

Monitoring the polymerization process of polypyrrole films by thermogravimetric and X-ray analysis

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Abstract The thermal behavior of different synthesized polypyrrole (Ppy) composites was studied in order to obtain quantitative information about the synthesis process and qualitative information about thermal stability of composites. An inorganic anion has been used as dopant ($\text{PW}_{12}\text{O}_{40}^{3-}$), and this has allowed obtaining a complete analysis of Ppy degradation process, since this anion does not degrade in the range of temperature used. In order to validate the quantitative information obtained by thermogravimetric analysis (TG), the work was completed with X-ray photoelectron spectroscopy (XPS) study, since the use of the N+/N or W/N ratios are useful to measure the doping level reached by the synthesis process. Also pyrolysis/gas chromatography/mass spectrometry (py-GC-MS) and differential scanning calorimetry (DSC) were used to obtain information of the products generated as a consequence of the degradation process. FTIR-ATR has been used to characterize Ppy powders.

Keywords Polypyrrole · Thermal stability · XPS · Pyrolysis · GC-MS

Introduction

Among the wide variety of electroconductive polymers, polypyrrole (Ppy) and its derivatives show a relevant interest due to their good electrical properties. It is feasible to obtain films and powders by means of several synthesis routes, thus obtaining invariably a black material which solubility is limited depending on the dopant and solvent employed. In the synthesis process, a cross-linking occurs so that the synthesized material becomes a thermoset and this fact makes processing difficult. The introduction of bulky anions reduces molecular interactions between polymer chains, and facilitates Ppy solubility [1].

In addition to this, one of the main problems that present the use of conductive polymers in technical applications is their thermal stability which is related to their thermal conductivity. It has been reported the influence of the thermal degradation of Ppy on its electrical conductivity [2–4]; the thermal treatments conducted in inert or air atmosphere can produce a decrease in its conductivity. So the improvement of thermal stability will have a positive effect on the long-term stability of conductivity.

Thermal methods of analysis, mainly thermogravimetry (TG), are probably the most widely used to investigate thermal degradation and polymer composition. The information available consists of the number of stages of degradation and a quantitative measurement of the mass loss for each stage. The major weakness of TG as a tool for studying polymer degradation is that it provides no information about the degradation products, thus making necessary the use of alternatives—complementary techniques. In the case of Ppy, little published studies can be found. Some studies have focused on the use of this technique for Ppy characterization [5–7]. These studies indicate that the thermal decomposition of Ppy occurs in several steps,

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but their definition highly depends on the test conditions and the nature of the dopant. During the synthesis of Ppy, some positive charges are generated in the structure; these positive charges must be compensated by a counter ion (also named dopant) to maintain the principle of electro-neutrality. These negative charges are supplied by an anion. Organic dopants have been traditionally used, as reported in bibliography, but they present some disadvantages because their degradation can interfere with Ppy signal [8], thus difficult the interpretation of results. In this study it has been used a dopant with inorganic nature ($\text{PW}_{12}\text{O}_{40}^{3-}$) that does not decompose in the range of Ppy degradation, and this allows the analysis of Ppy without interferences of the dopant degradation.

In order to validate the quantitative information obtained by thermogravimetry (TG) additional study with X-ray photoelectron spectroscopy (XPS) has been carried out, since the N+/N or W/N ratios are directly related to the doping level reached in the synthesis process. Also pyrolysis–gas chromatography–mass spectrometry (py–GC–MS) techniques and differential scanning calorimetry (DSC) have been used to obtain information about the species generated in the degradation process. FTIR has been used to characterize the material obtained in the chemical synthesis.

Experimental

Reagents

Analytical grade pyrrole, ferric chloride, anthraquinone sulfonic acid (AQSA) sodium salt were purchased from Merck. Analytical grade phosphotungstic acid hydrate was supplied by Fluka. Ultrapure water was obtained from an Elix 3 Millipore-Milli-Q RG system with a resistivity near to 18.2 M Ω cm.

Chemical synthesis of Ppy/ $\text{PW}_{12}\text{O}_{40}^{3-}$ and Ppy/AQSA

Pyrrole concentrations employed in chemical polymerizations were 0.5 or 2 g l⁻¹. The molar relations used in the chemical synthesis bath were pyrrole:FeCl₃:AQSA (1:2.5:0.6); when $\text{PW}_{12}\text{O}_{40}^{3-}$ was employed as counter ion the relation was 1:2.5:0.2. The molar relation of counter ion is three times lower when $\text{PW}_{12}\text{O}_{40}^{3-}$ is employed than

when AQSA is used, due to the fact that $\text{PW}_{12}\text{O}_{40}^{3-}$ has three negative charges; on the other hand AQSA only posses one negative charge. Pyrrole and counter ion are mixed in a solution. When FeCl₃ is added the oxidation of pyrrole to Ppy occurs and AQSA or $\text{PW}_{12}\text{O}_{40}^{3-}$ are incorporated in the Ppy structure as counter ions. Reaction elapsed during 150 min without stirring in a precipitates beaker. In the synthesis two parameters were varied; reaction temperature and pyrrole concentration. In some experiments there was an ice bath to lower the reaction temperature and the other experiments were done at 293–296 K. Two different concentrations of pyrrole were employed (0.5 and 2 g l⁻¹). Experimental conditions for the different samples can be observed in the Table 1. After the reaction, Ppy powders were filtered and dried in a desiccator during at least 24 h before measurements. Polymerization yield has been calculated, taking into account the average doping level obtained by the different techniques (0.2). Table 1 shows experimental conditions for the synthesis of different samples of Ppy.

Thermal degradation characterization

Thermogravimetric measurements were performed using a Mettler-Toledo TGA-SDTA 851e instrument, which allows heating rates from 274 to 473 K min⁻¹ up to a temperature of 1473 K. Dynamic tests were run from 303 to 1173 K at 293 K min⁻¹ heating rate. TG tests were performed in alumina crucibles where samples were placed without any previous treatment and experiments were run immediately. TG tests were carried out in nitrogen and air environment using a flow rate 200 mL min⁻¹.

The calorimetric analysis was carried out using a DSC Mettler-Toledo 821 (Mettler-Toledo Inc, Schwerzenbach, Switzerland). Samples of mass between 8 and 9 mg were used.

All samples were pyrolyzed with the use of a pyrolyzator (Pyroprobe® 1000 by CDS Analytical, Inc), interconnected with a GC/MS (6890N Agilent Technologies) equipped with a 5973N mass selective detector (MSD) (Agilent Technologies España S.L., Madrid, Spain). A 30 m long capillary column (HP-5 ms) 0.25 mm thickness, with a 0.25 μm stationary phase, which was programmed from 313 to 573 K at 283 K min⁻¹ and was subsequently maintained at the highest temperature for 5 min. The gas used was

Table 1 Experimental conditions for the synthesis of different samples of polypyrrole

Experiment	Dopant	Temperature/K	Pyrrole/g l ⁻¹	Polymerization yield/%
P1	AQSA	273	2	–
P2	$\text{PW}_{12}\text{O}_{40}^{3-}$	273	2	90
P3	$\text{PW}_{12}\text{O}_{40}^{3-}$	273	0.5	64
P4	$\text{PW}_{12}\text{O}_{40}^{3-}$	293–296	2	82

Helium with a 50:1 split ratio. The MSD was programmed to detect masses between 50 and 650 amu. Samples (around 1.2–1.1 mg) were pyrolyzed at 723 K for 10 s.

Spectroscopic characterization

Fourier transform infrared spectroscopy with horizontal multirebound attenuated total reflection (FTIR-ATR) was performed with a Nicolet Magna 550 Spectrometer equipped with DTGS detector. An accessory with pressure control was employed to equalize pressure in the different solid samples. A prism of ZnSe was employed. Spectra were collected with a resolution of 4 cm^{-1} , and 100 scans were averaged for each sample.

X-ray photoelectron spectroscopy analyses were conducted at a base pressure of 5×10^{-10} mbars and a temperature at around 173 K. The XPS spectra were obtained with a VG-Microtech Multilab electron spectrometer by using unmonochromatized Mg K_{α} (1253.6 eV) radiation from a twin anode source operated at 300 W (20 mA, 15 kV). The binding energy (BE) scale was calibrated with reference to the C_{1s} line at 284.6 eV.

Results and discussion

FTIR-ATR analysis

Figure 1 shows the spectra of Ppy/AQSA and Ppy/ $PW_{12}O_{40}^{3-}$ powders. It can be observed that different bands attributed to Ppy in both spectrums. One band centered at 1550 cm^{-1} associated to the pyrrole ring stretching vibration ($C=C$), $C-C$ stretching (1450 cm^{-1}) [6, 7], and $C-N$ stretching (1300 cm^{-1}) [9, 10]. The characteristic bands of the bending vibration of pyrrole can be observed

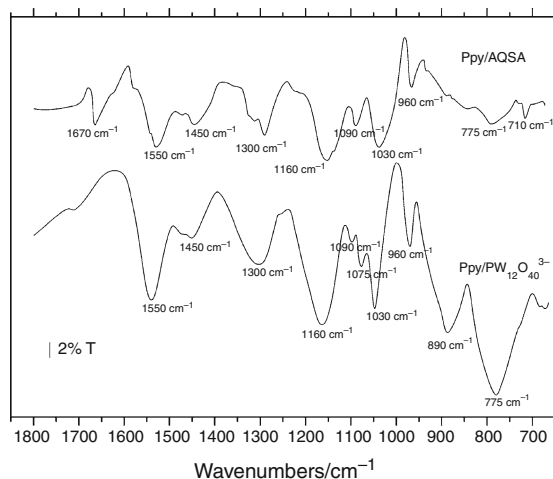


Fig. 1 Spectra of Ppy/AQSA and Ppy/ $PW_{12}O_{40}^{3-}$ powders

at 1160, 1030, and 775 cm^{-1} [11, 12]. Additionally, other bands can be observed, like $C-H$ in plane vibration (1090 cm^{-1}), $C-H$ bending vibrations (960 cm^{-1}) [13], and $=C-H$ out of phase vibration (890 cm^{-1}); the last band is not clearly observed in Ppy/AQSA spectrum.

Additionally to these bands it can be observed that the bands attributed to the counter ion. The band in the spectrum of Ppy/ $PW_{12}O_{40}^{3-}$ at 1075 cm^{-1} ($P-O$ stretching) [14, 15] indicates the presence of the $PW_{12}O_{40}^{3-}$. The other bands of $PW_{12}O_{40}^{3-}$ are overlapped with those of Ppy. In the spectrum of Ppy/AQSA two bands centered at 1670 and 710 cm^{-1} were observed, attributed to the AQSA structure (Fig. 1).

Quantitative analysis

TG analysis

We have combined thermogravimetric (TG) and differential thermal analysis (DTG) to determine the thermal stability of the polymer. For a correct analysis, it is necessary to consider the influence of dopant used in the synthesis process. Its nature can interfere with the interpretation of the results; if the dopant is organic, generally the mass loss will overlap the mass loss of Ppy, making difficult the analysis of results due to the two overlapped processes. The insertion of inorganic dopants in the structure of Ppy allows a more complete analysis by determining the mass loss ranges and degradation kinetic parameters [16]. In order to avoid this problem we have worked with an inorganic dopant ($PW_{12}O_{40}^{3-}$), since this compound shows higher thermal stability; this fact allows obtaining both qualitative and quantitative information about the degradation process. In oxidizing atmosphere as well as in inert atmosphere, the $PW_{12}O_{40}^{3-}$ shows a great range of thermal stability up to 1173 K; we can only observe a mass loss at about 473 K which represents a 3 wt% loss; this is probably due to the loss of hydration water of polyoxometalate (Fig. 2a). This behavior cannot be expected when using an organic dopant, as it is observed in the Fig. 2b AQSA degrades in the same temperature range that most polymers (Table 2).

This wide range of thermal stability allows a quantitative determination of Ppy and to obtain the main decomposition kinetic parameters of samples in different atmospheres. Independently of the atmosphere employed, the degradation passes in two steps. The first step begins at the 473–573 K range (Fig. 3), and it represents a small proportion of the total polymer mass loss when using an inert atmosphere. In this type of atmosphere the principal mass loss starts at about 773 K. In an oxidizing atmosphere the situation is inverted, so that the first jump acquires major relevance, though it begins at similar temperatures. Quantitatively, the sum of mass loss for both jumps is

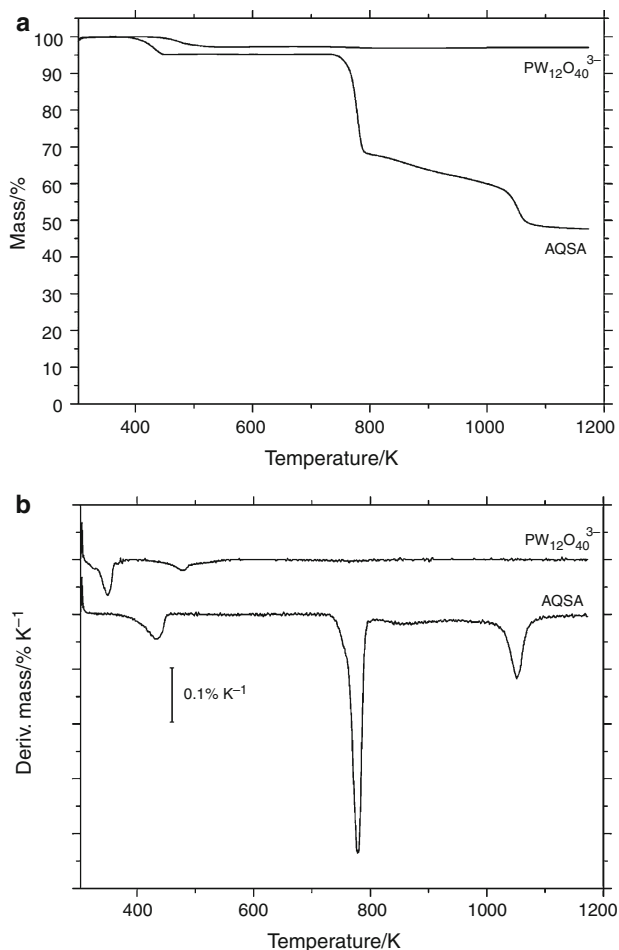


Fig. 2 Thermogravimetric analysis of $PW_{12}O_{40}^{3-}$ and AQSA. Relative mass loss derivate (N_2 atmosphere)

identical in both atmospheres and the differences between different samples are very small; in addition to this, changes in the synthesis conditions do not seem to alter the content of Ppy in a significant way.

In general, we can observe that the beginning of the decomposition is in good agreement with other studies described previously [17], but in this case due to the inorganic nature of the dopant we do not have interferences

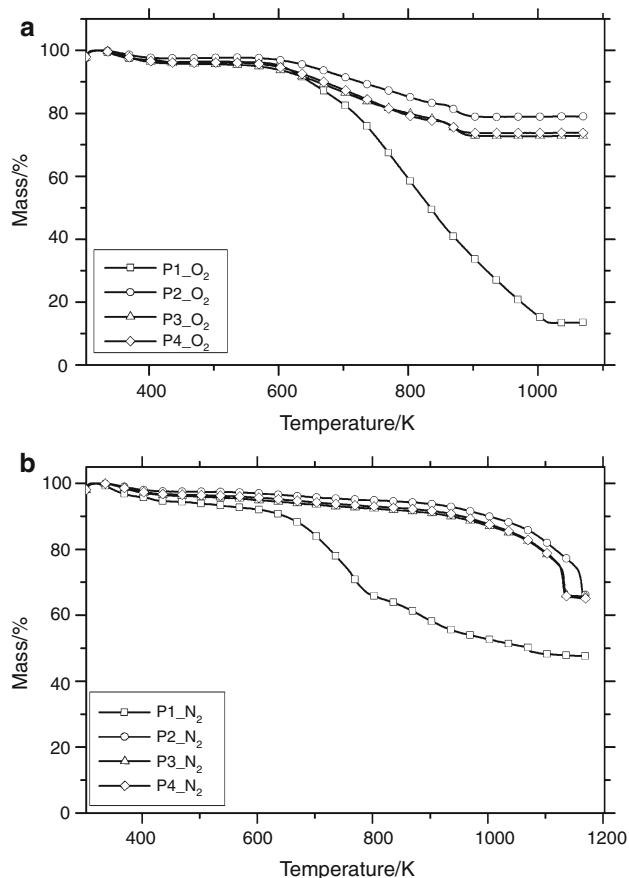


Fig. 3 Comparative curves of polypyrrole doped with $PW_{12}O_{40}^{3-}$ in air and N_2 atmosphere

and we can ensure that the observed mass loss is due to polymeric film, and not the dopant.

From the mass percentage of Ppy obtained experimentally by TG and using the molecular mass of the pyrrole (65.09) (considering that in the polymerization process 2 H^+ are removed) and $PW_{12}O_{40}^{3-}$ (2877.17), it is possible to calculate the number of positive charges per pyrrole molecule (doping level). The average value of the doping level obtained by means of TG is close to 0.22. The result does not depend on the atmosphere employed (air or N_2 atmosphere).

Table 2 Values of weight loss and doping level for the different samples

Sample	N_2 atmosphere				Air atmosphere			
	Mass loss/%				Mass loss/%			
	573–773 K	773–1173 K	Total	Doping level	573–773 K	773–1173 K	Total	Doping level
P2	2.8	29.3	32.1	0.218	15.2	14.2	29.4	0.238
P3	3.4	29.7	33.1	0.211	17.4	16.19	33.6	0.208
P4	2.0	28.2	30.2	0.231	18.8	13.94	32.7	0.214
Average			31.8	0.220			31.9	0.220

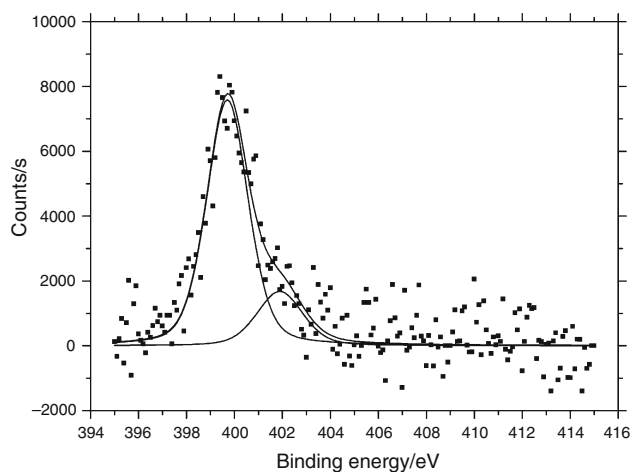


Fig. 4 High resolution XPS spectrum for N_{1s}

XPS analysis

To verify the validity of TG techniques, the obtained results of doping level have been contrasted with that obtained by means of XPS. It is possible to obtain some ratios from the information obtained about the powders surface composition. By using the atomic ratio W/N it is possible to determine the doping level. Using this ratio, obtained by XPS, the doping level is about 0.16, which is a bit lower than the value obtained by means of TG; this is probably due to the XPS experimental error. It is not possible to calculate the atomic ratio P/N , since the limit of detection of this technique does not allow detecting the presence of P in the sample, since it appears in a small concentration.

In Fig. 4 it is possible to observe the high resolution XPS spectrum of N_{1s} , which can be easily deconvoluted in two peaks. The peak located at 399.7 eV corresponds to amine ($-NH$)-type groups in the film [18] while the peak located at 401.7 eV can be assigned to protonated amines (N^+) [19]. So it is possible to calculate the percentage of pyrrole rings with positive charges and the total pyrrole rings thus obtaining the N^+/N ratio, which has a value of 0.19. This value is in more agreement with the value obtained by means of TG.

In Fig. 5 it is possible to observe the high resolution XPS spectrum of W_{4f} . The BEs of 35.1 and 37.2 eV correspond to the atomic environment of the W_{4f} , consisting in a coupling spin-orbit doublet ($W_{4f7/2}$ and $W_{4f5/2}$). The lowest BE corresponds to the contribution $W_{4f7/2}$, and the highest is related to the contribution $W_{4f5/2}$. Both contributions are due to an oxidation state W^{+6} [21,22].

The obtained results confirm that it is possible to use thermogravimetry as a quantitative technique; on the one hand the results are coincident independently of the experimental conditions used and on the other hand are

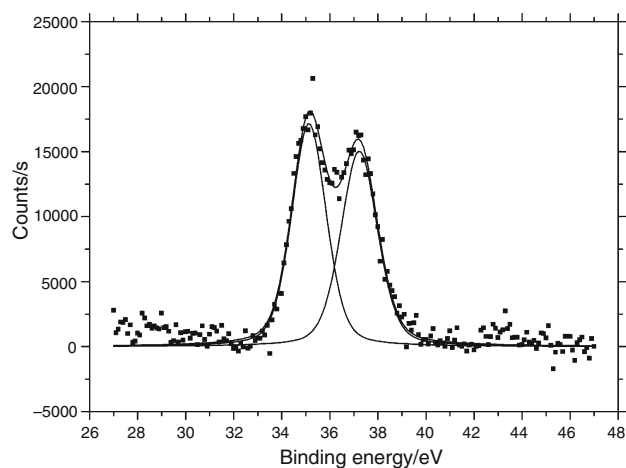


Fig. 5 High resolution XPS spectrum for W_{4f}

Table 3 Values of doping level obtained with different methods

Technique	Conditions	Doping level
Thermogravimetry	N_2 atmosphere	0.22
Thermogravimetry	Air	0.22
XPS	W/N	0.16
XPS	N^+/N	0.19
Average		0.20

similar to those obtained with XPS techniques. A summary of the results can be observed in the Table 3. The average doping level calculated by different techniques is 0.20, which indicates that of every five pyrrole molecules, one is positively charged.

Qualitative analysis

The total amount of Ppy does not depend on the testing method. When inert atmosphere is used, the degradation below 873 K concerns only a very small percentage of polymer, whereas in air atmosphere the degradation concerns the totality of the polymer. This fact is clearly observed when using DTG and DSC (Fig. 6), where the signal below 873 K is very low in nitrogen atmosphere, but very significant in air atmosphere.

When using inert atmosphere, the first jump would concern some Ppy chains poorly cross-linked to the three-dimensional network that forms the material. The Py-GMC analysis by means of direct insertion in atmosphere produces a very weak signal at 873 K (Fig. 7) where only the presence of the monomer is detected, $m/z = 67$, and the dimer and trimer have no significant presence in the totality of the analyzed samples (Fig. 7). This can be due to the fact that part of the monomer has not been oxidized by the $FeCl_3$ and has been retained inside the structure of the

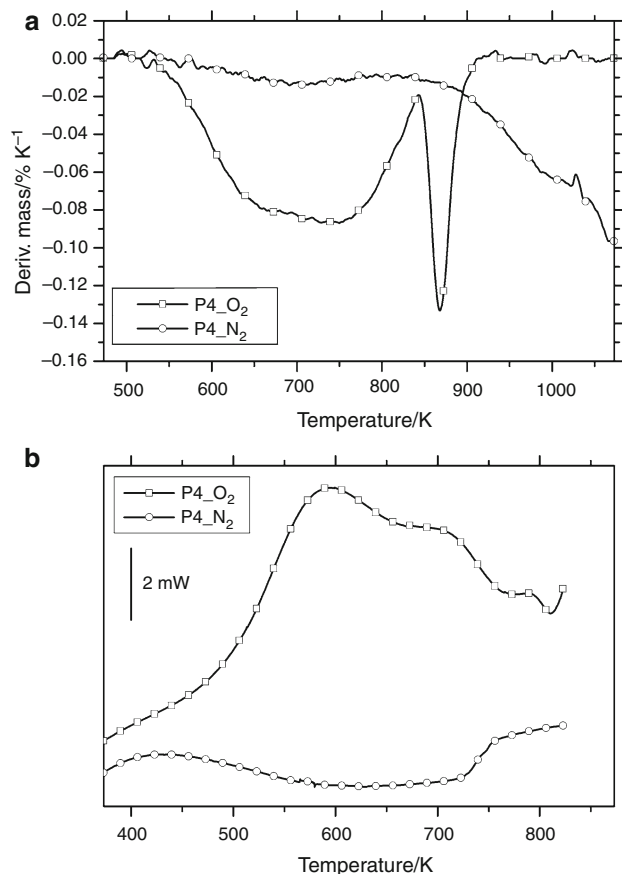


Fig. 6 DTG and DSC comparative of the sample 4 in N_2 and air atmosphere

polymer. When heating the material by TG, the evaporation of the pyrrole takes place, and therefore, it is removed from the structure. The m/z ratio is 67, so this peak corresponds to the pyrrole ring that has not lost both protons in the polymerization reaction; consequently they are monomer units that have not reacted in the synthesis process. Furthermore, the use of an inorganic dopant avoids the formation of some species related to dopant–Ppy interactions [20, 21].

If we compare samples when the synthesis temperature is varied (P2 and P4), we can observe that the sample synthesized at lower temperature (P2) is more stable than that synthesized at high temperature (P4) (Fig. 8). As the synthesis temperature increases, the reactions occur more quickly and some non-polymerized pyrrole molecules can remain as monomer in the polymer structure. Regarding the synthesis method for P2, the loss of volatiles does not begin until 523 K, whereas in sample P4 the degradation begins at about 473 K. If we compare samples at pyrrole concentrations (P2 and P3) we can observe that samples with higher pyrrole concentration (P2, 2 g l^{-1}) are more stable than that with lower pyrrole concentration (P3, 0.5 g l^{-1}) (Fig. 8). This can be explained if we take into account that

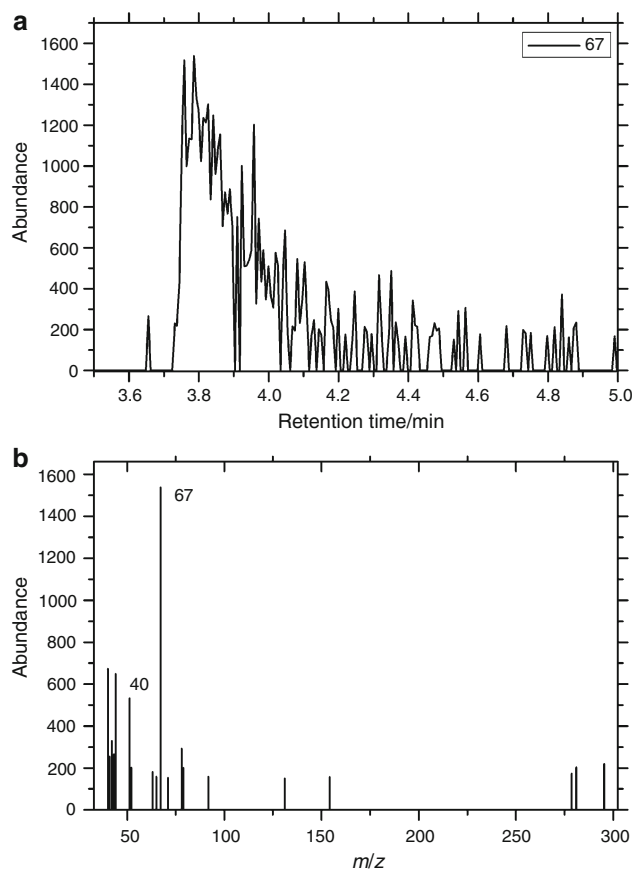


Fig. 7 Py–GC–MS spectrum of sample 4

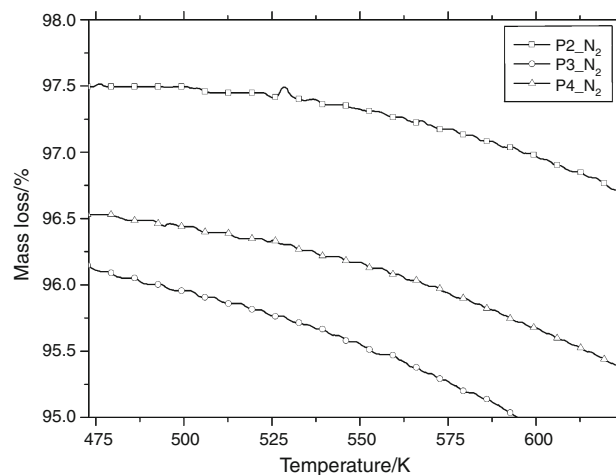


Fig. 8 Magnified comparative curves of polypyrrole doped with $PW_{12}O_{40}^{3-}$ in N_2 atmosphere in the zone 473–623 K

low reactive concentrations lead to a slow a reaction since the diffusion is difficult. Pyrrole monomer oxidation is more difficult since some of these monomers could be trapped by the Ppy structure.

So we can conclude that to obtain the most stable material, the synthesis process must be carried out in an ice bath and high pyrrole concentration (2 g l^{-1}). The polymerization yield of the synthesis reaction follows similar trend (Table 1). Low temperatures and high pyrrole concentration lead to high polymerization yield and then the probability of incorporation of non-oxidized pyrrole molecules decrease. This is in agreement with the obtained results with TG analysis. Polymers showing higher polymerization yield are more stable in the temperature range 473–523 K since they possess lower amounts of non-polymerized pyrrole.

Conclusions

The use of an inorganic anion $\text{PW}_{12}\text{O}_{40}^{3-}$ as dopant in the synthesis of Ppy has allowed us to obtain qualitative and quantitative information about the thermal behavior of the synthesized polymer. From a quantitative point of view we can determine the doping level by means of TG with identical results for both inert and oxidizing atmosphere. The comparison with other techniques such as XPS is satisfactory, and indicates that the doping level of the synthesized polymers is near to 0.2.

Qualitatively, the analysis in inert atmosphere indicates that Ppy degradation of Ppy starts at relatively low temperatures (473–523 K), concerning a small percentage of the synthesized material, being the pyrrole monomer the only significant degradation product. Lower temperature during polymer synthesis (273 K) and higher pyrrole concentrations (2 g l^{-1}) lead a higher stable polymer (the degradation of the polymer starts at 523 K) in comparison to synthesis process carried out at room temperature or low pyrrole concentration (0.5 g l^{-1}) (polymer degradation starts at 473 K).

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