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THERMAL ANALYSIS, CONDUCTING PROPERTIES AND ELECTROCHEMICAL APPLICATIONS OF SOME CONDUCTOR-DOPED POLYMERS. PART 2.

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ABSTRACT

Polymers of *para*- and *meta*-diethynylbenzene and 2,6-diethynylpyridine, massively doped with iodine, were analysed by TG, DTG and DSC techniques and their conductivity values were measured. Some analytical results, obtained using a polymeric ion selective electrode (selective to NH_4^+) and an enzyme urea sensor, both based on a PVC membrane containing poly-*para*-diethynylbenzene, are also reported.

INTRODUCTION

In the first part of this research the detailed thermoanalytical characterization (TG, DSC) of the polymers of *para*- and *meta*-diethynylbenzene and 2,6-diethynylpyridine was performed [1]. The conductivity characteristics of these polymers have also been studied. The actual conductivities of the polymers (when completely dry and free from any doping agent) are of the same order as insulating substances (10^{-12}–10^{-13} ohm^{-1} cm^{-1}).

This is in perfect agreement with the results of our electrochemical studies [2,3] into the use of these polymers as materials for polymeric membrane ion sensors [4,5]. The addition of these polymers to common PVC membranes does not vary the electrical resistance of the membranes or the sensitivity to H^+ or other ions. However, if these polymers (in particular poly-*para*-diethynylbenzene) are doped with iodine and are then added in low concentration to a PVC membrane, an increase in sensitivity of the membrane to ions such as H^+, NH_4^+, K^+ and Na^+ occurs. This membrane can then be used as a sensor membrane without the need for the addition of ionophore [4,6]. These observations have induced us to study the conductivities and thermal properties of these iodine-doped polymers (as has been previously performed on the same polymers, but in the undoped state [1]).

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The results are briefly described in this paper. In addition, electroanalytical data obtained using an ion selective electrode, based on a PVC membrane containing 5% of doped poly-*para*-diethynylbenzene, are reported.

EXPERIMENTAL

Polymers

Poly-*para*-diethynylbenzene, poly-*meta*-diethynylbenzene and poly-2,6-diethynylpyridine were prepared as described in a previous paper [1]. The same polymers, in the iodine-doped form, were obtained by dissolving the polymers in tetrahydrofuran with the addition 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 was obtained [3,7].

TG and DSC analysis

The TG, DTG and DSC curves of the doped polymers were obtained using a Mettler TG 50 thermobalance and a Mettler DSC 20, coupled with a Mettler TC 10A-TA processor system and a Swiss dot-matrix printer. The measurements were carried out in an air stream (flow rate, 100 ml $\min^{-1}$) at a heating rate of 5 °C $\min^{-1}$ for the TG and DSC experiments.

Conductivity measurements

Conductivity measurements were performed using a Keithley 169 Multimeter, with a Teflon measurement cell and two gold discs of 2 cm in diameter [8].

Polymeric membrane electrode assembly

The polymeric membrane electrodes were assembled using the same procedure as adopted in refs. 4–6. The electrochemical cell was analogous to that described in refs. 4 and 6.

The polymeric membranes were obtained by dissolving PVC (165 mg) in tetrahydrofuran (3 ml) with the addition of bis(2-ethylhexyl)sebacate (330 mg) as plasticizing agent and 5% (w/w) of the conductor-doped polymer. The solution was evaporated in a Petri dish (5 cm in diameter). A membrane ($\leqslant$ 0.1 mm thickness) was obtained and this was cut into discs of 10 mm in diameter. The discs were glued to the bottom of a PVC tube using an adhesive obtained by dissolving PVC in cyclohexanone. The solution contained in the PVC tube was NH_4Cl (10^{-2} mol l^{-1}). An Ag/AgCl reference electrode was dipped into this solution.

Enzyme immobilization on membrane

The enzymatic membrane was prepared in the following way. Urease (10 mg) was mixed with polyazetidine prepolymer solution (PAP) (200 μl). The solution was stratified on the ion selective membrane and was left for 24 h at 4°C. The resulting enzyme membrane was about 40–50 μm thick. The PVC–enzyme membrane was cut into discs and glued to the bottom of a PVC tube, as reported above. The sensor was assembled as described above.

Apparatus for potentiometric measurements

Potentiometric measurements were carried out using an Orion research potentiometer microprocessor ionalyser 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 electrode (as reference) were also used to obtain the calibration curve. The solutions to be analysed were magnetically stirred and thermostatted at 20°C. In the potentiometric measurements (both for the calibration line and for the standard addition method) the initial volume was 25.0 ml.

The enzymatic measurements were carried out in a similar manner; however, the medium used was 0.02 mol l^{-1} tris buffer solution at pH 8.

Reagents

All the reagents used were of analytical reagent grade: polyvinylchloride (PVC) and bis(2-ethylhexyl)sebacate were supplied by Fluka (Switzerland); urease, E.C. 3.5.1.5, was obtained from 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, DE (U.S.A.); all the other reagents (of analytical grade) were obtained from Merck, Darmstadt (F.R.G.)

RESULTS AND DISCUSSION

Thermal analysis (TG and DSC) was performed using essentially the same experimental conditions as adopted and discussed in ref. 1: flowing air, 100 ml $\min^{-1}$; heating rate, 5°C $\min^{-1}$; temperature range, 20–900°C.

The thermograms of doped poly-*para*-diethynylbenzene and doped poly-*meta*-diethynylbenzene are shown in Figs. 1 and 2. In Fig. 3, the TG and DTG curves of a sample of poly-2,6-diethynylpyridine doped with iodine are shown (it is clear that this sample is substantially iodine (66% (w/w)) owing to the very low solubility of the polymer in the doping medium). On comparing the three thermograms, it can be seen that the first step, which is

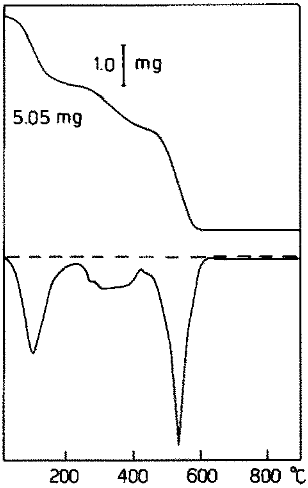

Fig. 1. TG and DTG curves of poly-*para*-diethynylbenzene doped with iodine in flowing air (100 ml min^{-1}) at a heating rate of 5°C min^{-1}.

present in all three cases, is essentially due to iodine loss. This was confirmed by bubbling the vapour evolved during this step into a starch–water solution (violet colour formed). Therefore it is possible to obtain useful information on the degree of doping from the TG curves by determining the iodine content of the polymers.

The thermoanalytical data (related to this TG step) of the three polymers are summarized in Table 1. The data on the oxidative degradation of the

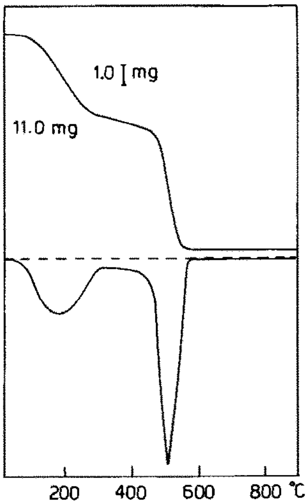

Fig. 2. TG and DTG curves of poly-*meta*-diethynylbenzene doped with iodine in flowing air (100 ml min^{-1}) at a heating rate of 5°C min^{-1}.

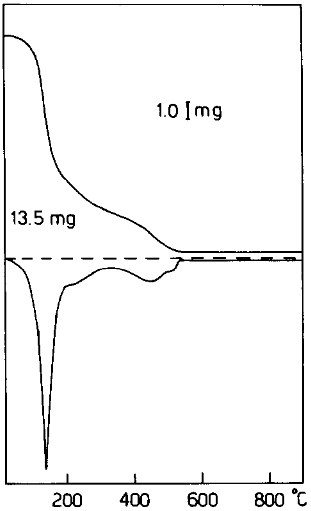

Fig. 3. TG and DTG curves of a sample of poly-2,6-diethynylpyridine doped with iodine in tetrahydrofuran. As explained in the text 66% (w/w) of the sample is iodine owing to the low solubility of the polymer in the doping medium. Air flow rate, 100 ml $\min^{-1}$; heating rate, $5\,^{\circ}\mathrm{C}\ \min^{-1}$.

polymers, which occurs in one or two steps, are reported in the same table. The DSC curves of poly-*para*-diethynylbenzene and poly-*meta*-diethynylbenzene, doped with iodine, are shown in Figs. 4 and 5. A marked exothermic transition is observed related to the oxidative degradation of the

TABLE 1

Thermal analysis of doped polymers in air (100 ml $\min^{-1}$) at a heating rate of $5\,^{\circ}\mathrm{C}\ \min^{-1}$

Polymer doped with iodine	First step (iodine loss)		Second step			
			1st substep		2nd substep	
	Weight loss (%)	PDT	Weight loss (%)	PDT	Weight loss (%)	PDT
Poly-*para*-diethynylbenzene	32.1	25	19.3	215	48.9	425
		110		315		535
		215		425		640
Poly-*meta*-diethynylbenzene	36.3	30	60.0	315		
		182		500		
		315		575		
Poly-2,6-diethynylpyridine [a]	66.0	30	15.6	210	18.1	340
		135		220		450
		210		340		570

PDT, procedural decomposition temperature. [a] Reported data for doped poly-2,6-diethynylpyridine are only illustrative because, as explained in the text, the sample is essentially iodine (66% (w/w)).

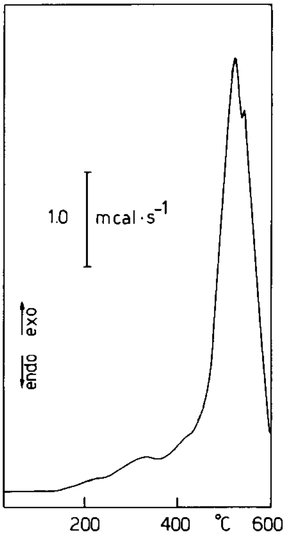

Fig. 4. DSC curve of poly-*para*-diethynylbenzene doped with iodine in flowing air (100 ml min^{-1}) at a heating rate of 5 °C min^{-1}.

polymers. In comparison with the TG and DSC curves of the same undoped polymers (reported in ref. 1) no exothermic step corresponding to a weight increase and occurring at around 200 °C (see also Figs. 6 and 7) is observed Moreover, the presence of traces of solvent (as a residue of synthesis or doping) cannot be seen in the TG and DSC curves of the dried doped

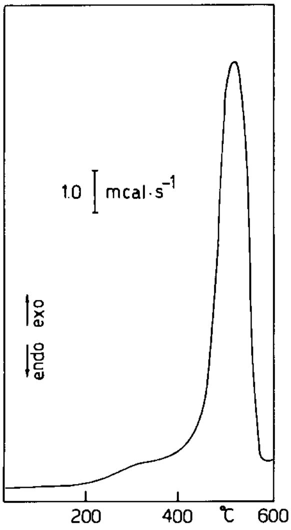

Fig. 5. DSC curve of poly-*meta*-diethynylbenzene doped with iodine in flowing air (100 ml min^{-1}) at a heating rate of 5 °C min^{-1}.

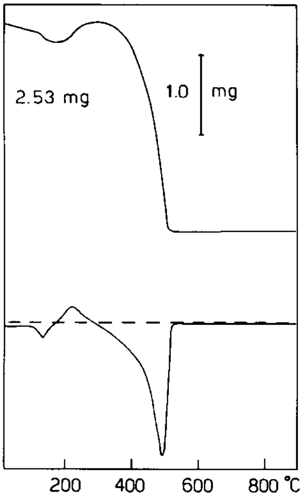

Fig. 6. TG and DTG curves of undoped poly-*para*-diethynylbenzene dissolved in tetrahydrofuran as in the doping process and then roughly dried. Air flow rate, 100 ml min^{-1}; heating rate, 5 °C min^{-1}.

polymers (Figs. 1–5). These curves can be compared with the TG and DSC curves (Figs. 6 and 7) of undoped poly-*para*-diethynylbenzene containing about 8% of solvent. In this case, a feeble endothermic transition can be seen in the DSC curve between 30 and 160 °C, corresponding to the evaporation of traces of solvent. This is also observed in the TG curve of the same

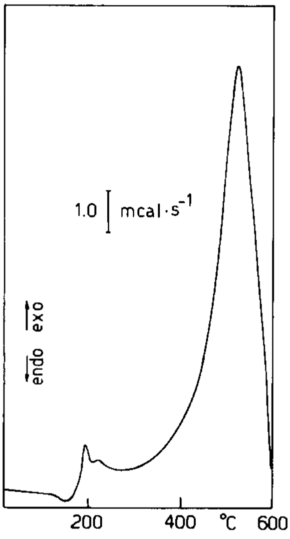

Fig. 7. DSC curve of undoped poly-*para*-diethynylbenzene dissolved in tetrahydrofuran as in the doping process and then roughly dried. Air flow rate, 100 ml min^{-1}; heating rate, 5 °C min^{-1}.

TABLE 2

Conductivity values and percentage iodine content (by weight) of all the polymers doped with iodine

Polymer	Conductivity σ (ohm^{-1} cm^{-1}) (SD (%) $\approx$ 2)	Iodine content from TG analysis (SD (%) $\approx$ 3)
Poly-*para*-diethynylbenzene	2.5×10^{-4}	32.1
Poly-*meta*-diethynylbenzene	1.5×10^{-4}	36.3
Poly-2,6-diethynylpyridine [a]	3.2×10^{-4}	66.0

[a] Reported conductivity data for doped poly-2,6-diethynylpyridine are only illustrative, because, as explained in the text, the sample is essentially iodine (66% (w/w)).

polymer in Fig. 7 of ref. 1. It can also be seen that the polymers are practically unchanged during the solubilization in tetrahydrofuran and the following drying process (as during the doping with iodine). This is shown by the comparison of Fig. 1(a) of ref. 1 with Fig. 6 of this paper.

It can be concluded that the high conductivity values of the polymers doped with iodine, reported in Table 2, can be attributed to the iodine doping and not to the traces of residual solvent (as observed in the undoped and incompletely dry polymers [1]). From Table 2, it also appears that if the dopant is in large excess the conductivity values obtained for polymers with different degrees of doping and for polymers after the loss of some iodine are always of the same order as in Table 2.

All these results are in perfect agreement with the different behaviour observed when doped and undoped polymers are used in ion selective polymeric membranes. Table 3 summarizes the main analytical results obtained in this study aimed at the characterization of an ion selective electrode based on a PVC membrane containing 5% of poly-*para*-diethynylbenzene doped with iodine. From the values of the slopes it can be

TABLE 3

Analytical data and characterization of the ion selective electrode based on a PVC membrane containing 5% of poly-*para*-diethynylbenzene doped with iodine and of the enzyme sensor for urea

Species determined	Range of linearity (mol l^{-1})	Slope (millivolts per decade of concentration)	Correlation coefficient
H^+	4.5×10^{-4}–1.4×10^{-1}	+53.5	+0.9987
NH_4^+	5.0×10^{-4}–1.6×10^{-1}	+54.1	+0.9998
K^+	5.0×10^{-4}–1.6×10^{-1}	+37.6	+0.9941
Na^+	5.0×10^{-4}–1.6×10^{-1}	+28.6	+0.9848
Urea	2.0×10^{-3}–3.8×10^{-2}	+40.1	+0.9971

Response time, <10 s; precision in the linearity range, as "pooled SD (%)" $\leqslant 1.8$.

deduced that the sensitivity of the polymeric membrane sensor is different for each cation. The response to NH_4^+ is almost Nernstian, with a good correlation coefficient. The range of linearity is generally almost the same (about 2.5 decades) for all the cations.

The ion selective electrode was employed to determine urea. The ammonium ion was determined using the ion selective electrode containing immobilized urease on its membrane. NH_4^+ was assumed to be formed according to the enzymatic reaction

$$(NH_2)_2CO + 2H_2O + H^+ \xrightarrow{\text{urease}} 2NH_4^+ + HCO_3^-$$

The analytical data are reported in Table 3. The range of linearity is about one decade; the value of the slope is quite satisfactory even though it is not Nernstian; the correlation coefficient is high and the response time is short. The greatest problem with the enzymatic electrode is the very short lifetime which is probably due to the denaturation of the enzyme caused by the action of the doping agent.

CONCLUSIONS

The thermoanalysis results of these polymers are very useful as they indicate a marked difference between doped and undoped polymers and enable the percentage content of dopant to be determined easily and quantitatively. It is also confirmed that, in the case of doped polymers, the high conductivity values (Table 2) can be attributed to the presence of the dopant, rather than to the trace of solvent residue from the synthesis, as in the case of the undoped polymers [1]. Finally, it is clear that the thermoanalytical and conductimetric characterizations are particularly useful in choosing the best conducting polymer for application on sensor membranes and in explaining some experimental results obtained in this kind of application.

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