Thermo-analyses of polyaniline and its derivatives

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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

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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
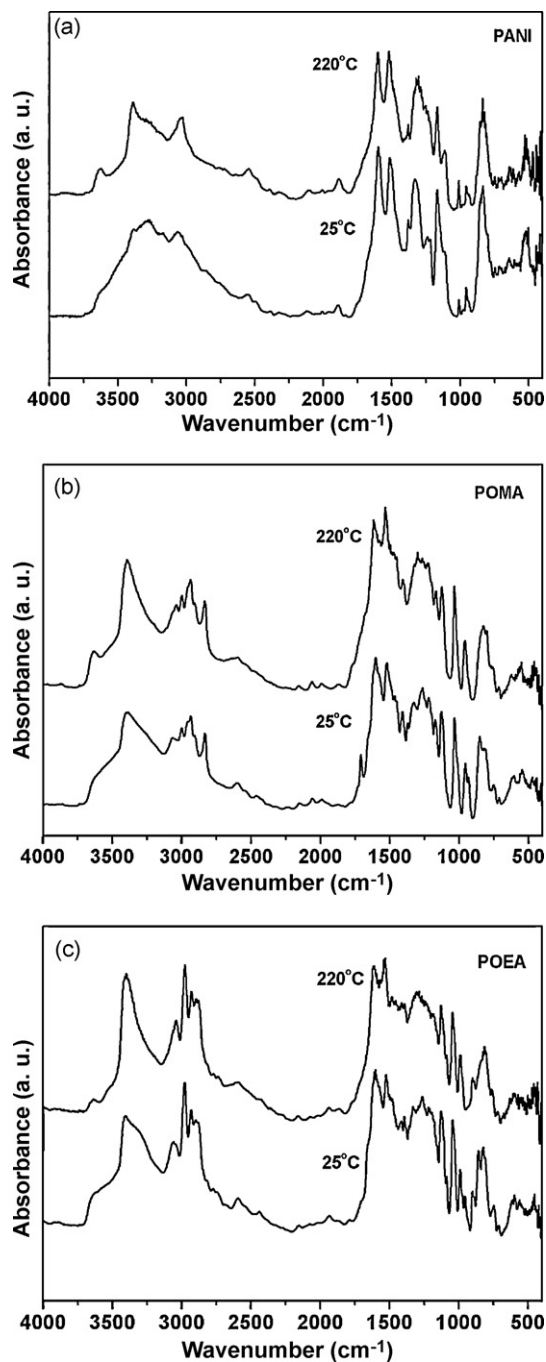

Fig. 1. DRIFTS spectra of (a) PANI, (b) POMA and (c) POEA, recorded without (room temperature, 25 °C) previous thermal treatment and after thermal treatment at 220 °C during 1 h under nitrogen (N$_2$) gas atmosphere. Temperature ramp: 10 °C/min.

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. 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,
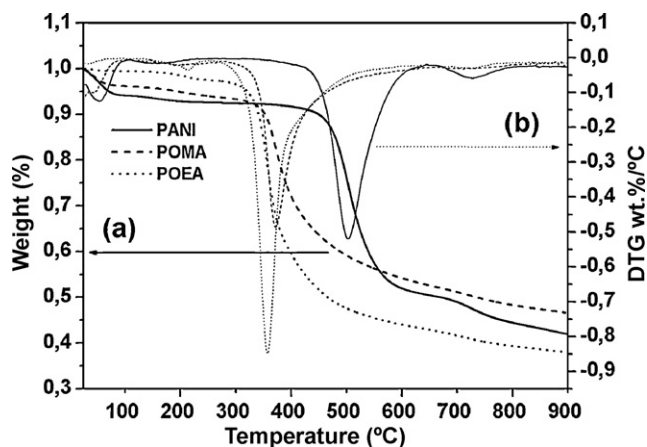
Fig. 2. Weight loss (TGA) (a) and derivative thermal gravimetric analysis (DTG) (b) results for PANI (solid line), POMA (dot line), and POEA (dash line), respectively. TGA temperature ramp: 10 °C/min under nitrogen gas (N₂) atmosphere.
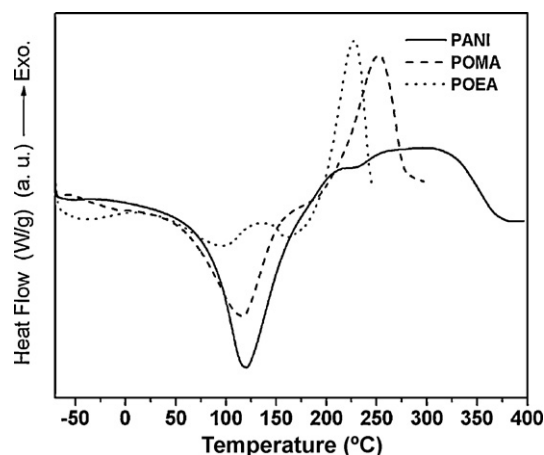

Fig. 3. DSC results for PANI, POMA, and POEA. DSC temperature ramp: 10 °C/min under nitrogen gas (N₂) atmosphere.

might be due to re-crystallization followed by crosslinking isomerization reaction (see schema of Fig. 4) [21,22]. Fig. 5 shows the UV–VIS spectra for samples of the EB form of PANI, POMA and POEA, treated at different temperature ranges, which were then dissolved in DMAc. These results (Fig. 5) show that the solubility of the treated samples in DMAc decreased after the thermal treatment done at $T_2 = 150$ °C and $T_2 = 220$ °C, which agree with the results presented in Fig. 3, which indicates that, even at $T_2 = 150$ °C, the crosslinking isomerization reaction might occur. The samples treated at $T_2 = 100$ °C showed no differences compared to the samples treated at $T_2 = 25$ °C. The sample treated at $T_2 = 220$ °C is insoluble in DMAc, which indicates that the extent of the crosslinking isomerization reaction is significant at $T_2 = 220$ °C.

The glass transition temperature (T_g) of PANI, POMA and POEA was determined by combining DSC and TMDSC. The adsorbed water

was first removed from the sample by heating the sample from room temperature (25 °C) up to 150 °C (heating rate of 10 °C/min) under nitrogen gas atmosphere, which was done by using the DSC technique in order to verify the water content removal (Fig. 6a). After the sample has reached the room temperature, it was then heated up from room temperature to 150 °C (heating rate of 5 °C/min) by using TMDSC technique (Fig. 6b). As it can be seen from Fig. 5b there is a baseline change in the TMDSC curve at ∼67 °C. The changes in the baseline might be due to structural changes in the polymer morphology due to the thermal treatment, *i.e.* the sample presented a glass transition after the thermal treatment, where the values for the glass transition temperature (T_g) are T_g(PANI) = 67 °C, T_g(POMA) = 68 °C, and T_g(POEA) = 70 °C, respectively. Similar results were observed by Ding et al. [15], where they reported a glass transition for PANI emeraldine base from TMDSC technique measurements.
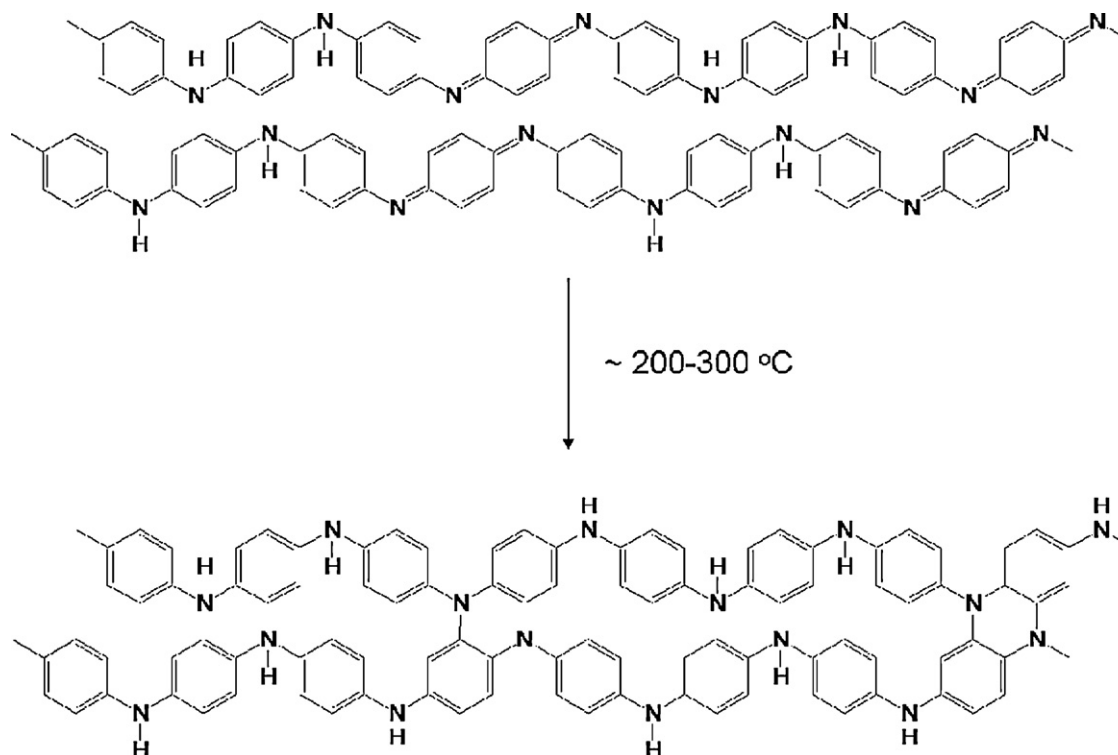
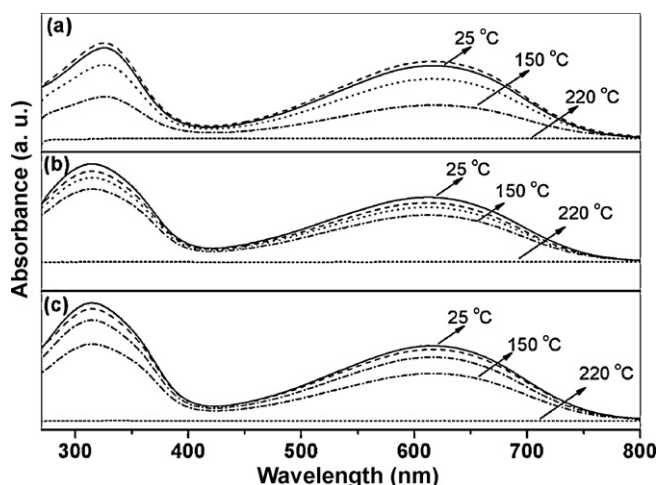**Fig. 4.** Scheme of PANI crosslinking isomerization reaction [15].

Fig. 5. UV–VIS spectra for samples of EB form of (a) PANI, (b) POMA and (c) POEA dissolved in dimethylacetamide (DMAc). The samples were treated at different temperatures, as indicated in the figure, prior dissolving in the solvent (DMAc). The UV–VIS spectra were recorded at room temperature (25 °C).
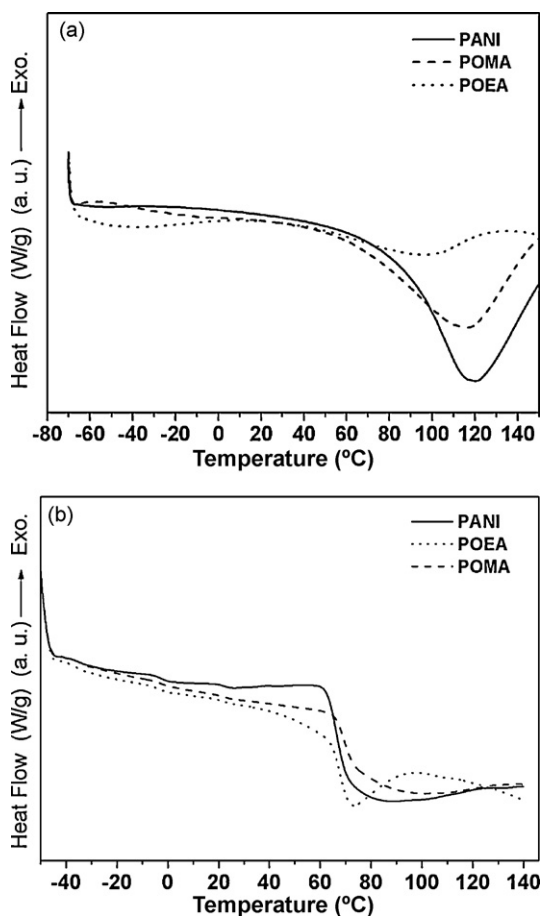

Fig. 6. Thermal analysis results for PANI, POMA, and POEA, under nitrogen gas atmosphere. (a) DSC measurements results from room temperature (25 °C) up to 150 °C; the samples were then cooled down to room temperature under nitrogen gas atmosphere before doing the TMDSC measurements. (b) TMDSC measurement results from room temperature (25 °C) up to 150 °C.

4. Conclusions

The thermal behavior of polyanilines, *i.e.* PANI, POMA, and POEA, in the form of emeraldine base, measured by using DSC and TMDSC techniques, might indicate that the crystallization and re-crystallization temperatures of POMA and POEA are lower than for PANI. This behavior is due to the presence of the alkoxy groups in the monomer aromatic ring. No change in the T_g values was observed in amorphous phase of the polymers, *i.e.* PANI, POMA, and POEA. The crosslinking isomerization reaction plays an important role on the polymer thermal stability. The combined results from DRIFTS and thermal analysis (TGA, DTG, DSC, and TMDSC) showed that PANI has higher thermal stability compared to POMA and POEA, which indicates the effect of the presence of alkoxy groups in the POMA and POEA systems on the crosslinking isomerization process. We believe that the extent of the crosslinking isomerization process is responsible for the higher thermal stability presented by PANI.

References

[1] F.L. Leite, L.G. Paterno, C.E. Borato, P.S.P. Herrmann, O.N. Oliveira, L.H.C. Mattoso, Polymer 46 (2005) 12503.
[2] W.F. Alves, D.H.F. Kanda, L.F. Malmonge, J.A. Malmonge, L.H.C. Mattoso, J. Appl. Polym. Sci. 105 (2007) 706.
[3] J.P.H. Lima, A.M. De Andrade, J. Mater. Sci.: Mater. Electron. 17 (2006) 593.
[4] E. Erdem, M. Karakisla, M. Saçak, Eur. Polym. J. 40 (2004) 785.
[5] W. Pan, S.L. Yang, G. Li, J.M. Jiang, Eur. Polym. J. 41 (2005) 2127.
[6] E.S. Matveeva, R.D. Calleja, V.P. Parkhutic, Synth. Met. 72 (1995) 105.
[7] X.-H. Wang, Y.-H. Geng, L.-X. Wang, X.-B. Jing, F.-S. Wang, Synth. Met. 69 (1995) 263.
[8] G. Aysegül, S. Bekirb, T. Muzaffer, Synth. Met. 142 (2004) 41.
[9] S. Chen, H. Lee, Macromolecules 26 (1993) 3254.
[10] A.J. Milton, A.P. Monkman, Synth. Met. 57 (1993) 3571.
[11] Y. Wei, G. Jang, K.F. Hsueh, Polymer 33 (1992) 314.
[12] Y. Wei, G. Jang, K.F. Hsueh, E.M. Scherr, A.G. Macdiarmid, A.J. Epstein, Polym. Mater. Sci. 61 (1989) 916.
[13] D. Gonçalves Jr., D.S. Dos Santos, L.H.C. Mattoso, F.E. Karasz, L. Akcelrud And, R.M. Faria, Synth. Met. 90 (1997) 5.
[14] L.H.C. Mattoso, S.K. Manohar, A.G. Macdiarmid, A.J. Epstein, J. Polym. Sci. Part A: Polym. Chem. 33 (1995) 1227.
[15] E.M. Scherr, A.G. Macdiarmid, S.K. Manohar, J.G. Masters, Y. Sun, X. Tang, M.A. Druy, P.J. Glatkowski, V.B. Cajipe, J.E. Fischer, K.R. Cromack, M.E. Jozefowicz, J.M. Ginder, R.P. McCall, A.J. Epstein, Synth. Met. 41 (1991) 735.
[16] L. Ding, X. Wang, R.V. Gregory, Synth. Met. 104 (1999) 73.
[17] V.G. Kulkarni, L.D. Campbell, W.R. Mathew, Synth. Met. 30 (1989) 321.
[18] D. Tsocheva, T. Zlatkov, L. Telemezyan, J. Therm. Anal. 53 (1998) 895.
[19] M.C. Gupta, S.S. Umare, Macromolecules 25 (1992) 138.
[20] W.A. Gazotti, M.A. De Paoli, Synth. Met. 80 (1996) 263.
[21] N.C. de Souza, J.R. Silva, J.A. Giacometti, O.N. Oliveira Jr., Thermochim. Acta 441 (2006) 124.
[22] H.S.O. Chan, L.M. Gan, T.S.A. Hor, S.H. Seow, L.H. Zhang, Thermochim. Acta 1 (225) (1993) 75.