Chemical polymerization of aniline in phenylphosphinic acid

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Abstract: The chemical polymerization of aniline was performed in phenylphosphinic acid (APP) medium using ammonium peroxidisulfate as the oxidizing agent, at 0 ºC and 25 ºC. The yield of polyaniline (PANI) was about 60–69 %. The polymerization process required an induction time 8–10 times greater than in other acids (hydrochloric, sulfuric). The average density of the obtained polymer was 1.395 g cm-3 for PANI-salt and 1.203 g cm-3 for PANI-base. The acid capacity of PANI depends on the synthesis parameters and the maximum value was 15.02 meq/g polymer. The inherent viscosity of PANI was 0.662 dl/g at aniline/oxidant molar ratios >2 and 0 ºC. The oxidation state was a function of the synthesis parameters and lay between 0.553–0.625, as determined from UV-VIS and titration with TiCl3 data. The PANI samples were characterized by measurements of their density, inherent viscosity, conductivity, acid capacity, FTIR and UV-VIS spectrum, and thermogravimetric data.

Keywords: chemical oxidation, aniline, phenylphosphinic acid, conducting polymers, polyaniline.

INTRODUCTION

Studies concerning the field of conducting polymers have opened up new and attractive domains of applications, due to the possibility of the synthesis of this new generation of polymers which combines the mechanical properties and attractive processability of traditional polymers with the electrical and optical properties of electronic conductors.1–21

PANI is a conducting polymer which can easily be synthesized by both chemical and electrochemical methods and seems to be the most studied due to its simple synthesis and its environmental stability. The general formula of PANI is the same structure in all cases and consists of a succession of reduced benzenoid nuclei and oxidized quinoid nuclei, but the method of oxidation affects the performance of the polymer and the reproducibility of the synthesis. The properties of PANI depend
on the monomer/oxidant molar ratio, pH, reaction temperature, nature of the used acid, the mode of doping and the structure of the monomer (presence of substituents). An important aspect of PANI synthesis is the nature of the acid. The role of the acid dissociation constant, $pK_a$, is known; in PANI, the protonation equilibrium involves the quinoid nucleus having two imine nitrogens with $pK_{a1} = 1.05$ and $pK_{a2} = 2.55$, therefore any acid is suitable as a dopant if its $pK_a$ value lies in this range. Any acid having a $pK_a$ around the value of the anilinium ion ($pK_a = 4.60$) would be suitable as the solvent and prevents overoxidation. Thus, the properties of conductive PANI are affected by the type of the employed dopant ion. The most preferred method of synthesis is to use either hydrochloric or sulfuric acid with ammonium peroxydisulfate as the oxidant. The synthesis has also been carried out in organic acids. The use of large anions as dopants increases the solubility of PANI. The conductivity of PANI is closely related to the redox state of the polymer, the $pH$ of the working medium and the type of the dopant anion. The type of dopant anion affects the stability, electrical conductivity, polymerization kinetics and yield of the polymer. The synthesis and characterization of PANI doped with different anions are critical since many properties of the final polymer are greatly influenced by the nature of the dopant ion.

In this study, the chemical polymerization of aniline was performed in the presence of aqueous solutions of phenylphosphinic acid, APP, the use of which has not been mentioned in the literature. The PANI samples were characterized by FTIR, UV-VIS, density, inherent viscosity, conductivity and acid capacity. The oxidation state of the PANI samples was determined by titration with TiCl$_3$ solution and from UV-VIS data.

EXPERIMENTAL

Chemicals
Aniline, freshly distilled and cooled to $-4 \, ^\circ C$, phenylphosphinic acid (C$_6$H$_5$PH(O)OH, APP, Aldrich), ammonium peroxydisulfate (Merck), ammonium hydroxide and N,N-dimethylformamide (DMF) were used.

Preparation of PANI-APP
PANI was obtained by oxidizing aniline in aqueous APP solutions with ammonium peroxydisulfate as the oxidizing agent. The mole ratio aniline/oxidant (A/O) was 1; 1.33; 2 and 4, and the aniline/APP ratio (A/APP) was 1/1, 1/2, 1/3, 1/4 (1; 0.5; 0.33; 0.25), at $0 \, ^\circ C$ and $25 \, ^\circ C$. The procedure was the same for all samples: first the aniline salt was formed by the dropwise addition of aniline (0.1 mol L$^{-1}$) to an aqueous solution of APP, under continuous stirring and precooling. To this solution, a precooled aqueous solution of ammonium peroxydisulfate (0.025 – 0.1 mol L$^{-1}$) was added dropwise under continuous stirring. The stirring was stopped after 24 h and the PANI was recovered by filtration and washed several times with a dilute APP solution. The resulting PANI was dried under a dynamic vacuum for 24 h. The product was converted to PANI-base form with ammonium hydroxide.

Characterization
The IR spectra were recorded in KBr pellets. The UV-VIS spectra were measured in DMF using a Specord M42 spectrophotometer. The conversion was calculated from grams of dry polymer.
without purification × 100/g aniline. The oligomer fractions (containing oligomeric and secondary products) were determined by the difference between % conversion and % dry polymer after purification. The yield (%) represents the grams of dry purified polymer per 100 g aniline.

The oxidation of aniline is exothermic, hence the temperature of the reaction mixture can be used to monitor the progress of the reaction. The temperature–time profile is well reproducible and was obtained using a high precision thermometer. It was more suitable to determine the induction time from the temperature–time profile, than from the maximum temperature. The induction time represents the time required to reach half of the total increase of temperature during the exothermal step. The inherent viscosities of 0.01 % solutions of the PANI samples doped with APP in sulfuric acid were determined using an Ubbelohde viscosimeter. The densities of the PANI samples were determined by the picnometer method, in decaline. The electrical conductivities were measured on press pellets by the two-probe method.

The acid capacities of the polymers were determined from the quantity of sodium hydroxide (0.005 mol L⁻¹) required for the titration of the polymer samples. The PANI powder was suspended in water and titrated by sodium hydroxide in a closed cell under nitrogen. The titration was performed very slowly, with incremental addition of 0.2–0.5 ml, and the delay between two consecutive additions required for pH stabilization was 15 min. The pH measurements were performed with a CG 841 SCHOTT instrument using a SCHOTT GERATEN N 2041A glass electrode. Three determinations were performed for each sample. The acid capacity, reported for 1 g of polymer, was determined from the neutralization curve.

The oxidation state of PANI was determined from the relative proportion between benzenoid and quinoid rings in the polymer chain. This method is based on the quantity of hydrogen needed to transform the quinoid rings in benzenoid rings (the conversion of emeraldine to leucoemeraldine). Experimentally it consists of the titration of PANI dissolved in acetic acid (80 %) with TiCl₃. It is known that the conversion of emeraldine to leucoemeraldine requires a theoretical quantity equal to 0.543 % H/gram emeraldine. The oxidation state was also determined from the UV-VIS absorbance spectrum of the polymer solution in DMF. The thermal analysis of the samples was performed with a TG 209 instrument (Netzsch) at a heating rate of 25 ºC/min in the temperature range 20 to 990 ºC, in a nitrogen atmosphere and a DSC 204 instrument (Netzsch) in a nitrogen atmosphere in the temperature range 20 to 500 ºC, at a heating rate of 25 ºC/min.

RESULTS AND DISCUSSION

The oxidative polymerization of aniline in APP is an exothermal process. An S-shape temperature–time dependence was observed (Fig. 1). The oxidative polymerization of aniline in acid media presents three distinctive stages. The first is slow and independent of the temperature. The active species in the polymerization process are formed during this stage. The second stage is faster and temperature dependent; polymer is formed due to propagation. The post-polymerization stage (third stage) is also temperature dependent, and the polymer undergoes protonation-deprotonation, and oxidation-reduction processes.

The obtained temperature–time profiles for the polymerization of aniline in APP indicated a long induction period, 8–10 times longer than the synthesis under the same condition in AS or in other known acids, mentioned in the literature (hydrochloric, picric). The induction time was determined from temperature–time dependence and represents the time required to reach half of the total increase in temperature during the exothermal step. Thus, for PANI obtained at an aniline/oxidant ratio of 1.33 and an aniline/acid ratio of 1/2 at 0 ºC in AS, the in-
duction time was 6.9 min, while in APP under the same condition, it was 65 min. With increasing synthesis temperature, the induction time decreases, hence, in APP under the same condition but at 25 °C, the induction time was 55 min.

UV-VIS spectra recorded during the polymerization process in APP indicate an absorption peak at 720 nm. This peak appears after the induction period necessary for the formation of cation-radical species, able to initiate the polymerization (Fig. 2). With time, the intensity of this peak increases, during the evolution of the polymerization. The broad absorption band, which first appeared between 700 and 840 nm, becomes narrower.

The induction time depends on the synthesis parameters. Comparing the absorbance at 720 nm when different APP concentrations are used (Figs. 3 and 4) it can be seen that the polymerization starts fastest in the aniline/APP 1/1 solution. This is in accordance with the results of Lux,23 i.e., the polymerization is suppressed in more acidic media. This is mainly attributed to the protonation of the an-
iline. The degree of protonation increases with increasing acid concentration. Thus, the degree of aniline protonation is lowest at an aniline/APP ratio of 1/1 and highest at an aniline/APP ratio of ¼ (Fig. 3).

![Graph showing absorbance at 720 nm versus time with an aniline/oxidant mole ratio of 1.33 for different aniline/APP mole ratios.]

![Graph showing induction time versus the aniline/oxidant and aniline/APP mole ratio, at 0 ºC.]

It increases with increasing APP concentration as a result of the slow formation of cation-radicals. The oxidation process of the protonated species is more difficult compared to that of unprotonated ones, and decreases linearly with increasing oxidant concentration (i.e. decreasing aniline/oxidant mole ratio).

With increasing amount of oxidant (decreasing aniline/oxidant mole ratio) and decreasing quantity of acid in the solution (Figs. 5 and 6), the rate of polymerization of aniline in APP solution increases. The polymerization rate can be assessed by the differential method in percent per minute from the conversion versus time profile, and is equal to the slope for a particular moment of the polymerization.

The IR spectra of PANI recorded in pellets indicate the presence of five characteristic peaks for all samples at 1580 cm⁻¹, 1490 cm⁻¹, 1307 cm⁻¹, 1145 cm⁻¹ and 826 cm⁻¹, which agrees with literature data.⁹,¹⁰,²¹
The peak at 3232 cm$^{-1}$ in each curve is attributed to N–H stretching vibrations. Its intensity is very sensitive to the concentration of APP, and increases with increasing acid concentration. The peaks at 1580 and 1490 cm$^{-1}$ are attributed to quinoid and benzenoid ring deformations, and are present in samples of PANI obtained by chemical means. Their positions are independent of whether the PANI is doped or not.

With increasing concentrations of acid and oxidant, the experimental data show: a decrease of the intensity of the peak characteristic of benzenoid rings at 1500 cm$^{-1}$; an increase of the intensity of the peaks due to quinoid rings at 1375, 1150, 1560–1570, 1470–1490 and 1630 cm$^{-1}$; a decrease of the intensity of the peak at 1630 cm$^{-1}$ due to overoxidation which results in a decrease in the amount of the quinoid structure and the appearance of characteristic peaks of benzoquinone at 885, 944, 1080, 1313 and 1654 cm$^{-1}$.

The intensity of the peaks ascribed to benzenoid and quinoid rings are qualitatively the same for an aniline/oxidant ratio in the range 2–4. The aniline/acid ratio used was between 1/1 and 1/2. The obtained PANI is, as a result, in the emeraldine form.
UV-VIS spectra of the PANI base were recorded in $N,N$-dimethylformamide. The spectra allowed the detection of the absorption maxima of polyaniline salt or base. PANI has absorptions due to the $\pi - \pi^*$ transition of the benzenoid ring at 333 nm, characteristic for the most reduced form of PANI, polyleucoemeraldine; the $\pi - \pi^*$ transition of the quinoid ring at 627 nm, characteristic for the partially oxidized form of PANI, polyleucoemeraldine form. Further oxidation to the fully oxidized form, polymernigraniline, results in a blue shift of the $\pi - \pi^*$ transition of the quinoid peak at 430 nm (due to the formation of semiquinoidic nuclei) and a band at 844 nm (due to the formation of an exciton centered on the quinoid nuclei).

The yield in PANI, its conductivity, inherent viscosities and density at different aniline/oxidant ratio a and aniline/APP are summarized in Table I.

<table>
<thead>
<tr>
<th>No. sample</th>
<th>A/O*</th>
<th>A/APP**</th>
<th>Yield %*</th>
<th>Conductivity S cm$^{-1}$</th>
<th>Inherent viscosity/dL g$^{-1}$</th>
<th>Density/g cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>1/1</td>
<td>52.61</td>
<td>54.82</td>
<td>0.07</td>
<td>0.625</td>
</tr>
<tr>
<td>2</td>
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<td>58.38</td>
<td>60.83</td>
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<td>1.33</td>
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<td>62.29</td>
<td>64.91</td>
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<td>0.44</td>
</tr>
<tr>
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<td>66.71</td>
<td>68.51</td>
<td>0.78</td>
<td>0.62</td>
</tr>
<tr>
<td>5</td>
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<td>48.91</td>
<td>50.96</td>
<td>1.92</td>
<td>1.06</td>
</tr>
<tr>
<td>6</td>
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<td>53.74</td>
<td>56.00</td>
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<td>0.91</td>
</tr>
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<td>60.21</td>
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</tr>
<tr>
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<td>4</td>
<td>1/3</td>
<td>46.79</td>
<td>48.76</td>
<td>1.68</td>
<td>1.07</td>
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<tr>
<td>10</td>
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<td>52.06</td>
<td>54.25</td>
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<td>53.97</td>
<td>56.24</td>
<td>0.92</td>
<td>0.73</td>
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<td>46.29</td>
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<td>0.35</td>
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<td>46.32</td>
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<td>48.47</td>
<td>50.51</td>
<td>1.80</td>
<td>1.11</td>
</tr>
<tr>
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<td></td>
<td>49.41</td>
<td>51.49</td>
<td>1.45</td>
<td>1.03</td>
</tr>
</tbody>
</table>

*O/A – aniline/oxidant; **A/APP – aniline/acid phenylphosphinic

The observed average yield was about 65 % in APP. The polymer yield increased almost linearly with decreasing aniline/oxidant ratio. The density determined for the polymer samples shows that the average value was about 1.395 g cm$^{-3}$ for the PANI-salt and 1.203 g cm$^{-3}$ for the PANI-base. The viscosity decreased significantly for aniline/oxidant ratios lower than 2. With increasing amount of oxidant in the reac-
tion medium, the concentration of formed radical cation increases and the resulting polymer chains are shorter, hence, the inherent viscosity is lower (Table I).

The conductivity shows a small tendency of increasing with increasing acid concentration (Table I) and decreasing with increasing induction time (Fig. 7).

A higher value of the electrical conductivity was obtained in more acid media (Table I). The conductivity increases with increasing proton concentration in the aqueous acid media, due to the formation of doped polymer, and due to the existence of a remanent quantity of acid retained by the polymer chain. At aniline/oxidant mole ratios < 2, the inherent viscosity of the PANI samples is higher (higher molar masses), and the conductivity should also be higher, because the electrical conductivity increases with increasing polymer chain length. It was experimentally observed that the molar mass of the PANI had almost no effect on the electrical conductivity. Such a behavior has been theoretically predicted for the cases when the charges hop from one polymer chain to another. These hops are faster compared to the life-time of the charge on the chain, i.e., when interchain transport occurs more readily than intrachain transports and decreases with the reaction temperature.

The oxidation state of PANI was estimated by calculating the intensity ratio of the peaks at 620 nm and 320 nm ($I_Q/I_B$) in each UV-VIS spectrum of the polymer samples and by the percent hydrogen necessary to reduce the PANI samples (Table II).

The ratio of quinoid and benzenoid units (i.e., C=N/C-N) was calculated on the basis of the following equation (Eq. 1).

A large quantity of oxidant favors the oxidation of the polymer chain and allows the formation of a polymer in an advanced oxidation state (pernigraniline) with an increased amount of quinoniminic rings.

The oxidation state ($Y$) of the obtained polymer was about 0.583 and both methods gave appropriated values which indicates that the PANI synthesized in APP was obtained in the emeraldine state (Fig. 8).
TABLE II. The IQ/IB ratio, acidic capacity and percent of hydrogen per gram polymer in dependence of the polymerization conditions

<table>
<thead>
<tr>
<th>No. sample</th>
<th>A/O*</th>
<th>A/APP**</th>
<th>IQ/IB meq/g polym.</th>
<th>% H/g dry polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0 °C 25 °C</td>
<td>0 °C 25 °C</td>
</tr>
<tr>
<td>1</td>
<td>4</td>
<td>1/1</td>
<td>0.75 0.78</td>
<td>13.0 12.76</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td></td>
<td>0.83 0.84</td>
<td>13.67 13.24</td>
</tr>
<tr>
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<td>1.33</td>
<td></td>
<td>0.76 0.77</td>
<td>13.96 13.36</td>
</tr>
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<td>1</td>
<td></td>
<td>0.67 0.68</td>
<td>10.55 10.04</td>
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<tr>
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<td>1/2</td>
<td>0.73 0.74</td>
<td>13.48 13.01</td>
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<td>14.53 13.98</td>
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<tr>
<td>16</td>
<td>1</td>
<td></td>
<td>0.87 0.89</td>
<td>15.2 14.44</td>
</tr>
</tbody>
</table>

*A/O – aniline/oxidant; **A/APP – aniline/phenylphosphinic acid

The acid capacity of the samples represent the quantity of base (meq) necessary for the neutralization of one gram of dry polymer and was determined from titration curves. With increasing quantity of oxidant and decreasing amount of acid, the acidic capacity decreases (Table II).

Solubility tests in solvents such as NMP, DMF, DMSO, indicate an enhanced solubility of doped PANI samples obtained in APP compared with the samples obtained in sulfuric acid (AS) under the same conditions. The highest solubility was obtained for PANI samples synthesized at aniline/oxidant mole ratio 2, aniline/acid mole ratio 1/2, at 0 °C (Table III).

The increase in the solubility was attributed to the presence of the voluminous phosphinate anion, which is able to undergo much stronger polymer–solvent interactions than polymer–polymer ones.
TABLE III. Solubility data of doped PANI samples obtained at an aniline/oxidant mole ratio of 2, and an aniline/acid mole ratio of ½ at 0 ºC

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Solvent NMP/g l⁻¹</th>
<th>DMF/g l⁻¹</th>
<th>DMSO/g l⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>–</td>
<td>0.042</td>
<td>0.006</td>
</tr>
<tr>
<td>APP</td>
<td>0.521</td>
<td>0.106</td>
<td>0.232</td>
</tr>
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</table>

The thermal stability of the polymers was studied by TG and DSC; the TG curves for some samples are presented in Fig. 9.

In general, the thermal behavior of PANI samples shows a characteristic “three step” weight loss, as can be seen from the DSC curves illustrated in Fig. 10, which show the endothermic peaks associated with mass loss.

During heating up to 150 ºC, the weight losses associated with the residual water present in all the PANI samples, lie between 5.98 % for PANI-AS (Fig. 9 curve A, B) and 8.82 % for PANI-APP (Fig. 9 curve C, D).

The water molecules are able to occupy dopant sites in polyaniline, hence, the residual water cannot be assumed to be humidity because all the samples were dried before the TG measurements. This process has also been observed by other authors.4,7,11,12–14

The weight loss in the temperature range 150 ºC to 400 ºC varied between 1.09 and 33.24 % for the PANI samples obtained in AS and doped with HSO₄⁻ ions and 15.56 and 24.20 % for the PANI samples obtained in APP and doped with APP. They are related to loss of dopant and degradation of the formed oligomer chains. Increasing the amount of oxidant in the reaction medium results in shorter polymer chain and, thus, the weight loss became higher. The use of a large amount of oxidant induces polymer degradation. With increasing acid concentration, and temperature of synthesis, the weight loss increases, due to an increase of the content of
dopant in the polymer samples. In the same domain, the PANI-APP samples showed two inflexion points, corresponding to the decomposition of the dopant. APP (Fig. 9 curve E) remains stable up to 200 °C, subsequently, the APP starts decomposing gradually up to 410 °C, with two maximum decomposition rates at 239.0 °C and 401.5 °C and with a weight loss of 60.86 % in this domain. The maximum weight loss (24.20 %) was observed for the PANI-APP obtained with an aniline/oxidant mole ratio = 1 and an aniline/APP ratio = 1/2 at 25 °C, and the minimum loss (15.56 %) was observed for the PANI-APP obtained with an aniline/oxidant mole ratio = 1.33 and an aniline/APP ratio = 1/1 at 0 °C.

In general, both the decomposition temperature and the weight loss are affected by the molar mass, and decrease with decreasing molar mass. The thermal stability of PANI synthesized in APP is lower than that obtained in AS. For example, for PANI-AS obtained at an aniline/acid ratio of 1/1 and an aniline/oxidant mole ratio of 1.33, the temperature corresponding to Δm = 50 % was 988.1 °C, and for PANI-APP synthesized under the same conditions, it was 489.2 °C. The 50 % (Δm = 50 %) weight loss for the PANI-AS samples obtained at an aniline/acid ratio of 1/1 and an aniline/oxidant mole ratio of 1.33 and 2 occurs at 988.1 °C and 877.1 °C respectively. This is in accordance with the inherent viscosity values, which are related to the molar weight. It was observed that the decomposition process occurred at higher temperatures with increasing aniline/oxidant mole ratio, due to the corresponding increase of the molar weight, as can be seen from the inherent viscosities (Table I). For the samples synthesized at the higher temperature, 25 °C, the 50 % (Δm = 50 %) weight losses appear at lower temperatures compared with the corresponding sample synthesized at 0 °C, due to the smaller molar weights; the differences were between 200 °C and 300 °C. In this case, the temperature assigned to the maximum decomposition rate varies between 230 °C and 300 °C.

All PANI samples indicate the first endothermic transition at approximately 130 °C, as can be seen in Fig. 10.

The first peak corresponds to the evaporation of water trapped inside the polymer or bonded to the polymer chain. The second and the third peak correspond to endothermic transitions due to the loss of acid dopant (AS and APP) and due to the decomposition of polymer chain starting around 400 °C, respectively.

Comparing the TG data with the DSC data, only for the PANI-APP samples prepared at 0 °C, did an additional peak at about 240 °C appear (Fig. 10 curves C, D), which does not correspond to the weight loss recorded on the thermograms. The presence of this peak can be assigned to the interaction of PANI and dopant, in this case APP, because this additional peak was not observed with the PANI-AS samples.

The maximum rates of weight loss observed on the thermograms correspond with the endothermic peaks on the DSC traces.
CONCLUSIONS

The experimental data show that PANI with a conductivity of 1.5 S cm\(^{-1}\) could be synthesized in APP. The polymerization process requires an induction time 8–10 times higher than in other common acids. The average yield was about 57%.

Fig. 9. Thermogravimetric curves for A: PANI – AS (A/O = 1.33, A/AS = 1/1, 0 °C); B: PANI – AS (A/O = 1, A/AS = 1/1, 0 °C); C: PANI – APP (A/O = 1.33, A/APP = 1/1, 0 °C); D: PANI – APP (A/O = 1.33, A/APP = 1/2, 0 °C); E: APP; F: PANI – AS (A/O = 2, A/AS = 1/1, 0 °C).

Fig. 10. DSC curves for A: PANI – AS (A/O = 1.33, A/AS = 1/1, 0 °C); B: PANI – AS (A/O = 1, A/AS = 1/1, 0 °C); C: PANI – APP (A/O = 1.33, A/APP = 1/1, 0 °C); D: PANI – APP (A/O = 1.33, A/APP = 1/2, 0 °C).
The average density of the PANI-salt was 1.395 g cm⁻³ and that of the PANI-base 1.203 g cm⁻³.

The acid capacity of the PANI samples lay between 13.16–15.02 meq/g polymer.

The inherent viscosity of the PANI samples have maximum values (0.625 – 0.662 dl/g) at an aniline/oxidant mole ratio >2.

The UV-VIS and titration with TiCl₃ data show that the oxidation state of the obtained polymer was about 0.583.

REFERENCES