Journal of Thermal Analysis and Calorimetry, Vol. 59 (2000) 721–727

RELAXATION TRANSITIONS IN THERMALLY TREATED POLYANILINE FILMS

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(Received November 10, 1998; in revised form October 31, 1999)

Abstract

Thermally treated films of polyaniline-emeraldine base (PANI-EB) cast from NMP solution were studied by using differential scanning calorimetry. Dependence of the thermodynamic parameters of the relaxation transitions on temperature and annealing period as well as the effect of the thermal history of the samples upon the crosslinking processes were investigated. For the first time DSC analysis of PANI-EB films after prolonged ageing was performed.

It was found that relaxation transitions can be registered only for crosslinked PANI-EB. The crosslinking processes proceed both upon short-time heating of the polymer studied over 80°C and during long-time storage at room temperature.

Keywords: ageing, annealing, DSC, polyaniline, relaxation transition

Introduction

Polyaniline (PANI) prepared by oxidative polymerization of aniline is an electrically conductive [1–4] but very hygroscopic [4–13] polymer possessing poor processability. The study of the thermal behaviour and thermal transition temperatures such as glass transition (T_g) of the polymer is of great importance for the potential thermal processing.

Kobayashi *et al.* found [14] that the conductivity of chemically synthesized PANI at room temperature varies with the time and the temperature of annealing. The results show an initial increase of regularity of the polymer chain, and subsequent phase transition to the loose-packed and ordered structure during annealing.

Yen Wei *et al.* [6, 8] reported relaxation transitions of annealed PANI-emeraldine base (EB) films cast from a solution in N-methylpyrrolidone (NMP) and containing various amount of residual solvent depending on the time and temperature of annealing. On increasing the annealing temperature (from 90 up to 150°C) T_g values determined by dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) increased from 140 up to 190°C and from 105 up to 150°C, respectively. T_g value (220°C) of a dry film (NMP content lower than 0.5 mass%) have been recorded only by DMTA.

It has been also suggested that the thermal treatment of PANI leads to crosslinking between the macromolecules resulting in a two-dimensional polymer

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

structure of phenasine type [12, 15–18]. The GPC chromatograms of the unaged and aged powdered polymer samples showed [4] that the high molecular mass fractions increase from about 20 to about 57% after annealing at 200°C for 6 h.

Other investigations of the isothermal evolution of water [13], HCl [19, 20] and NMP [21] from powders and films of chemically synthesized PANI showed that the thermal stability of conductive PANI depends on the sample form and on the environment – air or inert atmosphere.

In this paper we studied thermally treated films of PANI-EB cast from NMP solution by using DSC. The dependence of the thermodynamic parameters of the relaxation transitions and of crosslinking processes proceeding upon heating on the temperature and ageing period as well as the effect of the thermal prehistory of the samples upon the crosslinking processes were also investigated.

Experimental

PANI-EB powder was synthesized according to the procedure described by Wei *et al.* [8] and was dried under vacuum at 60°C for 24 h. Free standing 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 differential scanning calorimeter Perkin Elmer DSC 7 in argon atmosphere is the temperature range (–50)–(+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 approximately 10 mg were sealed in standard aluminum pans with holes.

Films as received and aged for one year in air at room temperature and at –30°C were investigated. Other set of samples of unaged film were thermally treated before

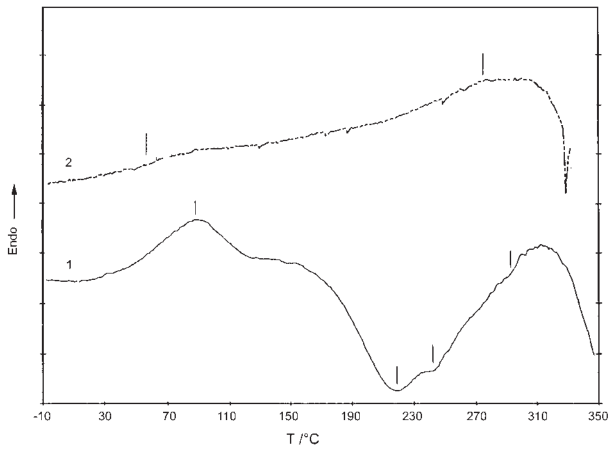

Fig. 1 DSC curves of initial PANI-EB, registered upon heating up to 350°C (1 – first scan, 2 – second scan)

scanning in two different ways: (a) heating to 150°C at 10°C min^{-1} in the calorimetric chamber followed by fast cooling; and (b) annealing at 80°C for 30 min.

Results and discussion

As is seen from Fig. 1, two well pronounced effects – endothermal and exothermal were observed upon heating of PANI-EB film up to 350°C (curve 1). In our previous paper [22] we reported that the endothermal effect registered in the range from ambient temperature up to about 120°C is related only to evaporation of water but not to the evolution of oligomeric aniline products or residual solvent. It was also found that the water molecules are hydrogen bonded with amine nitrogen atoms of the polymer chains and could be easily removed (activating energy of 12.6 kJ mol^{-1} [22]). This broad endothermal peak registed upon heating of the initial PANI-EB film does not allow to observe relaxation transitions in this temperature range (Fig. 1, curve 1). However, they appear during the second heating up to 350°C when the absorbed water and the residual solvent have been removed (up to ca. 90 and 200°C, respectively), and the polymer has already been crosslinked during the first heating (Fig. 1, curve 2) [22]. We are interested in finding out whether DSC is able to record the relaxation transitions of PANI films pretreated at the conditions mentioned above.

After the thermal treatment up to 80°C for 30 min and up to 150°C as described in the Experimental section, the endothermic peak in the temperature range of 30 to about 120°C does not occur any more (Fig. 2, curves 2 and 3). It was found that annealing at 80°C for 30 min is sufficient for removing the water absorbed in the film (about 2 wt.%). Although mass losses were not detected during the following heating,

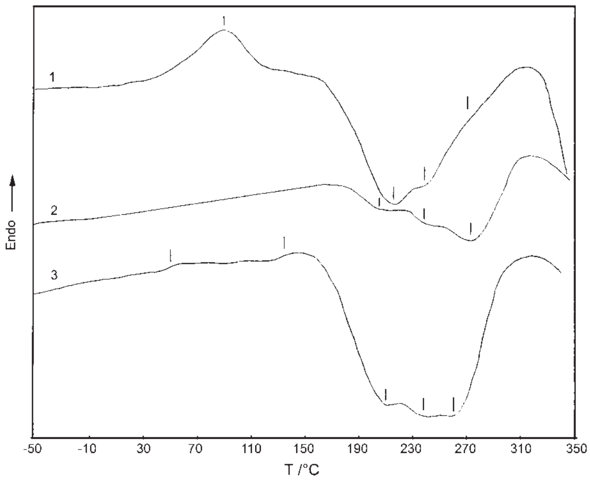

Fig. 2 DSC curves of PANI-EB, registered upon heating up to 350°C (1 – initial film, 2 – after annealing at 80°C for 30 min, 3 – after heating up to 150°C and subsequent fast cooling)

relaxation transitions in this region were not registered again (Fig. 2, curve 2). Thus, the removal of the moisture from the PANI-EB film is not sufficient for the relaxation processes to be observed.

In this region, however, after heating the film up to 150°C followed by fast cooling at 200°C min^{-1} in DSC-7, the relaxation transitions both low and high-temperature (LTRT and HTRT, respectively) were registered upon the subsequent heating (Fig. 2, curve 3). They are similar to the above mentioned effects observed upon the second scanning up to 350°C of the initial film (Fig. 1, curve 2). It was found [8, 22] that processes of rearrangement and crosslinking occurred upon heating of PANI-EB to a temperature over 150°C. Thus, it could be supposed that the crosslinking starts at temperature beyond 80°C and relaxation transitions could be registered by DSC only for crosslinked PANI-EB. The temperature of HTRT (T_{g_2}) determined after preliminary heating up to 150°C, is significantly lower than that for the film heated preliminary up to 350°C (Table 1), since the degree of crosslinking attained in the temperature range of 80–150°C should be quite low. On the other hand, NMP molecules still present in EB films heated up to 150°C, act as plasticizer, thus resulting in a shift of T_{g_2} to lower temperature range due to the facilitated motion of the macromolecular segments.

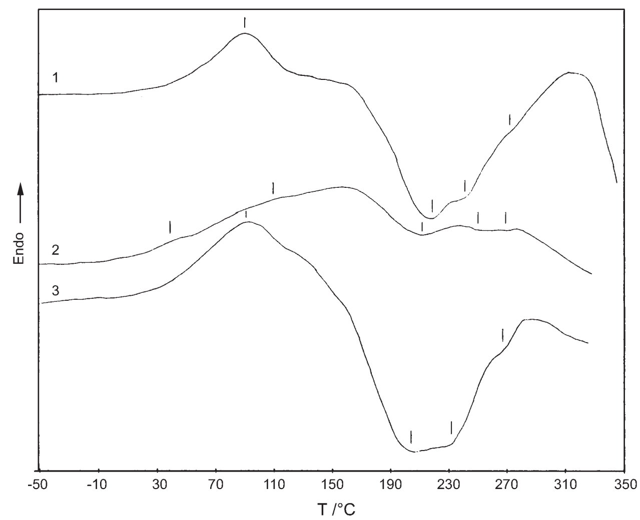

Fig. 3 DSC curves of PANI-EB, registered upon heating up to 350°C (1 – initial film, 2 – after ageing at room temperature, 3 – after ageing at – 30°C)

As is seen from Fig. 1 and Table 1, the conditions of preliminary thermal treatment do not affect the crosslinking parameters (temperatures T_{min_1}, T_{min_2}, T_{min_3} and enthalpy) of the exothermal processes proceeding upon heating.

We performed for the first time, DSC investigations of PANI-EB films after prolonged ageing (for one year).

Table 1 Thermodynamic parameters of thermally treated films of polyaniline–emeraldine base

	H^{endo}/J g^{-1}	T_{min_1}/°C	T_{min_2}/°C	T_{min_3}/°C	H^{exo}/J g^{-1}	T_{g_1}/°C	T_{g_2}/°C
Initial EB film	24.8	220	246	263	123.4	57.4	276
After 1 year at room temperature	3.7	212	248	270	20.4	50.4 (40*)	251 (110*)
After 1 year at –30°C	34.4	208	237	270	172.6	51.1	252
After 30 min at 80°C	–	210	244	276	108	–	–
After heating to 150°C	–	214	244	265	117.3	56.0	132

*Determined upon first heating to 350°C.
H^{endo} – heat of water evaporation; T_{min_1}, T_{min_2}, T_{min_3} – temperatures of the exothermal effects, H^{exo} – enthalpy of crosslinking; T_{g_1} and T_{g_2} – temperatures of the relaxation transitions (LTRT and HTRT, resp.)

The data in Table 1 show substantional reduction in the heat of water evaporation (H^{endo}) (amount of absorbed water, respectively) after ageing of PANI-EB film for one year at room temperature. The total enthalpy of the exothermal effects (H^{exo}) related to the crosslinking processes proceeding at temperatures over 150°C, is also manifold lower. It can be supposed that the changes in the values of the two parameters (H^{endo} and H^{exo}) and in the direction of their variation are also due to the crosslinking of PANI-EB molecules, taking place at room temperature. The network formed hampers both the absorption and the desorption of water. This assumption can be proved by the fact that after keeping the film at –30°C for one year, small or no changes of the values of the parameters of both endothermal and exothermal processes are observed (Fig. 3, curve 3; Table 1), since the crosslinking process would have been suppressed at such a low-temperature.

There is still another proof for the proceeding of crosslinking in air at room temperature. LTRT and HTRT were registered upon both the first (Fig. 3, curve 2) and the second heating of the aged film (Table 1). Their temperatures (T_{g_1} and T_{g_2}, respectively) determined during the first scanning are much lower than those for the initial unaged PANI-EB (Table 1). In our previous paper [22] it was shown that the relaxation transitions occur after heating the PANI samples up to 350°C which results in crosslinking. We supposed that LTRT is related to the motion of non-crosslinked low molecular chains and of chain ends of the polymer crosslinked at amine functionality during the first heating. We consider HTRT is due to the motion of macromolecular segments between the crosslinking points. T_{g_1} and T_{g_2} determined upon second heating of the aged film are also lower than those before ageing. We assume that this is due to the 'loose' network formed under ageing conditions described above. As is seen from Fig. 3, curve 2 and from the values of the thermodynamic parameters shown in Table 1, the degree of crosslinking taking place during the first heating is very low. Due to the complicated rearrangement of PANI-EB segments of already crosslinked aged film, additional crosslinking upon the following heating is getting suppressed. For that reason, T_{g_1} and T_{g_2} determined during the second heating after keeping the film for one year, are lower than those of the initial film before ageing registered under the same experimental conditions (Table 1).

In conclusion, as a result of the thermal DSC study of PANI-EB films cast from NMP solution it can be stated that relaxation transitions can be registered only for crosslinked polymer. It was also found that crosslinking processes proceed both upon short-time heating of the polymer studied over 80°C and during the long-time storage of the film at room temperature.

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We appreciate the financial support provided by the Ministry of Education, Science and Technology.

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