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H-bonding in entrapped water in poly(*o*-methoxyaniline): Results from a differential scanning calorimetry study

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Abstract

Differential scanning calorimetry (DSC) was used to investigate entrapped water in poly(*o*-methoxyaniline) (POMA) in powder form. Two endothermic peaks were attributed to removal of water molecules that were adsorbed with distinct energies. By obtaining thermograms at various heating rates, we succeeded in applying Kissinger's approaches to estimate activation energies for the water adsorbed. The values obtained were ca. 25 and 53 kJ/mol, which correspond to H-bonding interactions, probably at the amine and imine centers of POMA, respectively.

Keywords: Poly(*o*-methoxyaniline); H-bonding; Entrapped water; Differential scanning calorimetry

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1. Introduction

The adsorption process of poly(*o*-methoxyaniline) in layer-by-layer (LBL) films has been studied in detail in the recent years [1–5], with particular emphasis on the driving forces for adsorption. In addition to the ionic interactions that are inherent in the paradigm of the LBL technique, H-bonding has also been shown to occur for several polymers [6,7], including parent polyaniline [8] (PANI) and poly(*o*-methoxyaniline) (POMA) [1]. Using experiments with thermally stimulated desorption of POMA layers, Raposo and Oliveira [1] calculated activation energies for adsorption corresponding to three types of interaction: ionic attraction, H-bonding and van der Waals interactions. The importance of H-bonding was also clear in the results where an efficient adsorption of polyanilines was obtained from solution pHs at which the polymer was not doped [8]. In the latter case, ionic attraction could not be responsible for adsorption, which was attributed to H-bonding. Furthermore, H-bonding leads to non-self-limited adsorption of polyanilines [8], in which adsorption of the same polymer continued indefinitely when the substrate + film was immersed several times in the polymer-containing solutions and rinsed in between two immersion steps. H-bonding is usually demonstrated with FTIR spectroscopy of the LBL films, and has been suggested to be associated with entrapped water in the polymer film, even in cases where the film is dried. In PANI water molecules are believed to form H-bonds with the acid groups of the polymer. Two possible ways have been proposed for water to adsorb onto PANI [9–11].

In this work we investigate the adsorption of water molecules in doped POMA via differential scanning calorimetry. Measurements are carried out for POMA in the form of powder, which allows a detailed study of adsorption energies. The activation energy was determined by means of Kissinger [12] method.

2. Experimental details

POMA was synthesized according to the procedures established by Mattoso and Bulhões [13] in the powder form. The DSC measurements were performed with a DSC 2090 from TA Instruments. Samples of POMA in the form of powder and with ∼30 mg were introduced into sealed aluminum pans and DSC runs were taken with heating rates of 3, 5, 8, 10, 13 and 17 °C/min, between 50 and 300 °C, under nitrogen purge. Calibration for the temperature was carried out using an indium standard, melting temperature of 156.6 °C, on every other run to ensure accuracy and reliability of the data obtained. X-ray diffraction data were obtained for samples of POMA powder with a Rigaku Rotaflex Ru 200B diffractometer in a

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multipurpose chamber with a RINT2000 goniometer. Measurements were taken by changing the 2θ angle at 1°/min from 5° up to 60° in order to investigate the crystallization properties.

3. Results and discussion

POMA powder was encapsulated in aluminum crucibles and subjected to heating–cooling cycles with various heating rates (α). Fig. 1 shows a thermogram obtained at $\alpha = 10\,^\circ$C/min with exothermic and endothermic peaks. Because POMA is hygroscopic, the glass transition may be masked by endothermic reactions if the transition temperature, T_g, occurs in the same region of irreversible reactions. Endothermic reactions may be water evaporation while exothermic processes may be associated with crosslinking of polymer chains. The hypothesis of removal of water is consistent with the thermogravimetric analysis by Matveeva et al. [17]. An endothermic peak (A) appears between 100 and 150 °C in Fig. 1, which is attributed to removal of water molecules. In order to confirm that water was removed in the first endothermic peak, the following control experiment was carried out: the POMA powder was initially heated at $\alpha = 17\,^\circ$C/min up to 117 °C, then cooled down to room temperature and heated again with the same heating rate of 17 °C/min up to 300 °C. The inset in Fig. 1 shows that the first peak is not present in the second heating as the water had been removed during the previous heating–cooling cycle.

The exothermic peaks (B) between 150 and 200 °C may be related to recrystallization or crosslinking, as suggested in the literature [14]. Recrystallization may be ruled out on the basis of X-ray diffraction (XRD) data shown in Fig. 2 where the POMA heated up to 290 °C exhibits no diffraction peaks, unlike the case of POMA with no heating. The latter sample displays Bragg peaks at 2θ regions of 5° and 30°, which is consistent with the literature [15]. The decrease in POMA crystallinity upon heating is probably due to deprotonation, as suggested by Mattoso and Bulhões [13]. The exothermic peaks must therefore be associated with crosslinking, analogously to what occurs for emeraldine base PANI [16]. The endothermic peak (C) at 225 °C is probably due to evaporation of remaining entrapped water that is more strongly adsorbed onto the polymer chains. One could argue that this strong adsorption is actually chemisorption, but there is evidence in the literature pointing to the absence of chemisorption in POMA [1,3,4,17]. We shall comment upon this result later on when analyzing the activation energies.

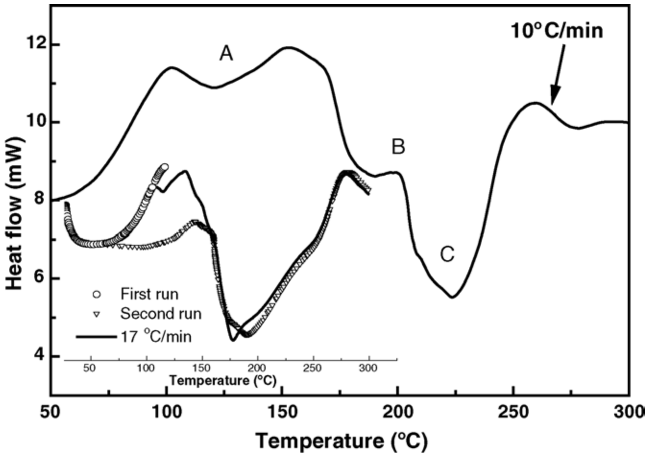

Fig. 1. DSC thermogram for POMA powder with $\alpha = 10\,^\circ$C/min. In the inset the thermograms were obtained at 17 °C/min.

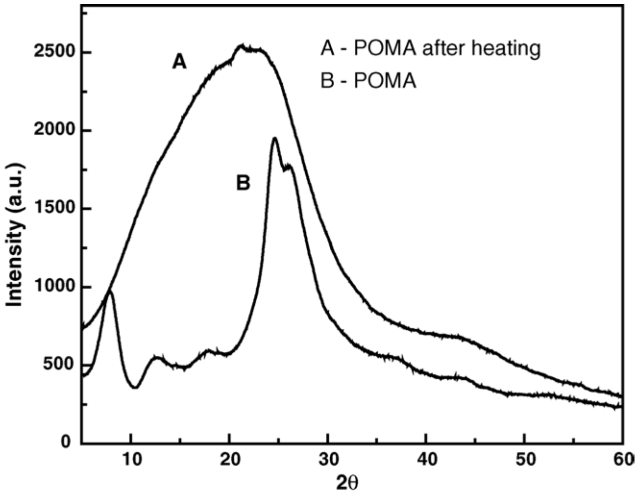

Fig. 2. Diffractograms for POMA powder prepared under two conditions: no heating (curve B) and after being heated to 290 °C (curve A).

The activation energies (E_a) of the endothermic peaks may be estimated using the method of Kissinger in which the temperature of a given peak (T_p) is related to the heating rate (α). Six values of α were employed, 3, 5, 8, 10, 13 and 17 °C/min. In the Kissinger's method $-E_a/R$ is obtained from the slope of the graph of $\ln(\alpha/T_p^2)$ versus $10^3/T_p$, where R is the gas constant. The results for the first and second endothermic peaks are shown in Figs. 3 and 4, respectively. Table 1 summarizes the peak temperatures (K) and the activation energies.

The activation energy for the first endothermic peak is approximately $E_a \approx 25$ kJ/mol, which according to Matveeva et al. [17] corresponds to a water molecule weakly bound to the polymer. The latter would give an energy value of ca. 21 kJ/mol,

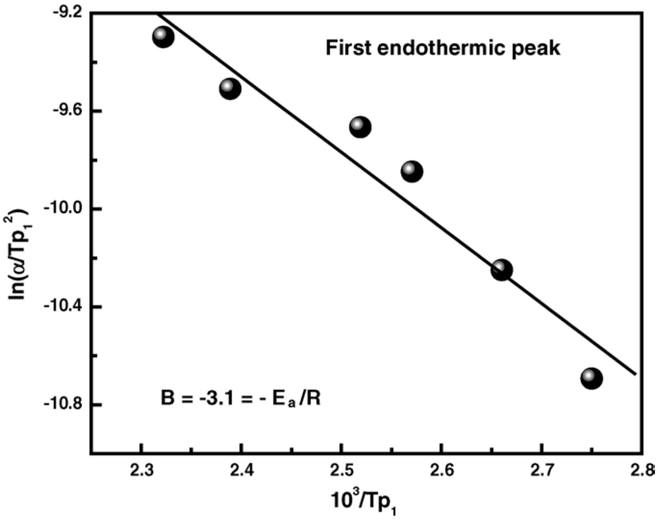

Fig. 3. The Kissinger plot for the evaluation of the activation energy for the first endothermic peak.

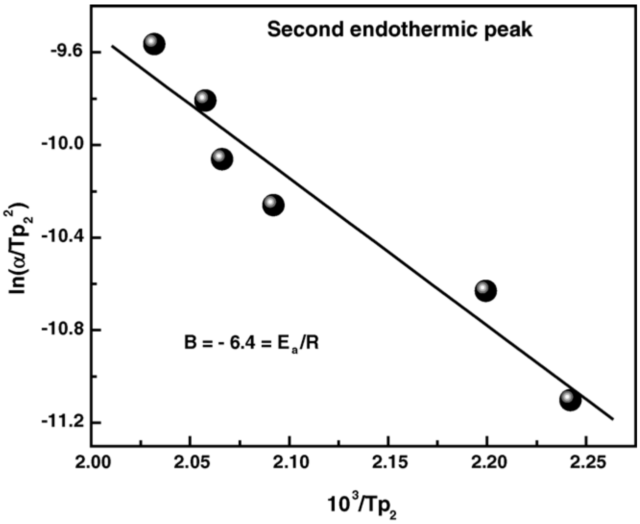

Fig. 4. The Kissinger plot for the evaluation of the activation energy for the second endothermic peak.

Table 1
Heating rates, peak temperatures for the endothermic peaks, activation energies and pre-exponential factor from Kissinger's methods

Heating rate (°C/min)	T_{p1} (K)	T_{p2} (K)
3	363	446
5	376	455
8	389	478
10	397	484
13	419	486
17	431	492
Activation energy	E_a (kJ/mol)	E_a (kJ/mol)
Kissinger	25.5 ± 1.4	53.2 ± 1.8
Pre-exponential factor	3.7×10^2 min^{-1}	1.6×10^5 min^{-1}

which is the energy required to remove water from conducting PANI [10,11]. According to Table 1, E_a for the second peak is ca. 53 kJ/mol. The presence of two peaks is consistent with the DSC thermogravimetric analysis by Matveeva et al. [17], who suggested that water molecules are "reversibly" adsorbed on the amine and imine centers with activation energies of 21 and 62 kJ/mol, respectively. Our data indicate, therefore, that entrapped water has similar effects on POMA in comparison with PANI. The mechanisms for adsorption of water in polyanilines have been addressed by Alix et al. [18], who suggested that water molecules H-bond with acid centers of PANI, while Lubentsov et al [11] considered two forms of adsorption for PANI. The importance of water for polyanilines has been demonstrated because of the effects induced by water, such as changes in conductivity, crystalline structure and chemical properties.

4. Conclusions

DSC measurements were carried out to investigate entrapped water in powder POMA samples. Two forms of adsorbed water were identified, with adsorption activation energies of ca. 25 and 53 kJ/mol, analogously to the results for parent PANI [17]. Entrapped water is believed to be adsorbed via H-bonds with amine and imine centers in POMA. This confirms the importance of H-bonding in the adsorption process of polyanilines, which is responsible for adsorption of dedoped POMA [1] and non-self limited adsorption [8]. The adsorption energies estimated here are also consistent with the energies for POMA adsorption onto glass, i.e. 20 kJ/mol, which was dependent on the breaking of H-bonds between water molecules and POMA [1].

Acknowledgments

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