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THERMAL ANALYSIS AND CONDUCTING PROPERTIES OF POLYMERS OF DIETHYNYLBENZENE AND DIETHYNYLPYRIDINE

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ABSTRACT

The TG, DTG and DSC curves in air and nitrogen and the related thermogravimetric and calorimetric data of the polymers obtained by polymerization of *para*- and *meta*-diethynylbenzene and 2,6-diethynylpyridine are reported and discussed. The conductivity properties of these polymers were studied as a function of the residual solvent content (as determined by TG analysis).

INTRODUCTION

For some years a research group has been working in our department on the synthesis, characterization and applications of polymers with claimed, or supposed, conducting properties [1]. In particular, the possibility of the use of some of these polymers (doped or undoped) as components of new electrochemical sensor membranes has been investigated [1–4]. In this paper results of studies on the thermoanalytical characterization of some of these undoped polymers, in particular those of *para*- and *meta*-diethynylbenzene and 2,6-diethynylpyridine, are described. In addition, an important correlation between the conductivity values of these polymers and the content of residual solvent from synthesis is established. The real conductivity properties of the dried polymers are evaluated.

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EXPERIMENTAL

The preparation [1] of the polymers of *para*- and *meta*-diethynylbenzene and 2,6-diethynylpyridine (Fig. 1) was carried out as follows. The monomer (1 g) was added to 25 ml of a solution of CuCl (25 mg) in pyridine. Oxygen was bubbled through the solution at room temperature and with stirring. After 1 h, the precipitation of the polymer was favoured by the addition of 50 ml of methanol. The precipitate was filtered and washed carefully with methanol containing 1% w/w of hydrochloric acid. The residue was filtered and vacuum dried. The yield obtained was 90%–95%. The results of the elemental analysis agreed with the theoretical data.

The TG, DTG and DSC curves of the 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. Air or nitrogen was used with a flow rate of 100 ml min^{-1}. The heating rate was 5 °C min^{-1} for the TG experiments in air and for the DSC experiments. A heating rate of 10 °C min^{-1} was used for the TG experiments in nitrogen as explained below.

Conductivity measurements were carried out using a Keithley 169 Multimeter, with a Teflon measurement cell and two gold discs of 2 cm in diameter [5]. The IR spectra were obtained using a Perkin–Elmer 882 IR spectrophotometer and nujol as solvent. Karl–Fischer measurements were performed as described in a recent paper [6].

RESULTS AND DISCUSSION

All the curves obtained for poly-*para*-diethynylbenzene are summarized in Fig. 2. Figure 2(a) shows the TG and DTG curves obtained between 20 and 900 °C in dynamic air (100 ml min^{-1}) at a heating rate of 5 °C min^{-1}; Fig.

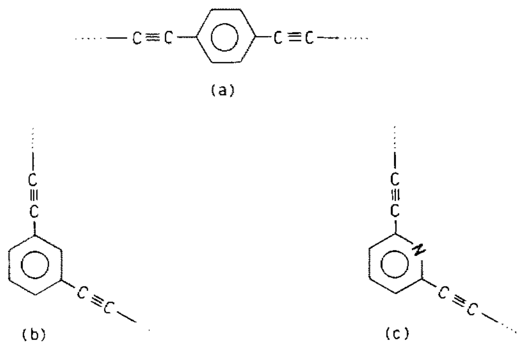

Fig. 1. (a) Poly-*para*-diethynylbenzene; (b) poly-*meta*-diethynylbenzene; (c) poly-2,6-diethynylpyridine.

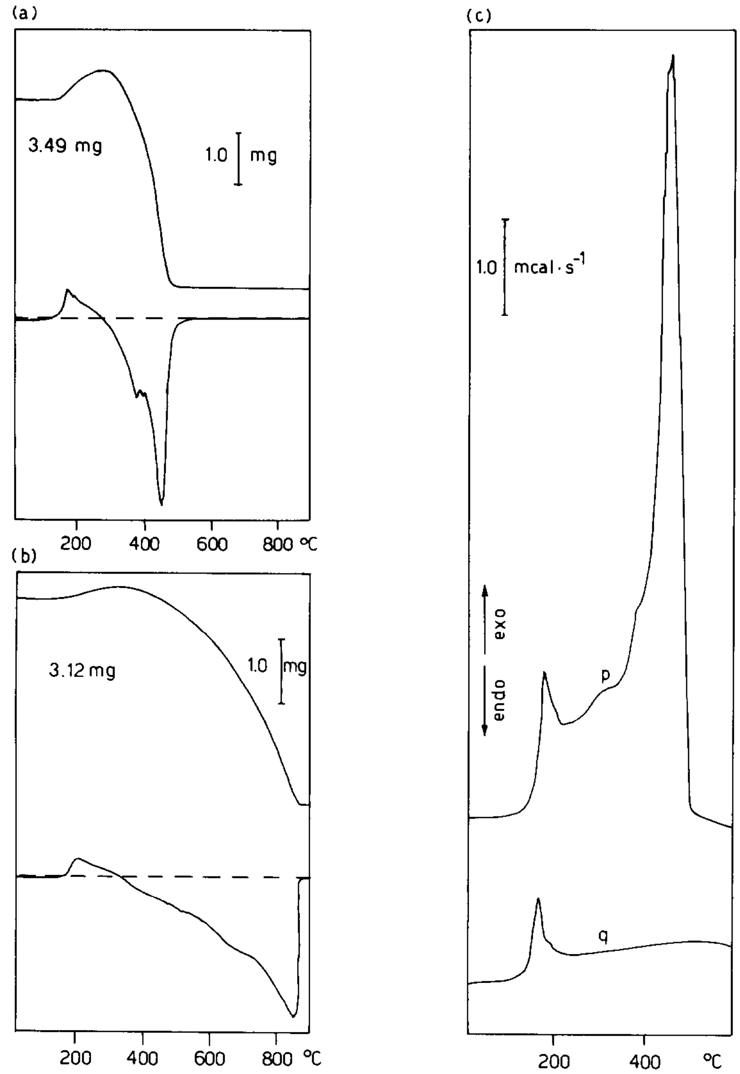

Fig. 2. Thermal analysis of poly-*para*-diethynylbenzene. (a) TG and DTG curves in flowing air (100 ml min^{-1}) at a heating rate of 5 °C min^{-1}; (b) TG and DTG curves in a nitrogen stream (100 ml min^{-1}) at a heating rate of 10 °C min^{-1}; (c) DSC curves: p, 1.26 mg of sample in an air stream; q, 1.53 mg of sample in a nitrogen stream; flow rate, 100 ml min^{-1}; heating rate, 5 °C min^{-1}.

2(b) shows the TG and DTG curves obtained over the same range of temperature in nitrogen (100 ml min^{-1}) at a heating rate of 10 °C min^{-1}; Fig. 2(c) shows the DSC curves obtained between 20 and 600 °C in dynamic air and nitrogen (100 ml min^{-1}) at a heating rate of 5 °C min^{-1}. In Figs. 3 and 4, the analogous curves for poly-*meta*-diethynylbenzene and poly-2,6-diethynylpyridine are shown.

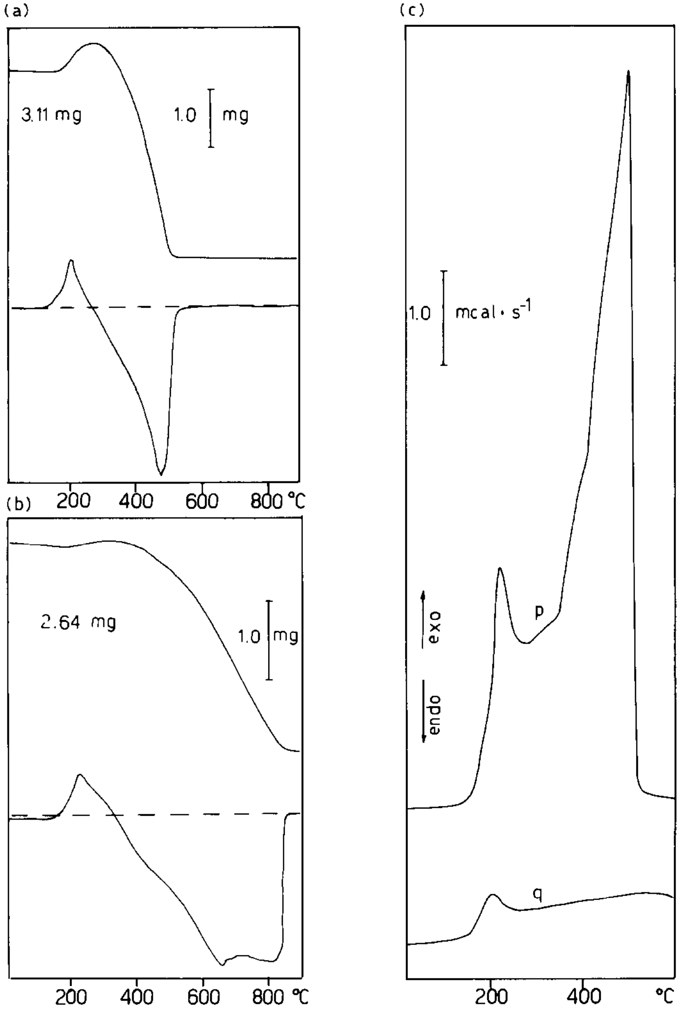

Fig. 3. Thermal analysis of poly-*meta*-diethynylbenzene. (a) TG and DTG curves in flowing air (100 ml min^{-1}) at a heating rate of 5 ° C min^{-1}; (b) TG and DTG curves in a nitrogen stream (100 ml min^{-1}) at a heating rate of 10 ° C min^{-1}; (c) DSC curves: p, 1.71 mg of sample in an air stream; q, 1.56 mg of sample in a nitrogen stream; flow rate, 100 ml min^{-1}; heating rate, 5 ° C min^{-1}.

From the experimental point of view, it can be observed that, on operating in air, it is necessary to adopt a fairly slow heating rate (5 ° C min^{-1}) otherwise,a very fast transition occurs at about 150 ° C, followed by the loss of matter from the crucible. This does not occur if a nitrogen stream is used so that, in this case, the thermogravimetric curves can be recorded at 10 ° C min^{-1}. The TG curves obtained in nitrogen at lower heating rates (i.e. 5 ° C min^{-1}) are not very different from those obtained at 10 ° C min^{-1}. However, this is the only positive aspect of the use of nitrogen. If the TG study is

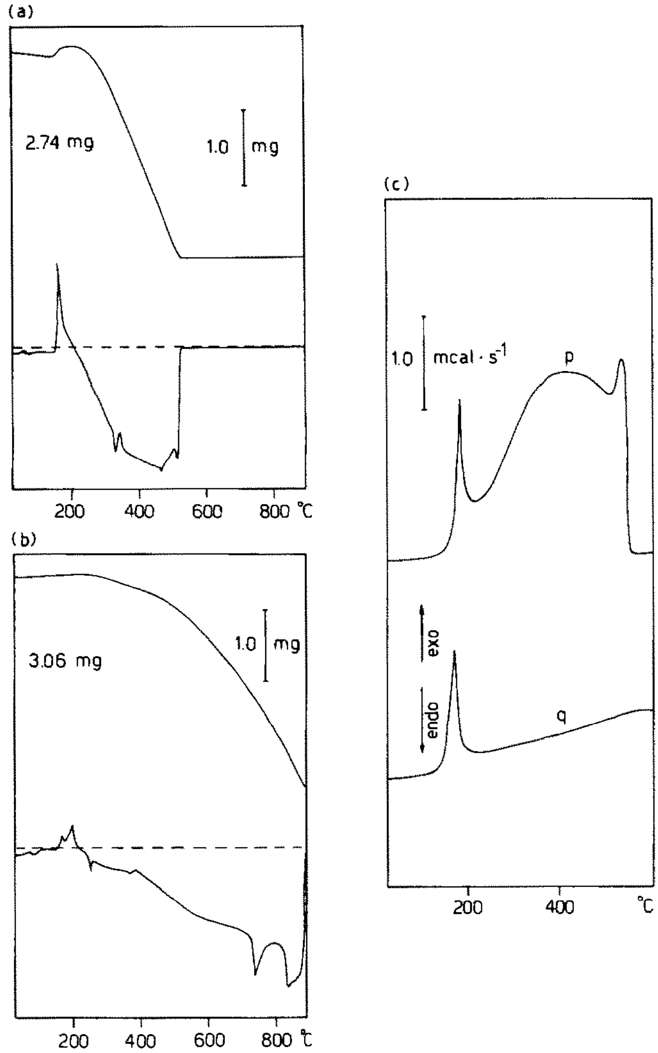

Fig. 4. Thermal analysis of poly-2,6-diethynylpyridine. (a) TG and DTG curves in flowing air (100 ml min^{-1}) at a heating rate of 5 ° C min^{-1}; (b) TG and DTG curves in a nitrogen stream (100 ml min^{-1}) at a heating rate of 10 ° C min^{-1}; (c) DSC curves: p, 1.10 mg of sample in an air stream; q, 1.55 mg of sample in a nitrogen stream; flow rate, 100 ml min^{-1}; heating rate, 5 ° C min^{-1}.

carried out in nitrogen, it is difficult to follow the second TG step completely. The second TG step is not complete even at 900 ° C, especially in the case of poly-2,6-diethynylpyridine (Fig. 4(b)), and this is a greater problem in the DSC curves (Figs. 2(c)–4(c), curves q).

All the thermogravimetric data obtained in air and nitrogen are reported in Tables 1 and 2 respectively. Initially, traces of solvent (a residue of the synthesis) are lost, if present (see TG curves of Fig. 7). For the TG curves of

TABLE 1

Thermal analysis of dried polymers in air (100 ml min^{-1}) at a heating rate of 5 °C min^{-1} (the sign (+ or −) before the found (%) values indicates an increase or a loss of mass respectively)

Polymer	Solvent loss		First step		Second step			
	Found (%)	PDT	Found (%)	PDT	1st substep		2nd substep	
					Found (%)	PDT	Found (%)	PDT
Poly-*para*-diethynylbenzene	−0.6	25	+14.6	135	−24.6	280	−89.2	380
		30		180		375		450
		125		280		380		540
Poly-*meta*-diethynylbenzene	−0.6	25	+16.4	135	−37.4	290	−78.4	425
		75		220		400		485
		130		290		425		550
Poly-2,6-diethynylpyridine	−0.8	25	+5.1	150	−25.0	220	−75.4	343
		30		170		330		470
		145		220		343		540

PDT, procedural decomposition temperature.

TABLE 2

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

Polymer	Solvent loss		First step		Second step			
	Found (%)	PDT	Found (%)	PDT	1st substep		2nd substep	
					Found (%)	PDT	Found (%)	PDT
Poly-*para*-diethynylbenzene	−0.6	23	+5.5	160	−48.8	328	−56.0	700
		35		200		675		835
		155		328		700		880
Poly-*meta*-diethynylbenzene	−0.7	25	+4.0	170	−62.2	330	−39.8	720
		40		225		660		820
		160		330		720		870
Poly-2,6-diethynylpyridine	−0.8	23	+0.7	160	−66.8	225	−31.4	780
		30		215		750		850
		150		225		780		> 900

PDT, procedural decomposition temperature.

Figs. 2–4 (obtained from polymers maintained for very long times (several months) in a vacuum drier) the solvent residue is of very little importance (always less than 1%). In the TG curves obtained in air (Figs. 2(a)–4(a)), two main TG steps are present. The first step (where an increase in mass is observed) corresponds to an exothermic transition in the DSC curves (Figs. 2(c)–4(c)). The second step, which is rather broad, corresponds to the total thermal decomposition of the polymer; this probably occurs in a number of steps, which are not well resolved. The second step has been tentatively subdivided into two main substeps (Table 1).

Some information on what happens to the polymers during the first step can be obtained from the IR spectra of poly-*para*- and poly-*meta*-diethynylbenzene before and after this first TG step (Fig. 5). The peak at 3300 cm^{-1} ($\equiv$C–H stretching) disappears and there is a contemporaneous small increase in the band at about 2200 cm^{-1} (this band is not very clear in the IR spectra of polymers which have not been heated). This seems to indicate that a further polymerization process occurs with an increase in the number of $-C\equiv C-$ groups in the polymeric chains and a disappearance of $\equiv$C–H terminal groups in the shorter polymeric chains. This interpretation is in good agreement with the darkening of the colour of the polymers which is observed at the end of the first step. In general, the colour changes from yellow (typical of a less extended conjugated system) to brown. The occurrence of a further polymerization can also explain the strong variations in wavelength and intensity of the typical band of the *para*-substituted benzene ring at about 830 cm^{-1} and of the typical bands of the *meta*-substituted benzene ring at about 680–790 cm^{-1}. These bands are clearly seen in the spectra of the polymers which have not been heated. Finally, the appearance of two broad bands at about 1600 and 1700 cm^{-1} can be interpreted as resulting from an oxidation process. The increase in mass during this step (which is clearly seen in the TG curves obtained in dynamic air, but is much less evident in the TG curves recorded in nitrogen) can be explained by this process. (The increase in mass is observed in nitrogen only because all oxygen traces present in the furnace are difficult to eliminate (the furnace used is not completely air tight)). The hypothesis of a process of oxidative polymerization is also in agreement with the exothermic transition of the DSC curve. This process may produce water, according to the reaction scheme

$$\equiv C{-}H + \tfrac{1}{2}O_2 + H{-}C\equiv \rightarrow \equiv C{-}C\equiv + H_2O$$

Residual water traces are present in the rapidly cooled final product as indicated in the TG curves of the polymers (heated until the end of the first step and then rapidly cooled) (Fig. 6) and by the Karl–Fischer test. The presence of moisture (7%–20% by weight) in the product was verified in several tests. This value is in reasonable agreement with the registered mass increase during the first TG step (Table 1). (It must be considered, however,

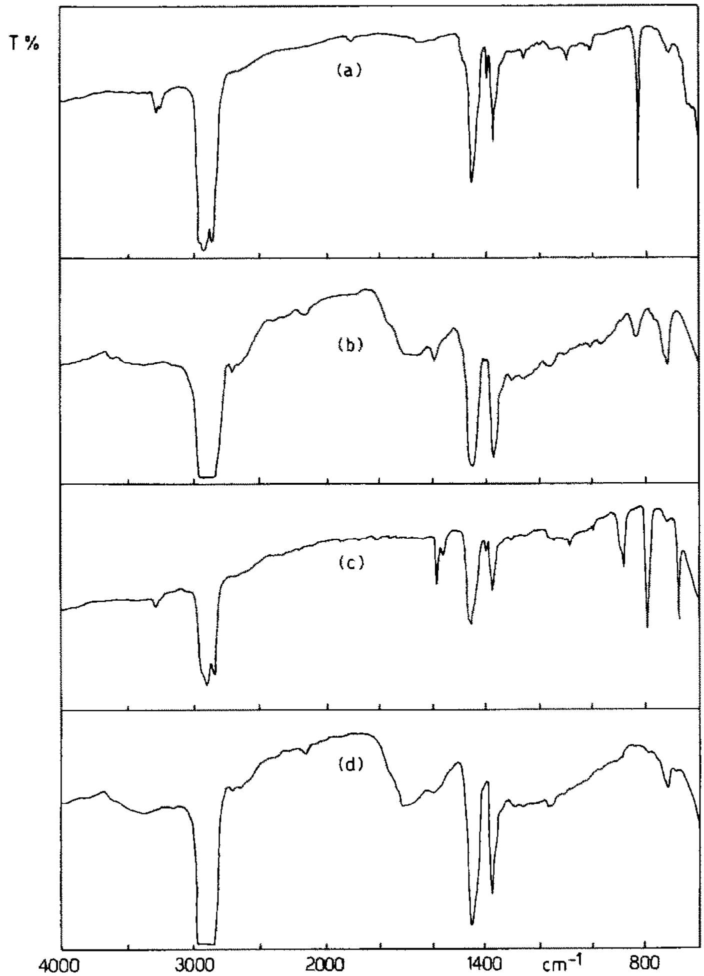

Fig. 5. IR spectra: (a) poly-*para*-diethynylbenzene; (b) poly-*para*-diethynylbenzene after heating up to the end of the first TG step (about 280 ° C); (c) poly-*meta*-diethynylbenzene; (d) poly-*meta*-diethynylbenzene after heating up to the end of the first TG step (about 280 ° C). Nujol as solvent.

that although the polymer was rapidly cooled, some of the water formed must have evaporated at the moment of its formation.) This polymerization process still seems to occur in a nitrogen stream, but probably in a different way.

If the TG curve of the polymer preheated to about 280 ° C is recorded, the first step (with an increase in mass) is no longer observed. This can easily be interpreted by assuming that the previous heating results in full polymerization of the sample and thus a second heating produces no effect (Fig. 6).

The second process, which is strongly exothermic in the DSC curves obtained in dynamic air and which occurs at about 450 ° C, agrees with the

TABLE 3

DSC data (peak temperatures and ΔH values) for the two main processes as shown in the DSC curves of the analysed polymers

Polymer	In air stream				In nitrogen stream	
	First process		Second process		First process	
	Peak temperature (°C) (SD (%) = 0.6)	ΔH (kcal g^{-1}) (SD (%) = 5.3)	Peak temperature (°C) (SD (%) = 0.6)	ΔH (kcal g^{-1}) (SD (%) = 5.3)	Peak temperature (°C) (SD (%) = 0.6)	ΔH (kcal g^{-1}) (SD (%) = 5.3)
Poly-*para*-diethynylbenzene	182.2	−0.24	472.2	−4.35	172.3	−0.13
Poly-*meta*-diethynylbenzene	227.7	−0.26	503.3	−4.12	201.5	−0.12
Poly-2,6-diethynylpyridine	172.7	−0.25	522.8	−4.28	167.5	−0.15

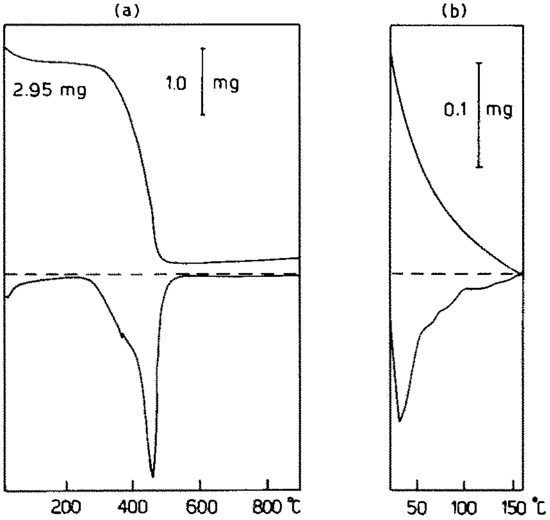

Fig. 6. TG and DTG curves of poly-*para*-diethynylbenzene previously heated at 280 °C and then rapidly cooled to room temperature: (a) full TG and DTG curves in the temperature range 20–900 °C; (b) TG and DTG curves (expanded scale) of the water loss process only. Flowing air, 100 ml min^{-1}; heating rate, 5 °C min^{-1}.

oxidative decomposition step of the corresponding TG curves. In the DSC curves obtained under nitrogen, this transition is practically absent and its sign is not apparent. The decomposition of the polymer in nitrogen occurs mostly at above 600 °C and by a different mechanism from that in flowing air.

In Table 3, the calorimetric data obtained from DSC (peak temperatures and ΔH values) for the first and second process in air are summarized. For the reasons discussed above only data for the first process can be obtained

TABLE 4

Variation in the conductivity values of poly-*para*-diethynylbenzene as a function of the percentage content (by weight) of the residual solvent from the synthesis process (as determined by TG analysis)

Time of polymer drying	Determined conductivity σ (ohm^{-1}cm^{-1}) (SD (%) ≈ 2)	Percentage (by weight) of residual solvent from synthesis as found by TG analysis (SD (%) ≈ 3)
Polymer dried in gooch after preparation	8.3×10^{-5}	38.2
Polymer dried for 4 days in a vacuum drier	1.4×10^{-6}	14.6
Polymer dried for 10 days in a vacuum drier	8.4×10^{-7}	10.6
Polymer dried for about 4 months in a vacuum drier	6.2×10^{-9}	4.3

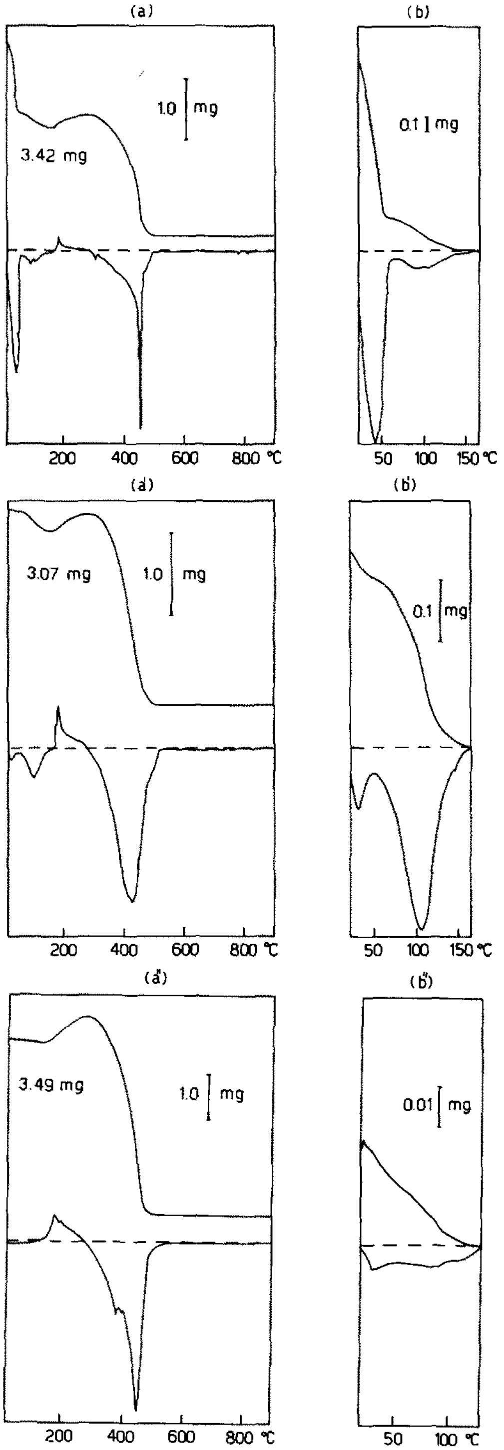

Fig. 7. TG and DTG curves of poly-*para*-diethynylbenzene with decreasing residual solvent from (a) to (a″): (a), (a′) and (a″), full TG and DTG curves in the temperature range 20–900 °C; (b), (b′) and (b″), TG and DTG curves, of the loss of solvent only (expanded scale). Flowing air, 100 ml min^{-1}; heating rate, 5 °C min^{-1}.

TABLE 5

Conductivity values and percentage of solvent (by weight) of all polymers dried for several months in a vacuum drier

Polymer	Determined conductivity σ (ohm^{-1}cm^{-1}) (SD (%) ≈ 2)	Solvent found (%) by TG analysis (see also Tables 1 and 2)
Poly-*para*-diethynylbenzene	1.5×10^{-12}	$<1\%$
Poly-*meta*-diethynylbenzene	5.5×10^{-13}	$<1\%$
Poly-2,6-diethynylpyridine	5.2×10^{-12}	$<1\%$

under nitrogen. A very interesting analytical application of the thermogravimetric measurements, is the determination of the amounts of residual solvent contained in the polymers, even after long drying times. This is possibly related to the conductivity characteristics of the compounds. For instance, in Table 4, the conductivity values of poly-*para*-diethynylbenzene are reported at different drying times (since preparation and after increasing lifetimes in the vacuum drier). The different amounts of solvent in the polymer (determined by thermogravimetric measurements (Fig. 7)) are also indicated in the same table. The conductivity values of the polymers containing $< 1\%$ by weight of residual solvent (as demonstrated by the TG curves, Figs. 2–4((a) and (b))) are given in Table 5.

These last two tables suggest that the fairly high conductivity values which are sometimes observed for these polymers (of the same order as those of semiconductors) can be attributed to the presence of residual solvent from the synthesis process (Table 4). When completely dry, the polymers show conductivity values of the same order as insulating materials (Table 5).

CONCLUSIONS

Thermal analysis of the polymers of *para*- and *meta*-diethynylbenzene and 2,6-diethynylpyridine was carried out. The fairly high conductivity values (semiconductors) obtained for these polymers can be attributed to residual solvent from the preparation process. The actual conductivity values of the polymers are much lower (of the same order as insulators).

ACKNOWLEDGEMENT

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