Thermochimica Acta 502 (2010) 43–46

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermo-analyses of polyaniline and its derivatives

William F. Alves[a,b], Everaldo C. Venancio[c,*], Fabio L. Leite[d], Darcy H.F. Kanda[e], Luiz F. Malmonge[e], José A. Malmonge[e], Luiz H.C. Mattoso[a,b]

[a] EMBRAPA Instrumentação Agropecuária, C.P. 741, São Carlos (SP), 13560-970, Brazil
[b] Dept. Química, Universidade Federal de São Carlos (UFSCar), São Carlos (SP), 13565-905, Brazil
[c] Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas (CECS), Universidade Federal do ABC (UFABC), Santo André (SP), 09210-170, Brazil
[d] Universidade Federal de São Carlos (UFSCar), C.P. 3031, Sorocaba (SP), 18052-780, Brazil
[e] Dept. Física e Química, Universidade Estadual Paulista Julio de Mesquita Filho, Ilha Solteira (SP), 15385-000, Brazil

ARTICLE INFO

Article history:
Received 21 August 2009
Received in revised form 6 January 2010
Accepted 2 February 2010
Available online 16 February 2010

Keywords:
Polyaniline
DSC
TGA
Poly(*o*-methoxyaniline)
Poly(*o*-ethoxyaniline)

ABSTRACT

In this work, is presented the thermal behavior of polyaniline (PANI) and its derivatives poly(*o*-ethoxyaniline) (POEA) and poly(*o*-methoxyaniline) (POMA), which were studied by using differential scanning calorimetry (DSC), modulated DSC (TMDSC), respectively, and thermal gravimetric analysis (TGA). The results from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and thermal analysis showed the formation of crosslinking isomerization reaction during the heating process. The results showed that the maximum weight loss and the crystallinity degree depend on the type of the aromatic ring substituent group, *i.e.* hydrogen, ethoxy or methoxy.

1. Introduction

Polyaniline (PANI) and its derivatives, *e.g.*, poly(*o*-methoxyaniline) (POMA) and poly(*o*-ethoxyaniline) (POEA) [1,2] have been intensively studied due to their electrical and optical properties associated with low costs, easy processability, its environmental stability and relatively simple method of synthesis [3,4]. The thermal analysis of conducting polymers, *i.e.* PANI, POMA and POEA, is crucial to define their performance on application processes of these materials [5]. Thus, thermal analysis of conducting polymers provides important information about the effect of morphological structure and other process, such as chemical reaction, which are sensitive to thermal effects (temperature changes), *e.g.*, crosslinking reaction processes among PANI chains. These processes have been studied by differential scanning calorimetry (DSC) [6–8] and dynamical mechanical thermal analysis (TDMTA) [9–12].

In this work, the glass transitions (T_g) for the chemically synthesized non-conducting form of PANI, POMA and POEA, in the powder form, were studied using modulated DSC (MDSC). The hypothesis of that a chemical crosslinking reaction occurs during the heating process was further confirmed by supporting experimental methods such as diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), DSC and TGA.

2. Experimental

PANI, POMA and POEA were chemically synthesized according to the method described in the literature [13,14]. The polymer obtained was a dark precipitate, with expected average molecular weight (M_W) of ~41,400 g mol^{-1} and polydispersivity (M_W/M_n) of 2.3. Dedoping was performed by treatment with a 0.1 M ammonium hydroxide aqueous solution for 16 h at room temperature (~25 °C) to yield the polymer in the emeraldine base form (EB). The polymer was then transferred to a glass desiccator without desiccant agent and then dried under dynamic vacuum for 24 h at room temperature (~25 °C).

A model Q 600 TA Instruments TGA was used to investigate the thermal stability of the polymers in the powder form in the temperature range from 25 to 900 °C, under N_2 gas atmosphere (50 ml/min), for the thermal treatment the system was first equilibrated at 220 °C for 1 h under N_2 gas atmosphere (50 ml/min). After the thermal treatment of PANI (EB), POMA (EB) and POEA (EB) the DRIFTS spectra were performed on a fully computerized Nicolet *NEXUS*® 670 using the software OMNIC. All the DRIFTS spectra

* Corresponding author at: Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas (CECS), Universidade Federal do ABC (UFABC), Rua Santa Adélia 166, Bairro Bangu, Santo André (SP), 09210-170, Brazil. Tel.: +55 11 49963166; fax: +55 11 49963166.
E-mail address: everaldo.venancio@ufabc.edu.br (E.C. Venancio).

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.02.003

were recorded on a Nicolet *NEXUS*® 670 spectrometer at a resolution of 1 cm^{-1} and using 64 scans. The temperature ramp used was 10 °C/min. In all experiments, PANI and its derivatives were present in equal amount, the total weight being at about 8.0 ± 1.0 mg. The thermal treatment of the EB powder was carried out by using a 2920 DSC Thermal Analysis under nitrogen gas purge (50 ml/min) and a heating rate of 10 °C/min, where the system was first equilibrated at −50 °C and then heated up to 150 °C. After the first run with the equipment on the DSC mode, the DSC Thermal Analysis equipment was switched to the TMDSC mode and then all subsequent runs were done with the DSC Thermal Analysis equipment in the modulated DSC (TMDSC) mode by using a 2920 modulated DSC. The TMDSC experiments were carried out as follows: the system was first equilibrated at −50 °C for 5 min, and then it was heated up to 150 °C using a heating rate of 5 °C/min with a period modulation of 60 s, and the temperature amplitude of modulation was ±1.0 °C.

The as prepared powder of the EB form of the samples, *i.e.* PANI, POMA and POEA, were treated at different temperature ranges as follows. It was used a 2920 DSC Thermal Analysis under nitrogen gas purge (50 ml/min) and a heating rate of 10 °C/min, where the system was first equilibrated at −50 °C and then heated up to T_2. The samples were then kept at T_2 for 2 h under N_2 gas atmosphere (50 ml/min). The thermal treatment was carried out at different temperatures, T_2 = 25, 50, 100, 150 and 220 °C, respectively. After the thermal treatment, 1.3 mg of the sample was dissolved in dimethylacetamide (DMAc) and then the UV–VIS spectra were recorded using a fully computerized Shimadzu spectrophotometer, model UV-1601PC, in a wavelength range of 900–250 nm.

3. Results and discussion

Fig. 1 shows the DRIFTS results for emeraldine base (EB) powder of PANI, POMA and POEA. The samples analyzed, with and without thermal treatment, showed differences in DRIFTS spectra, such as an increase in the absorption band at ∼1520 cm^{-1}, which is due to the axial bending of the benzoid–nitrogen (B–N) chemical bond, and a decrease in the absorption band at ∼1600 cm, which is due to the axial bending of the quinoid–nitrogen (Q–N) chemical bond. This result indicates the conversion of quinoid-like structures to benzoid-like structures due to the crosslinking isomerization reaction [15].

Fig. 2 shows the weight loss (TGA) of PANI, POMA, and POEA during heating treatment from room temperature (25 °C) up to 900 °C carried out under inert atmosphere (N_2). It can be observed a weight loss between 25 and 120 °C due to the removal of adsorbed water molecules [16–19], *i.e.*, 6 wt.% for PANI, 4 wt.% for POMA, and 1 wt.% for POEA, respectively. The weight loss observed between 382 and 640 °C (PANI), 300 and 600 °C (POMA), and 268 and 600 °C (POEA), respectively, are due to the polymer degradation. The differences observed for PANI (T_i = 382 °C), POMA (T_i = 300 °C) and POEA (T_i = 382 °C) for the thermal degradation temperature (T_i) are related to the crosslinking isomerization process that is taking place prior beginning of the degradation process. The crosslinking process might be affected by the size of the alkoxy substituent and subsequently the degradation process upon the thermal treatment. However, from these results it is not possible to state that the crosslinking process occurs through a different mechanism for the different types of polymer, *i.e.* PANI, POMA, and POEA. The presence of the alkoxy groups, *i.e.* methoxy (POMA) and ethoxy (POEA), results in a steric effect, which blocks the crosslinking chemical reaction. In the PANI system, where the monomer aromatic ring does not contain any alkoxy group, the crosslinking isomerization reaction proceeds as expected, *i.e.* the degree of crooslinking in polyaniline system is much higher than on POMA and POEA systems. These results suggest that the crosslinking isomerization process enhances the thermal stability of the polymer as it could be observed from the results presented in Fig. 2a. Fig. 2b shows a higher weight loss rate (maximum derivative value as shown in the dot line curve) for POEA, which indicates that there is also an effect of the size of the alkoxy group on the thermal stability of the polymer, *i.e.* larger alkoxy groups results in a polymer with lower thermal stability.

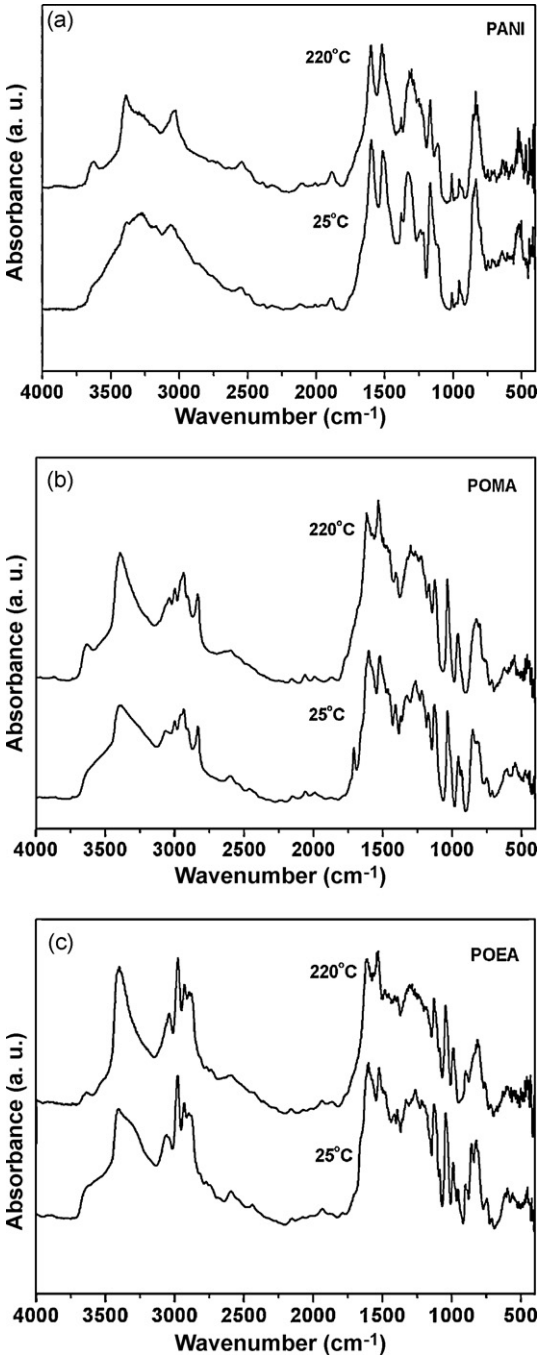

Fig. 1. DRIFTS spectra of (a) PANI, (b) POMA and (c) POEA, recorded without (room temperature, 25 °C) previous thermal treatment and after thermal treatment at 220 °C during 1 h under nitrogen (N_2) gas atmosphere. Temperature ramp: 10 °C/min.

Fig. 3 shows the DSC results (first scan) for PANI, POMA, and POEA, it can be observed two peaks in Fig. 3. The first peak, endothermic, with a maximum at ∼120 °C for PANI and POMA, and ∼110 °C for POEA, is due to removal of adsorbed water [20]. The second peak, exothermic, observed between 175 and 350 °C,