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THERMAL ANALYSIS, CONDUCTIVITY AND ELECTROCHEMICAL APPLICATIONS OF PHENYLACETYLENE AND BENZYLPROPARGYLAMINE POLYMERS. PART 3

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ABSTRACT

Benzylpropargylamine and phenylacetylene polymers were analysed using thermal analysis techniques (TG, DTG and DSC), those of phenylacetylene both undoped and doped with iodine or $FeCl_3$. Conductivity was also measured: the polymers with the best properties, from this point of view, were also added to PVC membranes, using which ion selective and enzyme electrodes were prepared and characterized.

INTRODUCTION

In two earlier publications [1,2], we examined and discussed the thermoanalytical and conductivity properties of doped and undoped polymers of diethynylbenzene and diethynylpyridine. This study demonstrated that TG and DSC analysis results were particularly useful not only for the characterization of the polymers, but also for the correct interpretation of the conductivity data, which are of great importance in order to establish their most suitable analytical application, such as the preparation of membranes for new ion selective electrodes [2–4]. The validity and utility of the information obtained in the previous studies persuaded us to extend the same research to study other interesting conductor polymers [5,6], i.e. those of polybenzylpropargylamine and of polyphenylacetylene (Fig. 1), the latter both in doped and undoped form.

In addition, analogously to our previous studies [2], a potentiometric PVC polymeric membrane sensor, containing doped polyphenylacetylene, was prepared and characterized for its response to some common ions such as H_3O^+, K^+, NH_4^+, Ba^{2+} and Al^{3+}. Another electrode, containing in its

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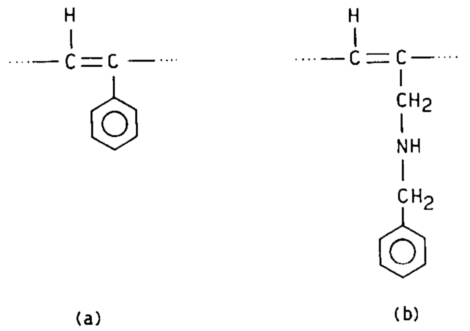

Fig. 1. (a) polyphenylacetylene, (b) polybenzylpropargylamine.

membrane undoped polybenzylpropargylamine, was tested as a sensor of some common anions, such as OH^-, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-}. Moreover the response of these ion-selective electrodes (ISEs) was modified by the addition of a biological mediator, the urease enzyme. The analytical results characterizing all these sensors are summarized in this paper.

EXPERIMENTAL

Reagents

PVC (polyvinylchloride) and bis(2-ethylhexyl)sebacate, used in the polymeric membrane preparation, were supplied by Fluka (Switzerland) and urease, E.C. 3.5.1.5, by Sigma, St. Louis, MO (U.S.A.); Polyazetidine prepolymer solution (PAP) (Hercules polycup 172.12% solids in H_2O) was purchased from Hercules Inc. (Wilmington, Del. U.S.A.); phenylacetylene and benzylpropargylamine monomers were supplied by Aldrich Chemical, Milan (Italy); all other organic solvents and reagents of analytical grade were from Merck Darmstadt (F.R.G.).

Polymers

Polybenzylpropargylamine (PBPA) and polyphenylacetylene (PPA) were prepared, the latter also in the doped form, using procedures reported in the literature [7,8]. Briefly, PPA was obtained from the reaction in hot refluxing conditions of the phenylacetylene monomer in CH_3OH, containing 0.2 mol l^{-1} of NaOH and chloro(1,5-cyclooctadiene)rhodium(I) dimer as catalyst. After addition of the methanol, the polymer was filtered off and dried. After dissolution in tetrahydrofuran, the solution was filtered and the polymer reprecipitated from the solution by adding methanol; the polymer was then washed with hexane/methanol (1 : 1) mixture, and finally vacuum dried. Polybenzylpropargylamine (PBPA) was obtained by adding a small volume of 0.1 mol l^{-1} NaOH solution in CH_3OH to the monomeric benzylpropargylamine, in the presence of the same catalyst. Chloroform was added to dissolve the residue and the polymer was precipitated from the solution obtained by adding *n*-hexane; after filtration, the polymer was separated and washed with *n*-hexane, and then vacuum dried.

Doping procedure

PPA was obtained in the iodine-doped form by dissolving the polymer in tetrahydrofuran and adding, to the solution, an amount of iodine corresponding to three times the weight of the polymer. After about 12 h, the solvent was evaporated under vacuum at room temperature and the doped polymer obtained. The $FeCl_3$-doped form of PPA was obtained by an analogous procedure, by adding to the tetrahydrofuran solution containing the polymer an amount of $FeCl_3 \cdot 6H_2O$ corresponding to 1.5 times the weight of the polymer.

Polymeric membrane preparation and ISEs or enzyme electrode assembly

The assembly of the polymeric (PVC) and sebacate membrane electrodes, containing 5% of doped or undoped conductor polymer, was performed using the same procedure adopted in previous research [4,9,10]. The electrochemical cell and internal Ag/AgCl reference electrode were also analogous to those described elsewhere [9,10], as was the external calomel reference electrode.

The response of these ISEs was then modified by operating in the presence of urease. With the ion-selective electrode based on a membrane containing PPA doped with iodine, the enzyme urease was free in solution, whereas it was immobilized in the PVC membrane in the case of the ISE modified by addition of PBPA to the PVC membrane. In this last case the enzymatic membrane, with immobilized urease, was prepared in the same way as was reported in a previous paper [2], by using polyazetidine prepolymer for the enzyme immobilization on the PVC membrane containing the conducting polymer. The assembly of the studied enzyme sensors was also carried out as previously described in detail [2,11].

TG and DSC analysis

The TG, DTG and DSC curves of the doped polymers were obtained using a Mettler TC 50 thermobalance and a Mettler DSC 20, coupled with a Mettler TC 10A-TA processor system and a Swiss dot-matrix printer. The atmosphere was an air stream with a flow rate of 100 ml min^{-1}; the heating rate used was 10 °C min^{-1} for both the TG and DSC experiments.

Apparatus for potentiometric or enzymatic measurements

Potentiometric measurements were carried out on an Orion research potentiometer microprocessor ionalyzer model 901 and a Radiometer REC 61 Servograph recorder. An automatic burette (Scott–Gerate TA 50), coupled to the potentiometer–recorder system and a saturated calomel reference electrode were also used to obtain the calibration curve. The solutions to be analysed were magnetically stirred and thermostated at 20 ° C. In the potentiometric measurements for the calibration line, the initial volume was 25.0 ml.

The enzymatic measurements were carried out using an analogous procedure; however, the medium used was 0.02 mol l^{-1} Tris buffer solution at pH 7.5.

Conductivity measurements

Conductivity measurements were carried out on a Keithley 169 Multimeter using a Teflon measurement cell with two gold disks of 2 cm diameter [2,12].

RESULTS

The TG and DTG curves of PPA and of PBPA between 20 and 900 ° C, in dynamic air (heating rate 10 ° C min^{-1}), are shown in Figs. 2 and 3. Table 1 summarizes the relative thermal data. In Figs. 4 and 5, the TG and DTG curves, recorded in the same experimental conditions, for PPA doped with iodine, or with iron(III) chloride, are reported. Table 2 shows the main thermic data corresponding to these TG curves. Figures 6 (a), (b), (c) and (d) shows the DSC curves, between 25 and 600 ° C, performed in the same dynamic air and heating rate conditions, for undoped PPA, for PBPA, for PPA doped with iodine and for PPA doped with $FeCl_3$, respectively. In Table 3, the conductivity values of all these polymers are reported, together with the values of the solvent residue, determined by TG analysis. In the case of PPA doped both with iodine and with $FeCl_3$, the variations in conductivity values are shown, along with the solvent residue left from the doping procedure. Table 3 also includes the iodine content of the PPA doped with iodine, determined by TG and, in the case of PPA doped with $FeCl_3 \cdot 6H_2O$, the crystallization water and iron(III) content of the polymer, the latter calculated on the basis of the percentage Fe_2O_3 residue found using TG at 800 ° C and derived by IR spectrometry from the Fe^{3+}–O stretching bands at 550 and 480 cm^{-1}.

Table 4 lists the main electroanalytical data obtained from the ion-selective electrode with the PVC membrane containing 5% PPA doped with

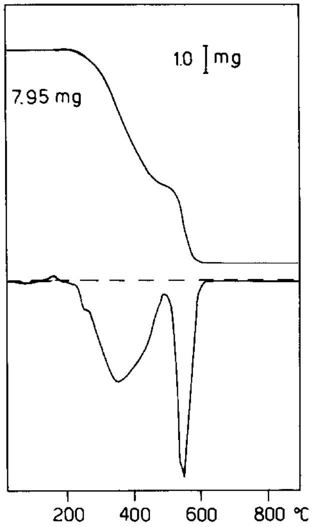

Fig. 2. TG and DTG curves of polyphenylacetylene in flowing air (100 ml min^{-1}) heating rate 10 ° C min^{-1}.

iodine, and also the data obtained from the ISE–enzyme sensor for urea, determined by modifying the response of the ISE with urease free in solution. Table 5 lists the main data obtained from the ion-selective electrode with the PVC membrane containing 5% PBPA and from the enzyme sensor for urea, obtained by modifying the response of the ISE with

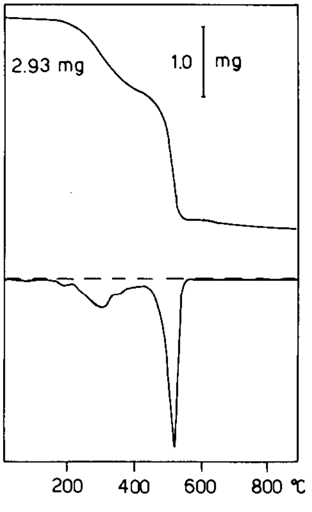

Fig. 3. TG and DTG curves of polybenzylpropargylamine in flowing air (100 ml min^{-1}) heating rate 10 ° C min^{-1}.

TABLE 1

Thermal analysis of dried undoped polymers in an air stream (100 ml min^{-1}) at a heating rate of 10 °C min^{-1}. The sign (+) or (−), before the found % values, indicates an increase or a loss of mass in the step respectively

Polymer	Solvent loss		First step [a]				Second step	
			(a)		(b)			
	found (%)	pdt [b]	found (%)	pdt [b]	found (%)	pdt [b]	found (%)	pdt [b]
Polyphenyl-acetylene	−0.6	24	+0.4	120	−63.5	190	−36.2	490
		75		160		350		545
		110		190		490		620
Polybenzyl-propargyl-amine	−0.8	25			−37.4	150	−58.8	445
		100				310		520
		140				445		580

[a] (a) and (b) are sub-steps.

[b] pdt = procedural decomposition temperature.

immobilized urease. Polymeric ISEs, containing PPA doped with iron(III) chloride, have such a short lifetime that their development was not pursued.

DISCUSSION

The experimental conditions of the TG and DSC curves are the same as in previous papers [1,2] i.e. in flowing air instead of nitrogen in order to

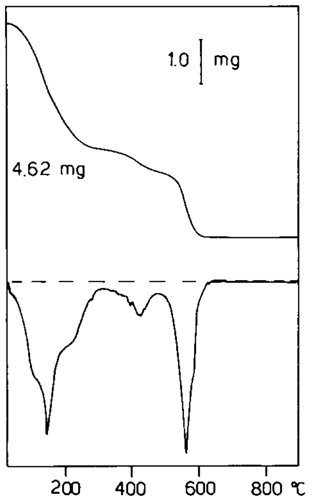

Fig. 4. TG and DTG curves of polyphenylacetylene doped with iodine in flowing air (100 ml min^{-1}) heating rate 10 °C min^{-1}.

TABLE 2

Thermal analysis of doped polymers (polyphenylacetylene) in an air stream (100 ml min^{-1}) at a heating rate of 10 °C min^{-1}. The sign (−) before the found % values indicates a loss of mass in the step

Doped polymer	Solvent and moisture loss		First step[a]				Second step[a]			
			(a)		(b)		(a)		(b)	
	found (%)	pdt[b]	found (%)	pdt[b]	found (%)	pdt[b]	found (%)	pdt[b]	found (%)	pdt[b]
Polyphenylacetylene doped with iodine	Solvent loss		Iodine loss							
	−0.6	24	−58.6	40			−10.8	306	−29.2	496
		30		130				420		560
		40		306				496		650
Polyphenylacetylene doped with $FeCl_3$	Solvent and moisture loss		Crystallization water loss		Crystallization water loss					
	−1.5	24	−5.5	75	−5.2	140	−41.0	210	−27.5	400
		38		120		160		350		420
		60		140		210		400		560

[a] (a) and (b) are sub-steps.

[b] pdt = procedural decomposition temperature.

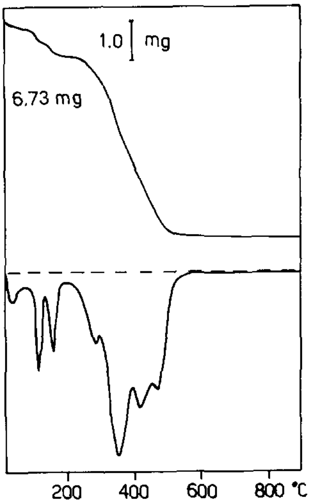

Fig. 5. TG and DTG curves of polyphenylacetylene doped with $FeCl_3$ in flowing air (100 ml min^{-1}), heating rate 10 °C min^{-1}.

ensure complete decomposition of the polymer within the temperature range which can be scanned by the available thermal apparatus. The heating rate was 10 °C min^{-1}; it was not necessary to operate with a lower heating rate, because the compounds under consideration do not decompose with excessive speed with a heating rate higher than 5 °C min^{-1} [1]. The thermal decomposition of the two undoped polymers, PPA and PBPA, which are practically anhydrous, begins in the range 150–190 °C and is complete by 580–620 °C. Table 1 shows essentially two main steps (see Figs. 2 and 3). However, in the case of PPA, after the loss of the last traces of solvent remaining from the synthesis ($\leq 0.6\%$) and immediately before the beginning of the first decomposition step at around 190 °C, a weak but characteristic oxidative polymerization process can be observed; this is clear at slightly higher temperatures in the case of the polymers of diethynylbenzene and of 2,6-diethynylpyridine [1]. This step is also demonstrated by the corresponding small increase in the mass of the sample (see the DTG curve of Fig. 2) and by the weak exothermic transition in the DSC curve (Fig. 6 (a)). The thermal data for this transition are reported in Table 1 as a sub-step of the first step. An analogous process is not observed in the TG curve of PBPA.

The thermal degradation of PPA doped with iodine (Fig. 4) or with iron(III) chloride (Fig. 5) begins with a very different trend. After the loss of the solvent traces remaining from the doping procedure (only a little in the case of the iodine-doped polymer ($\leq 0.6\%$) and somewhat more (1.5%) in the case of the iron(III) chloride-doped polymer), it is possible to observe in the first case a large step corresponding to loss of iodine from the polymer and, in the second case, a step corresponding to typical loss of crystallization

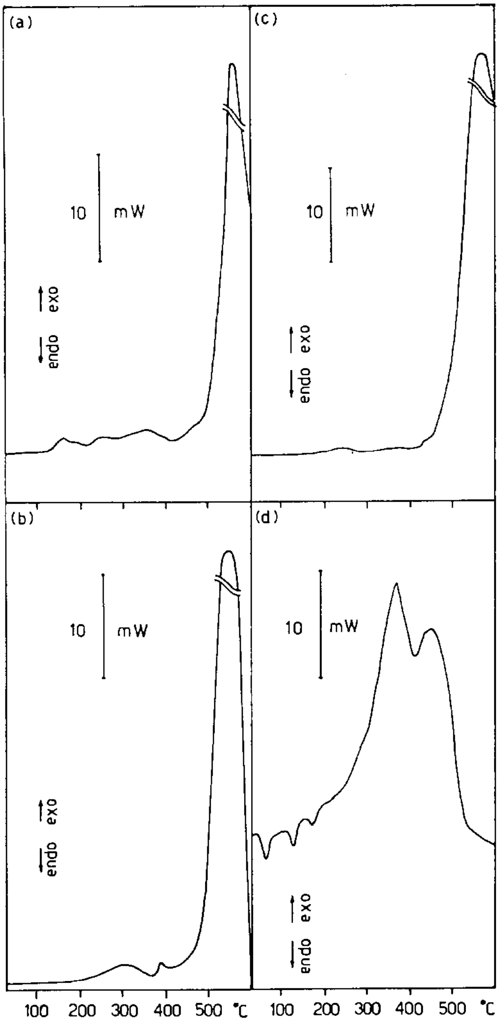

Fig. 6. DSC curves of: (a) polyphenylacetylene, 2.44 mg; (b) polybenzylpropargylamine, 1.74 mg; (c) polyphenylacetylene doped with iodine, 1.90 mg, and (d) polyphenylacetylene doped with $FeCl_3$, 2.44 mg; in flowing air (100 ml min^{-1}), heating rate 10 ° C min^{-1}.

water. This crystallization water is of course still bound to iron(III) chloride and is released in two characteristic well-defined successive steps clearly present in both the DTG (Fig. 5) and DSC (Fig. 6 (d)) curves. On increasing the temperature, the differently doped polymers then degrade in a similar manner with a strongly exothermic decomposition process, which can be divided into two sub-steps, as shown in Table 2. As can be observed, in contrast to the undoped polymers and to PPA doped with iodine, all practically anhydrous and free from solvent residue, the PPA doped with hexahydrated iron(III) chloride still retains part of the crystallization water of the iron salt and a small part of the solvent or moisture residual from the

TABLE 3

Conductivity values and % w/w of the solvent residue by TG analysis for the examined doped and undoped polymers and % w/w content of iodine, or of Fe^{3+}, and crystallization water by TG analysis of doped polymers. In all these TG analyses SD% = 3

Time of polymer drying	Determined conductivity σ ($ohm^{-1} cm^{-1}$) (SD% = 2)	% w/w of the solvent residue from synthesis, found by TG analysis	% w/w of iodine content by TG analysis	% w/w of the solvent and moisture residue by TG analysis	% w/w of crystallization water content by TG analysis	% w/w of Fe^{3+} by TG analysis
Polybenzylpropargylamine dried for 10 h in a vacuum drier	1.5×10^{-5}	0.8				
Polyphenylacetylene dried for 10 h in a vacuum drier	1.5×10^{-14}	0.6				
Polyphenylacetylene, doped with iodine and dried for 10 h in a vacuum drier	1.3×10^{-4}	2.8				
Polyphenylacetylene, doped with iodine, dried for 10 h in a vacuum drier and for 6 h at 50 ° C, in a Rotavator under vacuum	9.1×10^{-5}	0.6	58.6			

Polyphenylacetylene, doped with $FeCl_3$ and dried for 10 h in a vacuum drier	2.2×10^{-6}	7.7		
Polyphenylacetylene, doped with $FeCl_3$ and dried for 20 h in a vacuum drier	6.9×10^{-7}	4.4		
Polyphenylacetylene, doped with $FeCl_3$, dried for 10 h in a vacuum drier and for 6 h at 50 ° C, in a Rotavator under vacuum	1.8×10^{-7}	1.5	10.7	6.2

TABLE 4

Analytical characterization of the ion-selective electrode, with PVC membrane containing 5% polyphenylacetylene doped with iodine, and of the enzyme sensor for urea [a]

Species determined	Linearity range [b] $(\mathrm{mol\,l^{-1}})$	Slope $(\Delta \mathrm{mV}/\Delta \log c)$	Correlation coefficient
H^+	1.2×10^{-3}–2.1×10^{-2}	$+49.5$	$+0.9941$
NH_4^+	1.0×10^{-3}–5.1×10^{-2}	$+48.9$	$+0.9937$
K^+	1.0×10^{-3}–5.1×10^{-2}	$+29.8$	$+0.9991$
Ba^{2+}	1.0×10^{-3}–1.0×10^{-2}	$+15.4$	$+0.9958$
Al^{3+}	1.0×10^{-3}–2.0×10^{-2}	$+20.5$	$+0.9955$
Urea	1.5×10^{-3}–9.8×10^{-2}	$+38.5$	$+0.9983$

[a] Response time is <10 s, for the ISE and about 1 min for the enzyme sensor.
[b] Precision in the linearity range (as "pooled SD" % is $<2.1\%$.

doping procedure. It has not been possible to obtain the compound in a more anhydrous form, despite much effort. If it is heated to about 150 ° C, a partial loss of crystallization water and solvent residue is observed, but the product obtained is drastically altered: its TG curve is very different from that in Fig. 5; for instance, the thermal degradation begins at a temperature a little higher than room temperature, rather than at 210 ° C as in the case of the vacuum dried compound (Fig. 1), which has clear stoichiometrically defined characteristics, reproducible in other preparations. Attempts to prepare the product without crystallization water, by using anhydrous iron(III) chloride rather than the hexahydrate, were not successful. In this case the iron salt is practically insoluble in tetrahydrofuran and the doping process in the heterogeneous phase resulted in a product with characteristics very similar to those of the compound obtained after heating to about 150 ° C, as discussed above.

Table 3 lists the different conductivity values for all the polymers examined as well as the corresponding solvent trace values as found by TG. It

TABLE 5

Analytical characterization of the ion-selective electrode with PVC membrane containing 5% polybenzylpropargylamine, and of the enzyme sensor for urea [a]

Species determined	Linearity range [b] $(\mathrm{mol\,l^{-1}})$	Slope $(\Delta \mathrm{mV}/\Delta \log c)$	Correlation coefficient
Cl^-	2.0×10^{-4}–2.6×10^{-2}	-30.6	-0.9997
OH^-	8.0×10^{-4}–2.6×10^{-2}	-44.0	-0.9981
NO_3^-	2.0×10^{-4}–2.5×10^{-2}	-16.7	-0.9938
SO_4^{2-}	2.0×10^{-5}–2.6×10^{-2}	-14.3	-0.9969
PO_4^{3-}	5.0×10^{-5}–2.6×10^{-2}	-33.3	-0.9822
Urea	5.0×10^{-5}–1.6×10^{-3}	-47.3	-0.9963

[a] Response time is <10 s for the ISE and about 1 min for the enzyme sensor.
[b] Precision in the linearity range (as "pooled SD" %) is $<2.4\%$.

can be observed that the conductivity values of the two undoped polymers are markedly different: PBPA has a conductivity value of about 10^{-5} Ω^{-1} cm^{-1}, so that it can be considered a quasi-conductor, and also in the undoped form, whereas PPA has much lower conductivity values (about 10^{-14} Ω^{-1} cm^{-1}), so that, in the undoped form, this polymer is essentially an insulating compound, with a behaviour similar to that observed in a previous paper [1] for anhydrous polydiethynylbenzene. It is very interesting to observe that the TG data demonstrate the completely anhydrous state of these undoped polymers and the almost total absence of solvent residue ($\leq 1\%$) and also confirms the conductivity measurement results recently performed by our research group [12], but for which some uncertainties still existed, it not being valid to completely exclude the possibility that the large conductivity differences between the two polymers was attributable to differences in the solvent residue content of the two polymers.

Table 3 reveals that TG analysis can provide further information relevant to the determination of the real conductivity values of the polymers, in the case of PPA doped with iodine or iron(III) chloride. It can be observed, as on previous occasions [1,2], that the conductivity value decreases with the solvent residue percentage in the doped polymer. It can be also observed that PPA doped with iodine, similarly to undoped polymers, can be obtained in a completely anhydrous form practically free from any solvent residue ($\leq 1\%$), so that its real conductivity can be evaluated and was found to be about 10^{-5} Ω^{-1} cm^{-1}. It was thus confirmed that doping with iodine gives these polymers a higher degree of conductivity, as previously observed for doped poly-*para*-diethynylbenzene [2].

In contrast, PPA doped with $FeCl_3$ could not be obtained in a completely anhydrous form nor free from solvent residue, as discussed above. In this case, however, crystallization water molecules are coordinated by iron(III) ions and therefore take part in the stoichiometry of the compound, the conductivity of which (of the order of 10^{-7} Ω^{-1} cm^{-1}) can essentially vary as a function of the solvent or of the moisture traces still present in its composition, which can be minimized ($\leq 1.5\%$), by gentle thermal (50–60 ° C) treatments with vacuum dehydration, but not completely eliminated.

Lastly Tables 4 and 5 report the main electrochemical results obtained by ion selective or enzymatic sensors with a PVC membrane containing 5% of the best of the conducting polymers, on the basis of the results obtained: PPA doped with iodine, or undoped PBPA, which, even in the anhydrous state, were the most conducting of the polymers studied (conductivity of the order of 10^{-5} Ω^{-1} cm^{-1}). It can be observed that the ISE with iodine-doped PPA (Table 4) has a cationic response, with the highest sensitivity to H^+ and NH_4^+ (slope about +49 mV for log concentration decade). The urea sensor is an NH_4^+-sensing ISE coupled with a biological mediator (urease) which is free in solution; its slope is +38.5 mV for log concentration decade. The ISE with undoped PBPA in its membrane has an anionic response, with the highest sensitivity to the OH^- anion (slope −44 mV for log concentration decade). The urea sensor is a combination of an anionic ISE with the biological mediator urease which is immobilized on the PVC membrane; its slope is −47.3 mV for log concentration decade. The other characteristics of these sensors, reported in Tables 4 and 5, such as the response time, the linearity range and the reproducibility, are typical of ion-selective [4,9,10] and enzyme [11,13] electrodes.

CONCLUSIONS

The thermoanalysis (TG, DSC) of the polymers examined led to information concerning (1) the thermal stability, the main decomposition processes and the eventual further oxidative polymerization processes which can take place; (2) the solvent or moisture residue contents; (3) the real conductivity characteristics (Table 3); (4) the real content of dopant (iodine or iron(III)), or of crystallization water (Table 5) and (5) the choices which have to be made in order to prepare a polymeric membrane for use as the essential part of an ISE.

With respect to the experimental ISEs, with PVC, sebacate and conducting-polymer-based membranes, it can be observed that the response changes when the conducting polymer is changed, with anionic or cationic values of the slope, and that, in the cases considered, whilst the enzyme can be immobilized in the membrane when PBPA is used as the conducting polymer, when PPA doped with iodine is used, immobilization is prevented and inactivation of the enzyme results because of the denaturing actions of the dopant [11].

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