J Therm Anal Calorim (2009) 97:479–484
DOI 10.1007/s10973-009-0217-y

TG, EGA and kinetic study by non-isothermal decomposition of a polyaniline with different dispersion degree

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ICTAC2008 Conference

Abstract Polyaniline was obtained by oxidizing aniline in hydrochloric acid media with ammonium peroxidisulfate as oxidizing agent. Molar ratio aniline/oxidant was 1 and aniline/acid ratio: ½, at −5 and 400 °C, respectively, 800 mL water. The both compounds were studied using two different experimental strategies: the coupled TG-EGA (FTIR) technique by decomposition in dynamic air atmosphere and the kinetic analysis of TG data obtained at four heating rates (5, 7, 10 and 15 K min^{-1}). The kinetic analysis of the TG non-isothermal data was performed with the Flynn–Wall–Ozawa, Friedman's, and modified non-parametric kinetic (NPK) methods. By means of the coupled techniques spectroscopic arguments on the reaction mechanism were obtained, i.e. the oxidative degradation of the quinoine ring as the first step. The values of the activation energy by the three used methods are in good agreements. According to the NPK method, the termodegradation process consist in physical (diffusion) and chemical steps.

Keywords Coupled TG-EGA · Non-isothermal kinetics · Polyaniline

Introduction

Conducting polymers exhibit a wide range of novel electrochemical and chemical properties that has led to their use in a diverse array of applications including sensors, switchable membrane, anti-corrosive coatings, biosensors, electronic devices and rechargeable batteries [1–3].

Among the conductive polymers, polyaniline (PANI) is one of the most promising candidates for industrial applications due to its good conductivity, special doping mechanism and excellent chemical stability [1–3]. The intercalation in organic–inorganic hibrid compounds is a way to new and attractive materials [4, 5].

PANI is the simple 1,4 coupling product of monomeric aniline molecules, with the general formula:

$$-\left[(\mathrm{B}-\mathrm{N}=\mathrm{Q}=\mathrm{N})_y(\mathrm{B}-\mathrm{NH}-\mathrm{B}-\mathrm{NH})_{1-y}\right]_{n^-} \qquad (1)$$

where B is the benzene ring, Q the quinoine ring and y is the degree of oxidation ($0 \le y \le 1$)

The oxidation degree can be continuous modified, from the total reduced polymer, $y = 0$ (leucoemeraldine), through the half oxidized polymer, $y = 0.5$ (emeraldine), until the total oxidized polymer, $y = 1$ (pernigraniline) [6].

The PANI forms with $y \neq 0$ can be protonated by non-oxidizing acids, the protonation taking place on the imine nitrogen atoms [7].

Because thermal stability of PANI presents importance in materials manufacturing papers on this subject and reports of some correlations with synthesis conditions, based on thermogravimetic and differential scanning calorimetric analyses were published. Usually PANI undergoes several stages of weight loss associated with the release of water, dopant and chain decomposition [8–10].

Aniline polimerization is an exothermic process, the decomposition and crosslinking being influenced by some preparative parameters.

The topic of this work is to investigate the thermal behavior of a PANI in air atmosphere under non-isothermal

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conditions. The attention is focused on the influence the surface-to-volume ratio named as dispersion degree, an important characteristic by materials manufacturing. Because the polyaniline materials are sensitive in respect to oxygen and these materials will be used in air, the study on the thermal behavior was performed under dynamic air atmosphere.

Experimental

Synthesis

The sample were obtained by oxidizing freshly distilled reagent grade aniline (Chemopar Bucharest) in hydrochloric acid (Sigma Aldrich) medium with ammonium peroxidisulphate (Aldrich) as oxidizing agent. The molar ratio aniline:oxidant:acid was 1:1:2.

The dispersion degree was regulated by the amount of water used as reaction medium for a reaction mixture based on 0.4 mol of aniline. ESM1 was obtained in a volum of 800 cm^3 water, ESM2 in 400 cm^3, respectively.

In both cases the procedure was as follows:

- first the aniline salt is formed by the drop-wise addition of aniline in the aqueous solution of the acid, under vigorous stirring and cooling near 0 °C;
- a precooled aqueous solution of oxidant is drop-wise added under the same stirring;
- after the addition of the oxidant, the polymerization take place at -5 °C in 24 h;
- PANI is recovered by filtration, is washed several times with a dilute acid solution and dried in dynamic vacuum for 24 h.

In these conditions the oxidation degree was $y = 0.55$ and was determined by redox titration with $TiCl_3$ in 80% acetic acid.

Thermal analysis

The thermoanalytical curves, i.e. TG, DTG and heat flow (HF), were obtained on a Perkin-Elmer Diamond (TG/DTG/DTA) device, using Al crucibles in a dynamic air atmosphere (100 $cm^3\ min^{-1}$). The heating rates were 5, 7, 10, 15 and 20 °C min^{-1}.

Evolved gas analysis

The furnace of the thermobalance was coupled, by means of a Transfer Line (max. 10 s of delay) to the Gass-Cell of a Perkin Elmer Spectrum 100 device. The evolved gases were identified using a Gas Vapour Library (Sadtler Spectral Databases).

Results and discussions

Thermoanalytical curves

In Fig. 1 two typical curves are depicted. Some observations are noticeable:

- the both samples presents a good thermal stability; until 300 °C neither a thermal event observed;
- up to 300 °C a continuous and total mass loss take place, with an exothermal effect; it means that a thermooxidative degradation occurs;
- the maximum of DTG is with approximatively 100 °C higher than the maximum of the heat flow curve; this indicate a strong exothermic step at the begining of the thermal degradation.

At this step no significant differences between the two samples were observed. This means that the thermal behavior, is so far as it is characterized only by a TG/DTG/DTA diagram is sensitive in respect of the dispersion degree.

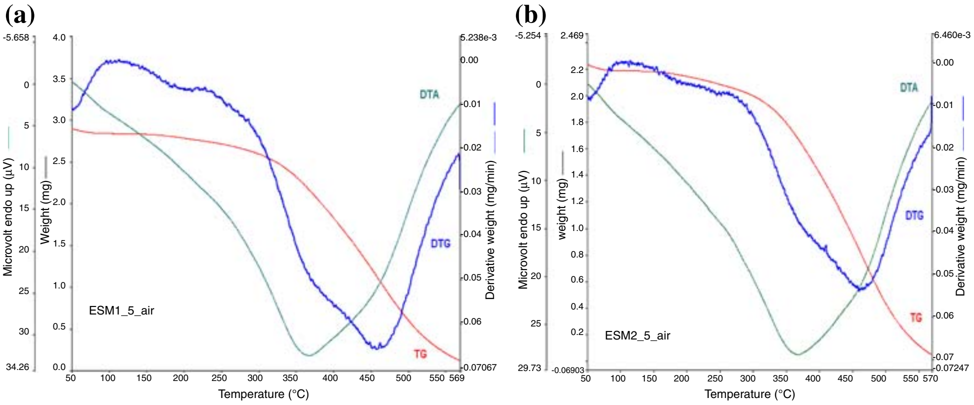


Fig. 1 The thermoanalytical curves for **a** ESM1; **b** ESM2 in air at heating rate 5 °C min^{-1}

Evolved gas analysis data

Supplementary informations from the evolved gas analysis (EGA) were expected. After connecting the transfer line and increasing the heating rate to 20 °C min^{-1}, the shape of the thermoanalytical curves was significantly changed (see Fig. 2). The four steps are very well separated.

The characteristics and the interpretation of these steps are systematized in Table 1. Even if the TG curve of ESM2 do not present well-definited steps (in comparison with ESM1), by inspecting the data in Table 1, a general thermodegradation mechanism, valuable for both samples, can be suggested:

(i) The thermooxidative degradation of the polymeric chain begin with the destruction of the quinoine ring; the observed exothermic effect is very high due to the high value of the enthalpy of formation for carbon dioxide and water ($\Delta H^0_{\mathrm{fCO_2}} = -394$ kJ mol^{-1}, $\Delta H^0_{\mathrm{fH_2O}} = -242$ kJ mol^{-1}). The presence of carbon dioxide in the evolved gass is supported by the spectra in Fig. 3.

(ii) Successive and parallel with the step (i), the degradation of amino/imino group takes place with the formation of nitrous oxide; the benzene appears in the evolved gases and is not oxidated due to the intrinsic thermal stability of the benzene ring and the small contact time of the evolved gases with the hot zone of the device. The presence of benzene and nitrous oxide in the evolved gass is assigned according to Fig. 4.

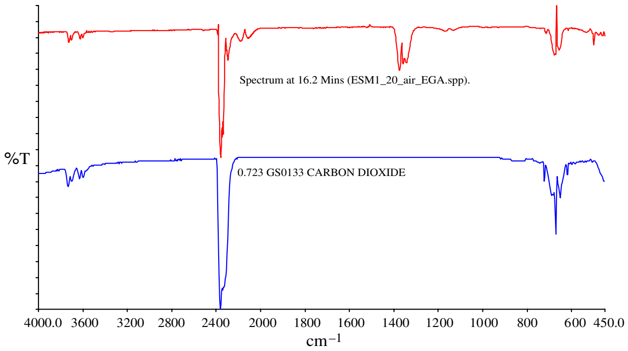


Fig. 3 Evolved gass spectrum at 360 °C (16.2 min) and the reference for carbon dioxide

Up to 450 °C a deep thermodegradation occurs and the composition of the evolved gass is more complicated, but benzene, carbon dioxide and nitrous oxide are present (see Fig. 5)

The dehidration step is not relevant for the thermodegradation mechanism; it is more important for synthesis.

The EGA data offer significant data for at first suggestions regarding the thermooxidative degradation of PANI, but not relevant differences by the two samples were

Fig. 2 The thermoanalytical curves at 20 °C min^{-1} obtained with connection of the transfer line to the IR gas cell: **a** ESM1, **b** ESM1

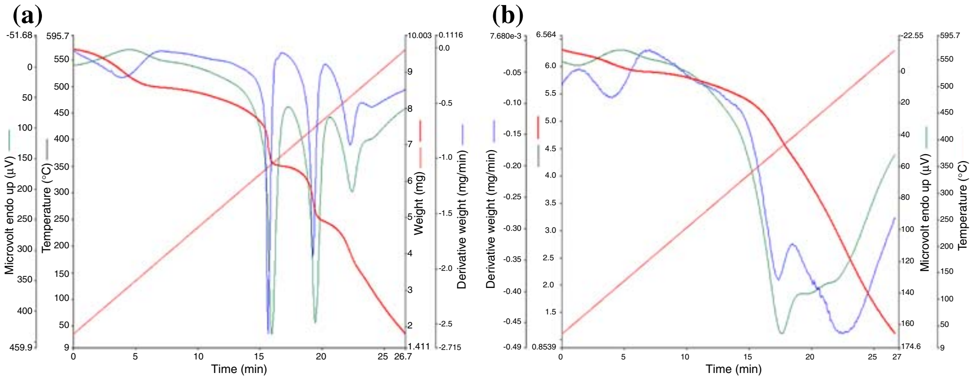


Table 1 Characteristics of the thermodegradation steps

Sample	Step	Heat flow max (°C)	Mass loss[a] (%)	Evolved gasses, assigned according to the FT-IR spectra of figures
ESM1	I	Endo 120	11.2	Water
	II	Exo 360	23.5	Carbon dioxide, see Fig. 3
	III	Exo 430	15.3	Benzene, nitrous oxide, see Fig. 4
	IV	Exo 480	>40	Benzene, carbon dioxide, nitrous oxide, see Fig. 5
ESM2	I	Endo 120	5.6	Water
	II	Exo 380		Carbon dioxide
	III	Exo 470	>90	Benzene, nitrous oxide

[a] $\Delta m_{\mathrm{s}}(\%) = \frac{m_{\mathrm{bs}} - m_{\mathrm{es}}}{m_{\mathrm{i}}}$; where $\Delta m_{\mathrm{s}}(\%)$ is the relative mass loss by step s, m_{bs} and m_{es} is the mass at the beginn, respectively, end of the step s, m_{i} is the initial mass of the studied sample

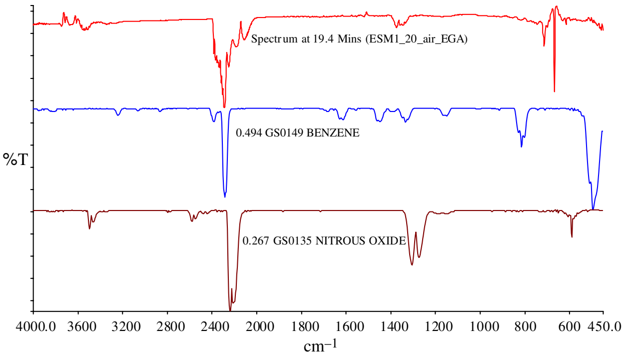


Fig. 4 Evolved gass spectrum at 430 °C (19.4 min) and the reference for benzene and nitrous oxide

observed. Therefore, a kinetic analysis of the TG data is necessary.

Kinetic analysis

The above mentioned TG/EGA data offer an image on the mechanism of the thermooxidative degradation of PANI, without any significant differences in relation with the dispersion degree. These differences are expected to be observed especially by the kinetic parameters. Therefore a kinetic analysis is compulsory.

The data processing strategy is based on the recommendation of the ICTAC 2000 Protocol [11], the used methods being essentialy isoconversional: the integral method of Flynn–Wall [12] and Ozawa [13] (FWO), the differential method of Friedman [14] (FR) and the modified non-parametric kinetic (NPK) [15]. This strategy was succesfully used in some of our previous paper [16–18].

The FWO method is based on the equation

$$\ln \beta = \ln \frac{A}{R \cdot g(\alpha)} - 1.052 \frac{E}{RT} - 5.331 \tag{2}$$

where $g(\alpha) = \int_0^\alpha \mathrm{d}\alpha / f(\alpha)$ is the integral conversion function, α—the conversion degree, β—the heating rate, T—the reaction temperature and E, A—the activation energy, respectively, the pre-exponential factor in sense of the Arrhenius equation. Being an integral method, the FWO method take into consideration the “history” of the sample, therefore a mean value is relevant if the variation of E versus α is not significant, and this is our case (see Fig. 6).

The FR method is essentially a differential method:

$$\ln\left(\beta \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln[A \cdot f(\alpha)] - \frac{E}{R \cdot T} \tag{3}$$

and reveals the dependence of E versus α. According to Fig. 7 this dependence is not significant and non-monotonous, so that a mean value is relevant.

By the NPK method, the reaction rate surface expressed by

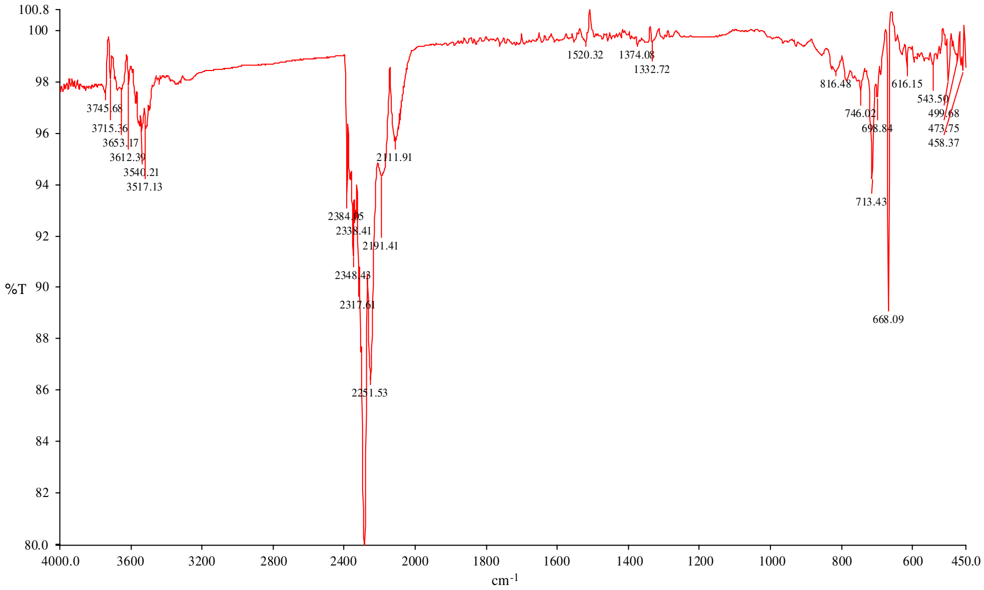
$$r = f(T) \cdot g(\alpha) \tag{4}$$

and obtained by interpolation of the experimental data, is discretizated into a square matrix M using the Singular Value Decomposition algorithm [19]:

$$M = U(\mathrm{diag} \cdot s)V^T \tag{5}$$

The u_1 vector, given by the first column of U is analyzed for the dependence on α; we suggest the Šestak–Berggren equation [20]:

Fig. 5 Evolved gass spectrum at 480 °C (22.3 min)



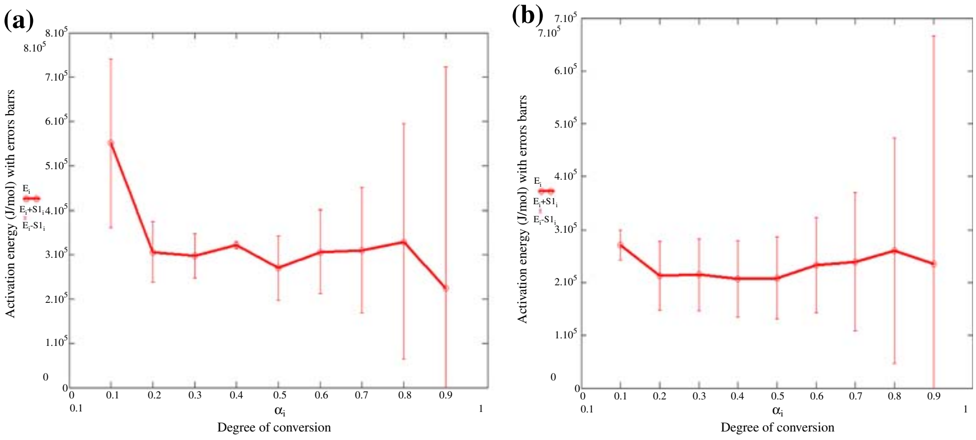


Fig. 6 E versus α variation according to FWO method: **a** ESM1, **b** ESM 2

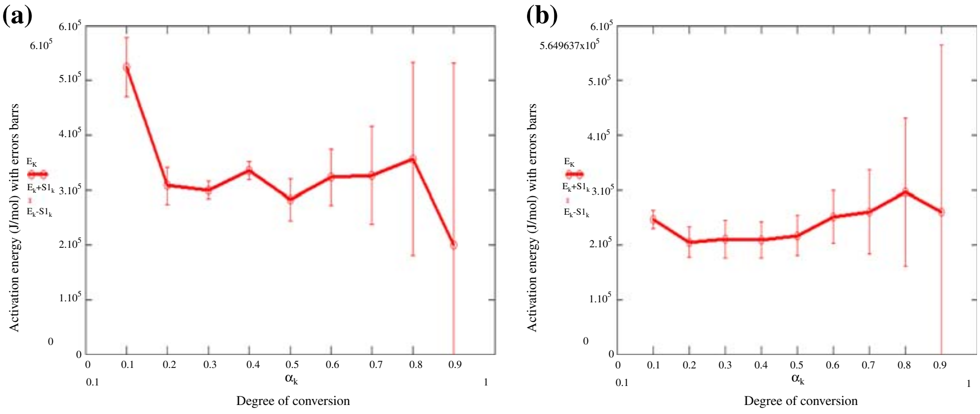


Fig. 7 Dependence of E versus α, according to FR method: **a** ESM1, **b** ESM2

$$g(\alpha) = \alpha^m (1-\alpha)^n \tag{6}$$

A similar vector v_1, corresponding to V, is checked for an Arrhenius temperature dependence.

By multi-step processes the matrix M became

$$M = \sum M_i \tag{7}$$

and the contribution of each step i is expressed by the explained variance λ_i, so that $\sum \lambda_i = 100\%$. The minimum threshold of significance is considered a value $\lambda \geq 10\%$. The most important data of the kinetic analysis are summarized in Table 2.

Regarding the FWO and FR methods, both give rather the same value of activation energy for the same sample, and the values corresponding to ESM1 is with 90 kJ mol^{-1} higher in comparison with the values for ESM2.

The NPK method offers more details. The thermooxidative degradation is a complex process with two significant steps. The values of the activation energy of the first step are very near to the corresponding values by FWO and FR methods. By inspecting the values of λ, m and n in Table 2, an increasing of the contribution of the second step with the increasing of the PANI dispersion degree was observed and also the contribution of the physical phenomenon became important ($m \geq 2$).

Table 2 Results of the kinetic analysis

Sample	Initial aniline conc.(mol L^{-1})	Mean value of E (kJ mol^{-1})		Parameters by NPK				
		FWO	FR	λ (%)	E (kJ mol^{-1})	A (min^{-1})	m	n
ESM1	0.5	324.0	328.5	56.4	344.3	8.23×10^{23}	5/2	1
				36.7	201.4	1.78×10^{11}	2	0
ESM2	1.0	231.4	239.7	80.2	221.0	2.51×10^{15}	0	2
				15.5	227.6	1.55×10^{15}	0	5/2

Conclusions

Polyaniline presents good thermal stability in air until 300 °C; up this temperature the thermooxidative proces starts with the degradation of the quinoine ring.

Under non-isothermal conditions the very exothermic oxidation to carbon dioxide is observed by a maximum of the Heat Flow curve with 100 °C before the maximum of the reaction rate was attained. Even if at normal pressure the thermooxidative degradation is continuous and total, by increasing the reaction pressure (due to the gas transfer line) a splitting of the process into three or four steps was observed.

Regarding the influence of the dispersion degree, only by means of a kinetic analysis were observed different thermal behavior of the samples. By the three used kinetic methods very near values for the activation energy were obtained. The values of the activation energy increases with increasing the dispersion degreee, and this is due to a higher contribution of diffusive phenomenons. The NPK method allowed an objective analysis of the relevance and the kinetics of the two elementary steps of the complex oxidative thermodegradation process.

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