

THERMOANALYTICAL STUDIES OF POLYANILINE 'Emeraldine base'

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Abstract

The thermal behaviour of polyaniline-'emeraldine base' (PANI-EB) was studied using thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). We assume that during heating over 150°C three exothermal processes proceed – reorganization and crosslinking between PANI-EB chains followed by post-polymerization. The low temperature relaxation transition for PANI-EB was registered for the first time by DSC. We suppose that it might be due to the motion of polymer chains non-crosslinked during the first heating, chain fragments resulting from high-temperature decomposition over 300°C and chain ends of the already crosslinked polymer.

Keywords: crosslinking, differential scanning calorimetry, polyaniline, post-polymerization, relaxation transition, TG

Introduction

Polyaniline (PANI) has been intensively studied recently due to its various and unique properties as well as to its environmental stability. However, very few of the studies deal with the thermal behaviour of the emeraldine salt form of PANI both as powder or film cast from solution [1–8]. Still fewer are the investigations on the thermal behaviour of the so-called 'emeraldine base' (PANI-EB) [1–3, 6, 9, 10].

PANI is known to be a hygroscopic polymer [1–13]. Some authors [3, 5, 8] assigned the endothermal effect registered by differential scanning calorimetry (DSC) in the range from ambient temperature up to approximately 140°C to the evaporation of water. It can interact with the polymer chain both during the synthesis and when absorbed from the air [14]. It is also known that PANI-EB films cast from solutions always contain some residual amounts of the solvent used, usually N-methylpyrrolidone (NMP), due to its high boiling point and to the hydrogen bonding with the polymer chains. Thus, Chen *et al.* [8] suggested the endothermal effect described above and registered after heating to 110°C to be re-

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sulting from the evaporation of the solvent, which proceeds in two stages at about 125 and 290°C, respectively.

Several papers [1, 3, 5, 6, 8, 15–20] reported a crosslinking process between PANI-EB chains, registered over 150°C by differential mechanical thermal analysis (DMTA) [1, 3, 8] and DSC and proved by various methods, e.g. gel permeation chromatography [21], dilatometry [19], IR spectroscopy [3, 8, 19, 20], wide angle X-ray diffraction [3, 6], mass spectrometry [6], solubility [3, 9, 19] and electronic paramagnetic resonance [9]. Crosslinking was supposed to be both physical at about 180°C [18, 19, 22, 23] and chemical over 200°C [1, 3, 6, 8, 18, 19]. The temperature strongly depended on the PANI-EB form (powder, tablet or film) and on the environment [6]. It was supposed that the process proceeds at the imine nitrogen atom [15–17] resulting in a two-dimensional polymer structure of phenazine type [9, 15–17, 20]. Crosslinking is a process favoured by impurities and defects in the chain [18, 19].

Data about the glass transition temperature (T_g) of EB are also scarce and rather controversial. By means of DMTA some authors have registered relaxation transitions in the chemically synthesized PANI-EB film cast from NMP solution [1, 3, 8, 18, 19]. Depending on the amount of the residual solvent in the film, T_g has been determined in the region of 105–220°C. DMTA studies by Chen *et al.* [8] showed three relaxation transitions in PANI-EB films. According to them, the T_g of such films varied between 99 and 158°C depending on the NMP content. To our knowledge this is the only paper presenting the DSC curve of a powdered PANI-EB sample, but relaxation transitions have not been registered.

The present paper reports on thermoanalytical studies of PANI-EB. The dependence of the relaxation transitions and their parameters on the heating rate and the form of polymer (powder or film cast from NMP solution), and the dependence of the structure and the thermal stability of PANI-EB on the presence of absorbed water and residual solvent were investigated.

Experimental

PANI-EB powder was synthesized according to the procedure described by Wei *et al.* [3] and was dried under vacuum at 60°C for 24 h. The film was obtained by casting 10% NMP solution onto a glass surface and the solvent was removed by heating at 135°C for 3 h.

Thermal studies were performed on a Perkin Elmer DSC 7 differential scanning calorimeter in an argon atmosphere in the temperature range of –60–350°C and heating rate of 10°C min⁻¹. Cooling was carried out at a rate of 200°C min⁻¹. The instrument was calibrated by using indium and lead as standards. Samples of about 8 mg were sealed in standard aluminum pans with holes.

Mass losses were determined by weighing the samples before and after each heating run to gradually rising programmed temperatures.

Thermogravimetric analysis (TG) was carried out on a Paulik-Paulik-Erdey, OD-102 apparatus (MOM-Budapest) in air using a scanning rate of $10^{\circ}\text{C min}^{-1}$.

Results and discussion

As seen from Fig. 1 presenting the heating curves of PANI-EB powder and film, two well pronounced effects – endothermic and exothermic, were observed. Literature data on the nature of both effects are quite controversial.

As mentioned above, PANI is a very hygroscopic polymer. The reversible weight changes in the polymer upon drying and wetting at about 30°C [10] with determined activation energy of $3\text{--}5\text{ kcal mol}^{-1}$ ($13\text{--}22\text{ kJ mol}^{-1}$) [10, 14] have been established. Matveeva *et al.* [10] supposed the existence of another form of water reversibly absorbed at the imine nitrogen with an activation energy of $15\text{--}18\text{ kcal mol}^{-1}$ ($63\text{--}75\text{ kJ mol}^{-1}$). A mechanism of the interaction between the water and the polymer chain has also been suggested [10, 12]. At first hydrogen bonds are formed and then water molecules dissociate. It was also assumed that absorbed water in PANI-EB and its removal cause structural changes in the polymer chains [6, 13].

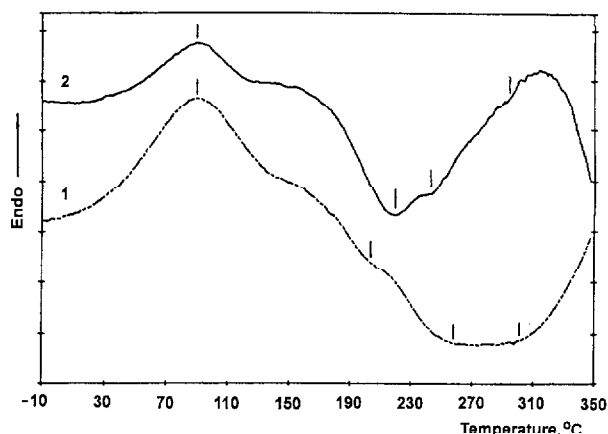


Fig. 1 DSC curves of initial PANI-EB samples, registered at a heating rate of $10^{\circ}\text{C min}^{-1}$ (1 – powder, 2 – film)

Figure 1 shows that the enthalpy of the endothermic effect in the region $30\text{--}120^{\circ}\text{C}$ for the powdered sample is twice that for the film (61 and 25 J g^{-1} , respectively). Mass losses (Fig. 2) in the same temperature region estimated by both methods described in the experimental part are also almost twice higher for powdered PANI-EB. This proves that the endothermic effect occurring at the first heating is not due to the solvent being removed (boiling point of NMP is 202°C). Only water is being evaporated in this temperature range. Moreover, we presume that the higher water content in powdered PANI-EB is due to its larger

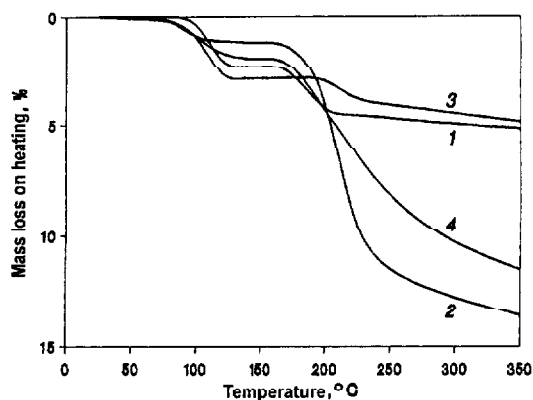


Fig. 2 Mass losses vs. final heating temperatures; DSC data (1 – powder, 2 – film); TG data (3 – powder, 4 – film)

specific surface and the absence of a physical network which has always been formed in the film.

The energy of water release in the temperature region described above was estimated according to Eq. (1) given by Matveeva *et al.* [10]. For both PANI-EB samples it is 12.6 kJ mol^{-1} and corresponds to the energy of the water absorbed at amine centers [10, 13, 14] ($13\text{--}22 \text{ kJ mol}^{-1}$).

During the second heating the endothermic effect did not occur (Fig. 3). Two relaxation transitions were observed instead. But when the two samples were left in air at ambient temperature for 24 h and scanned again, the endothermic effect (Fig. 4), having lower values of its main thermodynamic parameters, appeared again. The fact that the endothermic effect was registered again after keeping the samples in air, and the mass losses upon subsequent heating were equal to the

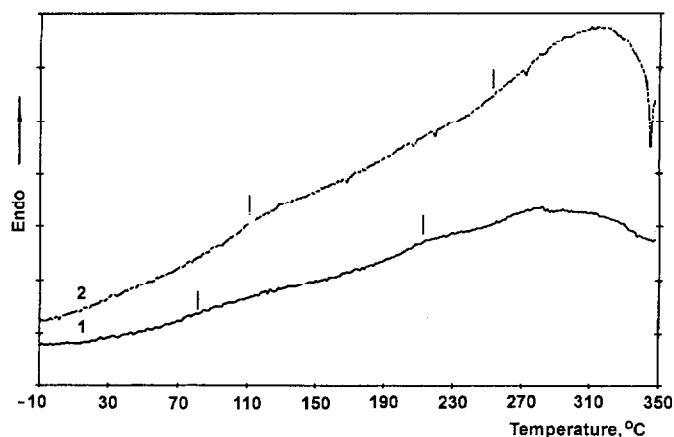


Fig. 3 DSC curves of PANI-EB samples after first heating to 350°C , registered at a heating rate of $10^\circ\text{C min}^{-1}$ (1 – powder, 2 – film)

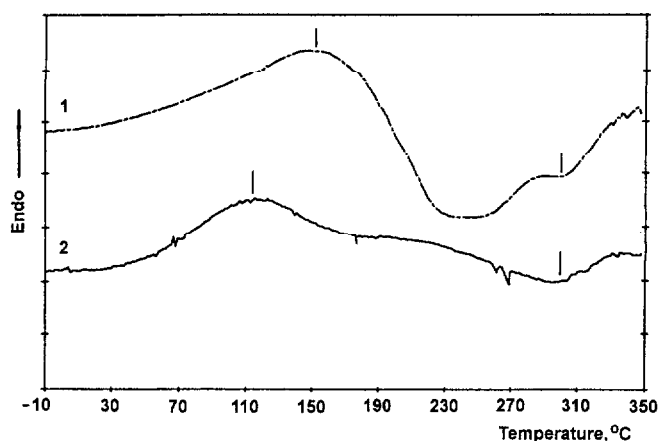


Fig. 4 DSC curves of PANI-EB film, registered at a heating rate of $20^{\circ}\text{C min}^{-1}$ (1 – first heating, 2 – after first heating up to 350°C and keeping in open air for 24 h)

amount of water absorbed from the air, enabled us to consider this effect as being of the same nature for both samples. Hence, it is due to the evaporation of water in both samples, but not to removal of the solvent present in the film. The decrease in the maximum temperatures (of about 20°C) of the endothermic peaks and of the enthalpies during the third heating (Fig. 4), as compared to those of the corresponding initial samples (Fig. 1) are most probably due to changes in the structure of emeraldine base after the first heating to 350°C followed by exposition to air. It allows water to be absorbed mainly on the surface, thus favouring its subsequent evaporation.

The maximum temperature ($T_{\text{max}}^{\text{H}_2\text{O}}$) of the endothermic peak registered during the first heating enhanced with increasing scanning rate (Fig. 5). At lower rates

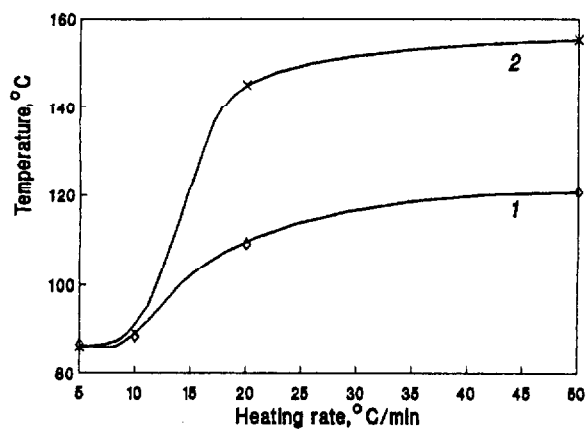


Fig. 5 Dependence of $T_{\text{max}}^{\text{H}_2\text{O}}$ on the heating rate (1 – powder, 2 – film)

(5 and 10°C min⁻¹) the diffusion processes of water to the surface of the powdered particles and of the film, respectively, were similar and their $T_{\max}^{\text{H}_2\text{O}}$ values were almost equal. When the scanning rate was higher than the diffusion rate, $T_{\max}^{\text{H}_2\text{O}}$ was shifted to higher temperatures. At scanning rates of 20 and 50°C min⁻¹ $T_{\max}^{\text{H}_2\text{O}}$ of the film was considerably higher than that of the powdered sample. It is also a result of the formation of a denser structure in the film which hinders the diffusion of water to the surface.

For powdered PANI-EB the mass losses registered by DSC in the region of 170–250°C were about 2.5 wt% (Fig. 2). We accept the statements of other authors [2, 5, 24] that they are due to the evolution of non-polymerized aniline and its oligomeric products. The mass losses for the film at temperatures exceeding 170°C were higher due to the evaporation of the solvent (NMP). As seen from DSC measurements, the mass losses of both samples in the region described above, differ by 8.5 wt% (2.5 and 11 wt% for PANI powder and film, respectively) which equals the content of residual NMP in the film. Similar data were obtained by TG showing that in the same region the mass losses of the powdered PANI and the film were about 1% and 7%, respectively.

An intensive broad exothermal effect in a wide temperature range was also registered in Fig. 1. It suggests overlapping of many exo- and endothermal processes taking place at temperatures exceeding 150°C (evolution of solvent and oligomers, crosslinking, breaking of hydrogen bonds, etc.) As was already mentioned, heating of PANI-EB at a temperature over 150°C leads to crosslinking. Previous DSC studies have shown an exothermal effect when heating a film cast from NMP solution, interpreted by the authors as reorganization [3], crosslinking [3, 8] or formation of new bonds [9]. It has been supposed that upon heating the residual solvent in the film acting as plasticizer [18, 19, 24] is evolved, thus forming a free space allowing the motion of the macromolecular segments [5, 19]. Hence, the processes in the film when heated, should proceed more easily in a narrower temperature region and at lower temperature. That is why, unlike the film, the maximum heating temperature of the powdered sample (350°C) is not high enough for completing the total exothermal process. Moreover, the curve of the film reveals three clearly separated minima at temperatures T_{\min_1} , T_{\min_2} and T_{\min_3} , respectively (Fig. 1). We can assume that the exothermal processes of reorganization, crosslinking and post-polymerization of residual aniline in the system might be responsible for these effects. Their separation is quite provisional, but nevertheless T_{\min_1} , T_{\min_2} and T_{\min_3} can be assigned to these processes based on the following considerations.

Figure 6 shows that for the PANI-EB film the exothermal effect at T_{\min_1} becomes less pronounced (i.e. the process is hindered) as the heating rate increases. As has been shown [3], the polymer chains rearrange (reorganize) in the presence of a plasticizer (NMP evaporates at about 250°C), which is suppressed upon faster heating. Because of the lack of a plasticizer in the powdered sample, the

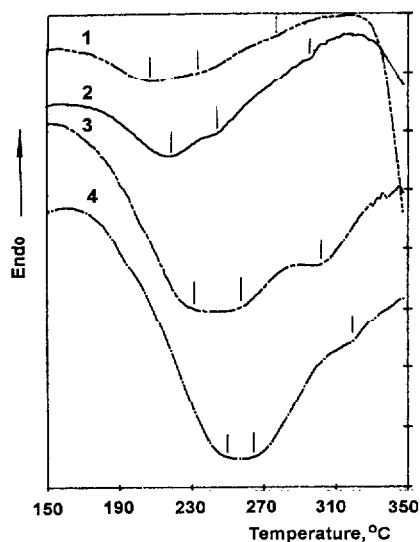


Fig. 6 DSC curves of PANI-EB samples, registered at various heating rates (1 – 5°C min⁻¹, 2 – 10°C min⁻¹, 3 – 20°C min⁻¹, 4 – 50°C min⁻¹)

segment rearrangement is hindered and it is very difficult to estimate T_{\min_1} . We confirm the statement of Wei *et al.* [6] that crosslinking in PANI-EB films seems to take place at temperature T_{\min_2} and is related to the rearrangement of molecules at T_{\min_1} . The more suppressed the reorganization, the more difficult the crosslinking. Therefore, it becomes more difficult to determine T_{\min_2} as the heating rate increases due to its shift to higher temperatures. As mentioned above, the crosslinking of a powdered sample is much more difficult and less complete at higher heating rates.

A third extremum with a temperature T_{\min_3} was registered for the first time for PANI-EB films cast from solution in the region from approximately 250 to 340°C, depending on the scanning rate. This effect is well manifested for the film and becomes more pronounced with increasing heating rate. Its nature needs further studies but most probably it is related to a post-polymerization process suggested in previous papers [25–29]. It has been supposed that EB does not represent the emeraldine oxidation state of PANI but an intermediate oxidation state between emeraldine and pernigraniline. In the presence of aniline a reduction (post-polymerization) by addition of aniline to EB chains is possible. At heating rates higher than 10°C min⁻¹ aniline cannot evaporate (like water) and post-polymerization presumably proceeds. This is why the exothermic effect with maximum temperature T_{\min_3} is better pronounced at higher scanning rates (Fig. 6). Since the reorganization and crosslinking processes have to be suppressed at higher heating rates, T_{\min_3} can be assigned to post-polymerization. Another proof is the fact that after two successive heatings of the film up to 350°C and exposure to open air for 24 h at room temperature, a similar exothermic effect with an in-

initial temperature of about 200°C appeared (Fig. 4). Its extremum is in the region where T_{\min} , during the first heating was observed. We suppose that under the influence of moisture and oxygen from the air PANI-EB might hydrolyze, evolving aniline which polymerizes during the third heating.

As seen from Fig. 2, the film, unlike the powder, loses mass in the region 300–350°C. This temperature region coincides with the region wherein the second exothermal effect occurs in the curves of films at low heating rates (Figs 1 and 6, curves 1 and 2). It has been established by TG studies that a PANI-EB film in inert atmosphere is thermally stable up to 420°C [1–3], while the powdered polymer remains stable even over 470–500°C [1, 2, 6, 30]. Thus, the exothermal effect over 300°C (Fig. 1) might be due to the progress of the decomposition of the already crosslinked film. We suppose this decomposition to be only thermal, but not oxidative, since in the mentioned range the mass losses are equal (about 1%) both under argon (DSC) and in air (TG).

During the second successive heating of film and powdered PANI-EB (Fig. 3) up to 350°C two relaxation transitions were registered – a low temperature (LTRT) and a high temperature (HTRT) one contrary to the statement of Wei *et al.* [3] that during the second heating no thermal effects occur in the range 25–300°C as a result of the crosslinking. We have for the first time registered by DSC a LTRT in the range from about 30 to about 80°C as did Wei *et al.* (beta-transition) by DMTA [3]. They suppose it to be connected with a local motion of segments of the polymer chains.

We suppose LTRT to be connected with the motion of: (a) non-crosslinked chains; (b) chain fragments resulting from high-temperature decomposition during the first heating; and (c) chain-ends of the polymer crosslinked during the first heating. As mentioned above, when heated PANI-EB undergoes several changes depending on the scanning rate. The lower the first heating rate the

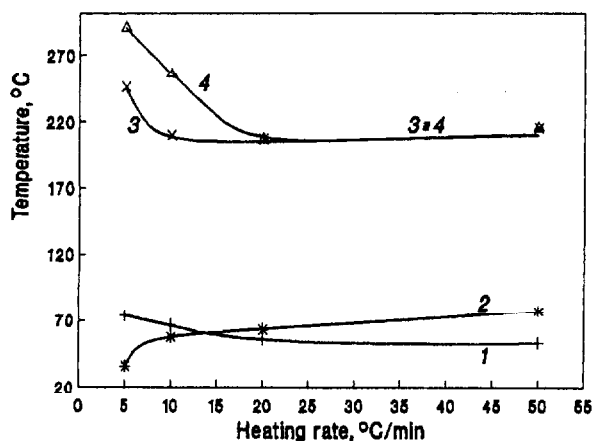


Fig. 7 Relaxation transition temperatures, registered after heating up to 350°C and subsequent cooling ($200^{\circ}\text{C min}^{-1}$) vs. the heating rate (1 – LTRT of powder, 2 – LTRT of film, 3 – HTRT of powder, 4 – HTRT of film)

higher the degree of crosslinking of the powdered sample. This explains the shape of curve 1 in Fig. 7, where the highest temperature of LTRT of the powdered sample was observed at the lowest scanning rate. However, the film exhibits the lowest LTRT temperature at the same scanning rate (Fig. 7, curve 2). This confirms that thermal decomposition takes place at heating rates 5 and $10^{\circ}\text{C min}^{-1}$ leading to formation of non-crosslinked chain fragments of lower molecular weight.

The HTRT recorded during the second heating can be assigned to the cooperative motion of the segments of the already crosslinked polymer. At low heating rates (Fig. 6) the exothermal crosslinking process in the film proceeds to the highest extent. The very dense network formed during the first heating up to 350°C determines the highest registered HTRT temperature (Fig. 7, curve 4). The increase of the scanning rate hinders the crosslinking process and the transition temperature drops. Crosslinking is more difficult to proceed in a powdered sample, since it does not contain plasticizer. Hence, when heated slowly, powdered PANI exhibits a lower HTRT temperature (Fig. 7, curve 3) than the film. Noteworthy is the fact that when the heating rate is 20 or $50^{\circ}\text{C min}^{-1}$ and decomposition is not observed, both samples have almost the same plots (Fig. 7, curves 3 and 4), which means that their degree of crosslinking is identical.

The above discussion evidenced that the residual NMP in the PANI-EB film, as well as its initial structure, determined its thermal behaviour which was therefore different from that of the powdered polymer. Calorimetric studies showed that the film absorbed a smaller amount of moisture, but it evaporated more difficultly. It was found that the film was easier crosslinked, but also decomposed more easily as compared to PANI EB powder.

In conclusion, it can be stated that the endothermal effect registered for PANI-EB in the range from ambient temperature to about 120°C is related only to evaporation of water but not to the evolution of oligomeric products or residual solvent. We assume that during heating over 150°C three exothermal processes proceed – reorganization and crosslinking between PANI-EB chains followed by post-polymerization in the region from approximately 250 to 340°C depending on the scanning rate. The low temperature relaxation transition was registered for the first time by DSC for PANI-EB. We suppose that it might be due to the motion of polymer chains non-crosslinked during the first heating, chain fragments resulting from high-temperature decomposition over 300°C and chain ends of the already crosslinked polymer.

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