) tend to confirm this purpose: the first drop of the pH is less important for AniP than for the other anilinium salts and the second is decelerated in the presence of the phosphate counter ion. The profile of the pH curves tends to underline that the induction and the propagation step in which the counter ion is expelled from the anilinium cation are slowed down for the phosphate counter ion.

Other authors [43] have studied the kinetics of the polymerization of aniline in the presence of various dopants of the same family, for example dicarboxylic acids. They showed that sterical hindrance due to the size of the dopant could affect both rates and attainable conversions. In the present work *ab initio* calculations have been performed on a series of six ionic clusters. For the sake of clarity, anilinium salts are named $((\phi - \mathrm{NH}_3^+)_n - X^{n-})$ with $X = \mathrm{Cl}^-$, SO_4^{2-}, $\mathrm{CH_3SO_3^-}$, $\mathrm{C_2H_5SO_3^-}$ $\mathrm{H_2PO_4^-}$ and $\mathrm{C_2H_5}$ $\mathrm{HPO_3^-}$ which are here respectively denoted Cl, S, MSo, ESo, P, EPo. Our aim was to gain a deeper insight into the contribution of the interaction energy of the cluster in the polymerization (see Table 1).

As suggested by the mechanism proposed elsewhere [44–50], the formation of the active species in the early stages of the oxidative polymerization of aniline, *i.e.* the cation-radical $\varphi\text{–NH}_2^{\bullet+}$, has as a prerequisite the dissociation of the cluster of the anilinium salt. Such clusters in solution may be viewed as “tight” (TC) and “loose” (LC) according to the interionic distances and the position of the corresponding minima on the potential energy surface (PES). The interaction energies, defined by the difference between the energy of the cluster $((\phi - \mathrm{NH}_3^+)_n - X^{n-})$ and the sum of the energies of $(\phi - \mathrm{NH}_3^+)_n$ and X^{n-} were calculated for each type of cluster.

Two categories of clusters are highlighted, *i.e.*, on one hand, the pure ionic clusters (AniCl, AniS, AniMSo and AniESo) and, on the other hand, ionic and H bounded clusters (AniP and AniEPo) (Table 1). The high interaction energies of AniP and AniEPo are related to the additional hydrogen bond type interactions involved in these clusters and are responsible for their greater stability.

The AniS cluster deserves a particular comment in that it is the only cluster consisting of three ionic components (all others are made of two parts). To start polymerization only one anilinium ion has to be removed from this cluster so the corresponding dissociation energy to be considered is that amounting to 11.4 kJ mol^{-1} [51].

On the whole, Table 1 shows a correlation between the interaction energy of the clusters and the polymerization kinetics. The calculated data are in agreement with the experimental results: the stronger the interaction energy is (AniCl < AniS < AniMSo ≈ AniESo<<AniP ≈ AniEPo), the slower the kinetics of the reaction (AniCl > AniS > AniMSo ≈ AniESo>AniP ≈ AniEPo).

The nature of the dopant is one of the parameters which could modify the conductivity properties [52–54]. Several parameters have been pointed out in the literature: the dopant size [52], the oxidation state, the inter- and/or intrachain interactions, involving the nature of the anilinium ion/counter ion pair [53,54].

The conductivity of the composite has been measured by a four probe method. All the composites containing 17 *wt%* PAni exhibit close conductivity values ranging from 4 × 10^{-2} to 1 × 10^{-1} S cm^{-1} as reported in Table 2.

Within this range, AniCl leads to a polymer exhibiting a higher conductivity than AniS, AniMSo and AESo which are above AniP and AniEPo.

The conductivity measurements of the PAni doped with inorganic dopants are in accordance with previous results [53–56].

Many applications involve thermal processing, therefore both composite formulations, *i.e.* doped PAni content and the dopant nature have been investigated on the conductivity performance at elevated temperature. The annealing curves for various composites exposed at 100 °C and 150 °C are reported in Fig. 5. The conductivity remains constant at 100 °C, whatever the nature of the dopant, whereas the conductivity drops at 150 °C within 40 h before stabilising.

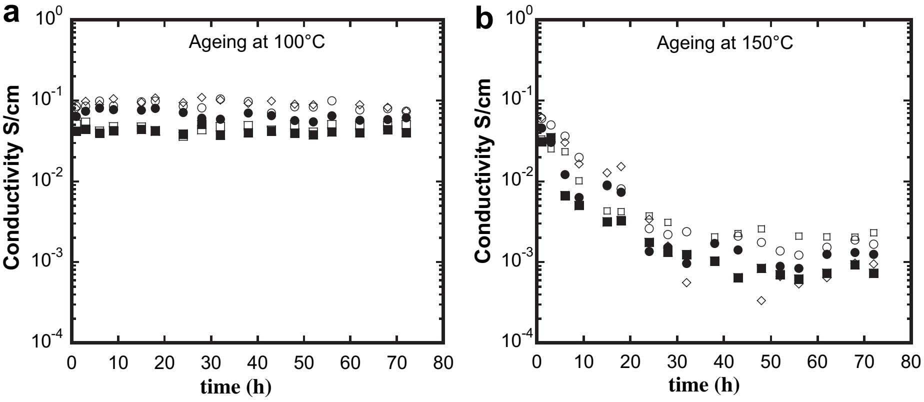


Fig. 5. Conductivity *versus* time plot of PAni-Cl (◇),PAni-S (○), PAni-ESo (●), PAni-P (□), PAni-EPo (■) at: (a) 100 °C and (b) 150 °C.

This behavior is usually attributed to the loss of water and to an evolution of the dopant resulting in partially reversible dedoping. Given that the dehydration may be considered to be the same for all the samples, it is possible to consider the influence of the nature of the dopant. PAni-Cl exhibits a decrease of 2 orders of magnitude in conductivity while the conductivity of PAni-P and PAni-EPo drops by only one order of magnitude. This feature could be explained by the thermal stability of these kind of dopants and also by the fact that these multivalent anions can act as cross-linking centers and protonate the imine units of different chains [57–59].

Several PAni composites were obtained *via* a facile route; the formulation (PAni content and dopant nature) is tunable and the composites exhibit a conductivity ranging from 4×10^{-2} to 1×10^{-1} S cm^{-1}. An effect of the dopant nature was observed on the kinetics and the thermal stability of the final composite properties. All these materials are suitable for the development of chemical sensors. Three representative samples were tested and compared, namely the PAni composites doped with HCl, H_2SO_4, or H_3PO_4.

3.2. Influence of the dopants on response of ammonia sensor

We previously showed that film composite containing an ICP such as PAni may be successfully employed in chemical sensor devices [26,60,61]. The active layer made of conducting composite was revealed to be sensitive (a pollution as low as 10 ppm ammonia was detected) and exhibited a short response time (a few minutes). Moreover tests showed that the sensor may be used several times in a row with high sensitivity and no need of servicing between exposures. Previous articles reported the results of composites made of poly(butyl acrylate) HCl-doped PAni and comparisons have been made between sensors containing 10, 15 and 20 *wt%* of HCl-doped PAni [26]. The influence of humidity on ammonia gas sensitivity has been studied on sensor containing 10 *wt%* of HCl-doped PAni [61]. In the present study, the effect of the nature of the dopant is studied *versus* the ammonia sensor response, all the other parameters remaining the same. These new conducting composites already showed improved properties as thermal stability and it is interesting to now evaluate their performance as sensor active layer.

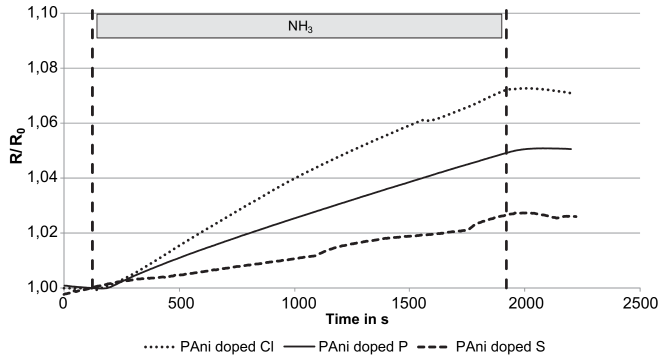


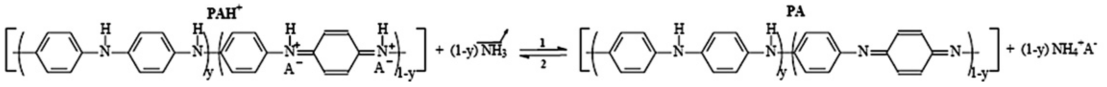
Fig. 6. Sensor behaviour when exposed in 100 ppm ammonia for 30 min in 50 rh% at 25 °C.

Table 3
Performances of chemical sensors, with $t_{expo} = 30$ min; R_{texpo} the resistance after 30 min of exposure, R_0 the resistance before exposure under ammonia pollution and S the sensitivity with $S = (R_{texpo}/R_0 - 1)/[NH_3]$.

Dopant	R_{texpo}/R_0	S (ppm^{-1})
Cl	1.0723	7.2×10^{-4}
P	1.0492	4.9×10^{-4}
S	1.0269	2.7×10^{-4}

Composites have been obtained from core-shell particles and named as follows: poly(Core-Shell). Three composites have been tested: Poly(BuA-PAni) using HCl, H_2SO_4 and H_3PO_4 as dopant to elaborate the active layer of an ammonia sensor. The devices have been exposed for 30 min–100 ppm of ammonia and sensor responses were monitored as showed in Fig. 6.

The principle of the ammonia sensor containing PAni as sensing material is described in the following equation (3).



(3)

When the sensor is exposed, ammonia takes up protons from PAni, to form energetically more favorable ammonium ions, NH_4^+. This is the PAni dedoping reaction leading to an increasing of the resistance of the composite. As soon as the composite is in atmosphere free of ammonia, the reaction is shifted towards the left.

The analysis shows the influence of the dopant nature in this process. For a better comparison, all the parameters have been reported within the Table 3.

The sensor performances have been evaluated at 25 °C and 50 rh%. This experimental method corresponds to the standard conditions for the development of a sensor for chemical detection in a working environment. Based on the results (Fig. 6 and Table 3), it is worth noticing several characteristics. First, the sensors have been exposed for 30 min, nevertheless the resistance value of the active layer increases continuously over this period without reaching saturation point. This result implies that higher ammonia concentration (in the case of gas leak for example) should be detected. Secondly, all the sensors are sensitive and exhibit a short response time (a few minutes). Third, the resistance value decreases again as soon as the sensor is exposed under "fresh air" free of ammonia pollution. This feature has been previously obtained [26] and is in accordance with the reversibility of the chemical reactions involved here.

It is interesting to consider that the chemical formulation of the active layer may be chosen from HCl-, H_2SO_4- or H_3PO_4-doped PAni. Moreover, H_3PO_4-doped PAni was revealed as the most thermally stable and may be then preferred for ammonia detection in relatively hot locations.

4. Conclusion

Various conducting composites have been obtained in a one step synthesis in water dispersed medium. An influence of the nature of the dopant has been observed on kinetics. *Ab initio* calculations showed that the stability of the anilinium salts (or in other words, the interaction energy of the ionic cluster) is a key parameter to explain the dependence of the polymerization kinetics on the type of the anilinium salt. The conducting properties of all the composites have been recorded from room temperature to 150 °C. The results showed that the composites are perfectly thermally stable up to 100 °C and the conductivity remains acceptable up to 150 °C. Three of these composites, namely poly(butyl acrylate)-PAni doped with HCl, H_2SO_4 and H_3PO_4 have been respectively tested in sensor devices. The film used as active layer was easily obtained after dehydration of the crude aqueous dispersion of the composite. The sensor performances have been recorded in a climatic chamber by taking into account parameters such as ammonia concentration, temperature and moisture. The results show that all the composites poly(BuA/doped PAni) are suitable to detect ammonia pollution whatever the PAni dopant is. Moreover, the performance devices may be classified from their chemical composition as follows: containing PAni doped by HCl $>$ doped by H_3PO_4 $>$ doped by H_2SO_4.

Further experiments are in progress: the behavior of these devices when exposed to lower ammonia concentration as well as the interfering agents (such as CO, CO_2, NO_2…) is currently under investigation.

Acknowledgments

The authors thank Oseo-Anvar for financial support. They also thank Mr. Abdel Khoukh from IPREM-EPCP for NMR experiments. Special thanks are also due to Dr. J.-L. Wojkiewicz, Dr. H. Plaisance from Ecole des Mines de Douai and Dr Alain Castetbon from IPREM-LCABIE, for helpful discussions. Authors gratefully acknowledge one of the referees for his/her particularly constructive remarks and Dr R. C. Hiorns for editing the manuscript prior to submission.

References

[1] Falcou A, Duchene A, Hourquebie P, Marsacq D, Balland-Longeau A. Synthetic Metals 2005;149:115–22.
[2] Pandey SS, Annapoorni S, Malhotra BD. Macromolecules 1993;26:3190–3.
[3] Nicolau YF, Ermolieff A. Synthetic Metals 1995;71:2073–4.
[4] Xia Y, Wiesinger JM, MacDiarmid AG, Epstein AJ. Chemistry of Materials 1995;7:443–5.
[5] Barthet C, Armes SP, Lascelles SF, Luk SY, Stanley HME. Langmuir 1998;14:2032–41.
[6] Kim BJ, Oh SG, Han MG, Im SS. Polymer 2002;43:111–6.
[7] Kohut-Svelko N, Reynaud S, Martinez H, Dedryvère R, Gonbeau D, François J. Langmuir 2005;21:1575–83.
[8] Rodrigues PC, Akcelrud L. Polymer 2003;44:6891–9.
[9] Rodrigues PC, Lisboa-Filho PN, Mangrich AS, Akcelrud L. Polymer 2005;46:2285–96.
[10] Gill M, Armes SP, Fairhurst D, Emmett SN, Idzorek G, Pigott T. Langmuir 1992;8:2178–82.
[11] Han MG, Armes SP. Journal of Colloid and Interface Science 2003;262:418–27.
[12] Han MG, Armes SP. Langmuir 2003;19:4523–6.
[13] Cairns DB, Armes SP, Bremer LGB. Langmuir 1999;15:8052–8.
[14] Khan MA, Armes SP. Langmuir 1999;15:3469–75.
[15] Perruchot C, Chehimi MM, Delamar M, Lascelles SF, Armes SP. Langmuir 1996;12:3245–51.
[16] Maeda S, Gill M, Armes SP, Fletcher IW. Polymer International 1995;11:1899–904.
[17] Khan MA, Armes SP, Perruchot C, Ouamara H, Chehimi MM, Greaves SJ, et al. Langmuir 2000;16:4171–9.
[18] Cairns DB, Armes SP, Chehimi MM, Perruchot C, Delamar M. Langmuir 1999;15:8059–66.
[19] Barthet C, Armes SP, Chehimi MM, Bilem C, Omastova M. Langmuir 1998;14:5032–8.
[20] Bai H, Shi G. Sensors 2007;7:267–307.
[21] Kukla AL, Shirshov YM, Piletsky SA. Sensors and Actuators, B: Chemical 1996;37:135–40.
[22] Nicolas-Debarnot D, Poncin-Epaillard F. Analytica Chimica Acta 2003;475:1–15.
[23] Prasad GK, Radhakrishnan TP, Kumar DS, Krishna MG. Sensors and Actuators, B: Chemical 2005;106:626–31.
[24] Tai H, Jiang Y, Xie G, Yu J, Chen X, Ying Z. Sensors and Actuators, B: Chemical 2008;129:319–26.
[25] Matsuguchi M, Io J, Sugiyama G, Sakai Y. Synthetic Metals 2002;128:15–9.
[26] Bouhadid M, Thévenot C, Ehrenfeld F, Redon N, Desbrières J, Grassl B, et al. Sensor Letters 2008;6:548–57.
[27] Özdeger E, Sudol ED, El-Aasser MS, Klein A. Journal of Polymer Science Part A Polymer Chemistry 1997;35:3813–25.
[28] Kohut-Svelko N, Dinant F, Magana S, Clisson G, François J, Dagron-Lartigau C, et al. Polymer International 2006;55:1184–90.
[29] Kohut-Svelko N, Joubert M, Reynaud S. Synthèse one-step de films conducteurs; 2005; 08172 [PCT: FR 05].
[30] Dunning Jr TH. The Journal of Chemical Physics 1989;90:1007–23.
[31] Becke AD. The Journal of Chemical Physics 1993;98:5648–52.
[32] Lee C, Yang W, Parr RG. Physical Review B 1988;37:785–9.
[33] Frisch MJ. In: CT W, editor. Gaussian 03. Gaussian, Inc; 2004.
[34] Gohaud N, Begue D, Darrigan C, Pouchan C. Journal of Computational Chemistry 2005;26:743–54.
[35] Szwarc M. Ions and ion pairs in organic reactions. NY: Wiley Interscience; 1972.
[36] Pliego Jr JR, Riveros JM. Journal of Physical Chemistry A 2001;105:7241–7.
[37] Smiechowski M. Journal of Molecular Structure 2009;924–926:170–4.
[38] Kohut-Svelko N, Reynaud S, François J. Synthetic Metals 2005;150:107–14.
[39] Stejskal J, Sapurina I. Journal of Colloid and Interface Science 2004;274:489–95.
[40] Sapurina I, Stejskal J. Polymer International 2008;57:1295–325.
[41] Plesu N, Ilia G, Pascariu A, Vlase G. Synthetic Metals 2006;156:230–8.
[42] Choi SJ, Park Moon S. Journal of Electrochemistry Society 2002;E26:149.
[43] Erdem E, Karakisla M, Sacak M. European Polymer Journal 2004;40:785–91.
[44] Wei Y, Tang X, Sun Y, Focke WW. Journal of Polymer Science 1989;27:2385–96.
[45] Wei Y, Hsueh KF, Jang G-W. Polymer 1994;35:3572–5.
[46] Wei Y, Hariharan R, Patel SA. Macromolecules 1990;23:758–64.
[47] Mattoso LHC, MacDiarmid AG, Epstein AJ. Synthetic Metals 1994;68:1.
[48] Rannou P. Synthèse, mise en oeuvre et vieillissement. Grenoble: University of Grenoble, France; 1998.
[49] Gospodinova N, Terlemezyan L, Mokreva P, Kossev K. Polymer 1993;34:2434–7.
[50] Gospodinova N, Mokreva P, Terlemezyan L. Polymer 1993;34:2438–9.
[51] A second minimum with a very weak interaction energy has also been located on the PES of AniS. It can be associated to a LC and is not expected to interfere energetically with the more stable TC (around this minimum the PES has been approximated to a grid of 10 single points).
[52] Kahol PK, Satheesh Kumar KK, Geetha S, Trivedi DC. Synthetic Metals 2003;139:191–200.
[53] Hatchett DW, Josowicz M, Janata J. Journal of Physical Chemistry B 1999;103:10992–8.
[54] Abdiryim T, Xiao-Gang Z, Jamal R. Materials Chemistry and Physics 2005;90:367–72.
[55] Zhang Z, Wei Z, Wan M. Macromolecules 2002;35:5937–42.
[56] Seong H, Jea H, Kyung W. Journal of Applied Polymer Science 2002;83:2245–54.
[57] Chan HSO, Ng SC, Ho PKH. Macromolecules 1994;27:2159–64.
[58] Motheo AJ, Venancio EC, Mattoso LHC. Electrochimica Acta 1998;43:755–62.
[59] Prokes J, Stejskal J. Polymer Degradation and Stability 2004;86:187–95.
[60] Stejskal J, Trchova M, Blinova NV, Konyushenko EN, Reynaud S, Prokes J. Polymer 2008;49:180–5.
[61] Bouhadid M, Redon N, Plaisance H, Desbrières J, Reynaud S. Macromolecular Symposia 2008;268:9–13.