

# Copolymers of Aniline and *o*-Methoxyaniline. II. Thermoanalytical Studies

Dimitrinka Tsocheva, Pavlina Mokreva, Levon Terlemezyan

Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Received 7 November 2005; accepted 14 September 2006

DOI 10.1002/app.25712

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A study on the thermal stability, thermodynamical parameters, especially relaxation transition temperature ( $T_g$ ), and their change upon irreversible reactions (crosslinking, postpolymerization, decomposition, etc.) taking place on heating of the undoped homo- and copolymers of aniline and *o*-methoxyaniline was performed by using differential scanning calorimetry. It was found that polyaniline and its oligomers might be responsible for the postpolymerization process

observed on heating thermograms of the polymers in their emeraldine base form. It can be stated that the proceeding of this process appears to be a reason for the higher thermal stability of polyaniline when compared with poly(*o*-methoxyaniline).

© 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2729–2734, 2007

**Key words:** polyaniline; poly(*o*-methoxyaniline); differential scanning calorimetry; copolymers; thermal stability

## INTRODUCTION

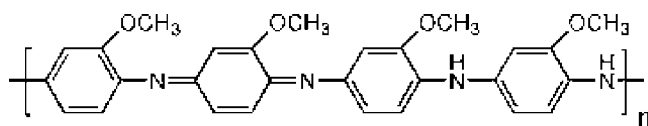
Polyaniline (PANI) is one of the most promising conductive polymers for commercial application, because of its unique electrical, electrochemical, and optical properties<sup>1,2</sup> as well as excellent environmental and thermal stability.<sup>3,4</sup> The main problem related to the usage of PANI is its poor processibility both in melt and solution, because of its backbone stiffness and strong interchain interactions. It is also known that PANI is generally nonsoluble in common organic solvents.

Several approaches have been attempted to improve the solubility of the aniline (ANI) polymers. It was recently reported that the polymers protonated with the so-called functionalized protonic acids such as camphorsulfonic acid,<sup>5,6</sup> dodecylbenzenesulfonic acid,<sup>7,8</sup> etc. PANI can be “dissolved” in several nonpolar or weakly polar solvents. These acids “compatibilize” PANI also with other polymers of similar molecular structure, facilitating the blending and processing by conventional technique.<sup>9–13</sup>

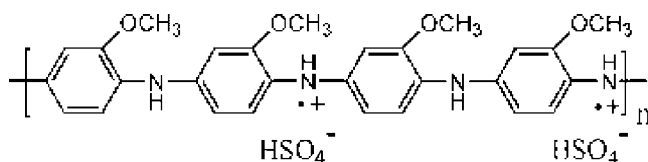
It was also found that the homopolymerization of ANI derivatives (e.g., alkyl<sup>14,15</sup> and alkoxy<sup>16–20</sup> ring-substituted ANIs) or their copolymerization with ANI results in better solubility of the obtained polymers. Copolymers of ANI and *o*-methoxyaniline (MANI) with good solubility characteristics had been recently prepared and described in our previous article.<sup>21</sup> The higher the MANI

content of the copolymer the better the solubility, however, at the expense of electrical conductivity. It is also of great importance to investigate the behavior of ANI homo- and copolymers and the change in their supramolecular structure at elevated temperature to which they can be exposed during application and storage.

In this article, we present a differential scanning calorimetry (DSC) study on the thermal stability, thermodynamical parameters, especially relaxation transition temperature ( $T_g$ ), and their change upon irreversible reactions (crosslinking, decomposition, etc.), taking place on heating of the undoped homo- and copolymers of ANI and MANI. The thermal stability of undoped poly(*o*-methoxyaniline) (PMANI-EB)



and doped in sulfuric acid medium (PMANI-ES)



was also compared.

## EXPERIMENTAL

The homopolymers of ANI and MANI as well as their high-conversion copolymers (~ 70% yield) with different content of ANI and MANI units were synthe-

Correspondence to: D. Tsocheva (tsocheva@polymer.bas.bg).

Contract grant sponsor: Bulgarian Ministry of Education and Science; contract grant number: CH-1403/2004.

sized by chemical oxidative polymerization, according to the procedure described in our previous article.<sup>21</sup>

A mixture of ANI and MANI was dissolved in 0.5M H<sub>2</sub>SO<sub>4</sub> in an ice bath. Aqueous solution of ammonium peroxydisulfate was added dropwise with continuous stirring to the obtained solution. The reaction mixture was stirred at 0–5°C for 6 h and then kept at 10°C for 20 h. The doped copolymer in the form of emeraldine salt (ES) was filtered and washed with 0.5M H<sub>2</sub>SO<sub>4</sub>. To prepare the emeraldine base (EB), the polymer salt was suspended in 0.1M NH<sub>4</sub>OH solution, stirred for 6 h, and filtered, followed by vacuum drying to constant weight.<sup>21</sup> Copolymers with ANI : MANI molar ratio of 80 : 20 and 50 : 50, hereafter called AM80/20 and AM50/50, respectively, were obtained.

A similar procedure was used to get both doped and undoped PANI and PMANI homopolymers.

Monomers and oligomers free samples of the undoped homopolymers and AM50/50 copolymer were obtained by simple solvent extraction at room temperature for 24 h. PANI and the copolymer were treated with chloroform, and PMANI was treated with acetone, since PMANI is completely soluble in chloroform.

Thermal studies of the polymers studied were performed on a Perkin–Elmer DSC 7, using argon as a purge gas. The apparatus was calibrated with indium and lead standards, for temperature and heat change. The DSC traces were recorded after removing the absorbed water upon heating up to 150°C in the calorimetric chamber and were presented normalized.

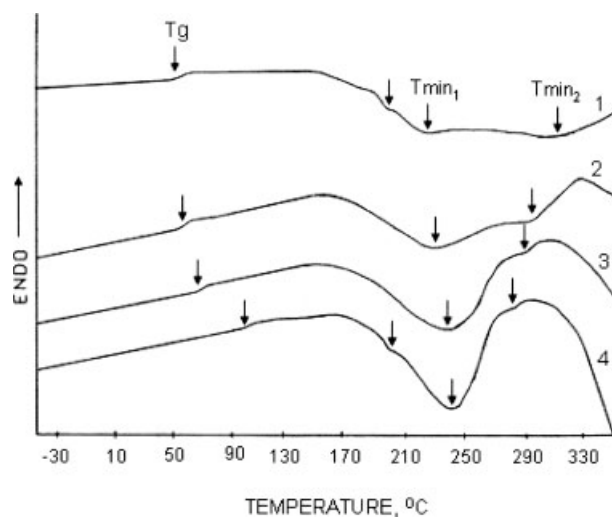
Calorimetric measurements were performed in the following ways:

1. Polymers were directly heated in the temperature range from –30 to 350°C at a heating rate of 10°C min<sup>–1</sup>, followed by fast cooling with a rate of 200°C min<sup>–1</sup>, and reheating the samples under the same heating conditions;
2. PANI-EB, PMANI-EB, and PMANI-ES were heated up to gradually rising programmed temperature (100, 120, 150, 170, 200, 220, 250, 270, 300, 330, and 400°C) with a heating rate of 10°C min<sup>–1</sup> and quenching after each heating run to determine the relaxation transitions and experimental mass loss. The latter was calculated by weighing the sample pans prior to ( $W_{in}$ ) and after ( $W_f$ ) each heating run in the calorimetric chamber according to the equation:

$$\text{Mass loss (\%)} = \frac{W_{in} - W_f}{W_{in}} \times 100$$

## RESULTS AND DISCUSSION

DSC traces of undoped homo- and copolymers of ANI and MANI in emeraldine oxidation state are pre-



**Figure 1** DSC curves of 1, PANI-EB, 2, AM80/20, 3, AM50/50, and 4, PMANI-EB, registered upon heating up to 350°C at a heating rate of 10°C min<sup>–1</sup>.

sented in Figure 1. They have been recorded after removing the absorbed water. A slight relaxation transition and a strong exothermic effect are observed for all the samples.

It is known that the PANIs are very hygroscopic polymers.<sup>22–25</sup> The water evaporation during the calorimetric study results in a broad endothermic peak, often masking the registration of relaxation transitions.<sup>26</sup> Thus, preliminary removal of the absorbed water appears to be obligatory. In the homopolymers studied, the water content, as determined by the equation given in the Experimental part, varies between about 4.4 wt % for PANI-EB and about 3.1 wt % for PMANI-EB, both heated directly up to 350°C. The maximum temperature of water evaporation and the activation energy of water release ( $E$ ) in the temperature range up to 150°C are presented in Table I.  $E$  was estimated according to the equation suggested by Matveeva et al.<sup>25</sup>

$$E = \frac{\Delta H^{H_2O}}{\Delta P} M^{H_2O}$$

where  $\Delta H^{H_2O}$  is the amount of heat evolved during the dehydration,  $\Delta P$  is the water mass loss, and  $M^{H_2O}$  is the molecular mass of water. The  $E$ -values corre-

**TABLE I**  
Temperature ( $T^{H_2O}$ ) and Activation Energy ( $E$ ) of Absorbed Water Release

Sample	$T^{H_2O}$ (°C)	$E$ (kJ mol <sup>–1</sup> )
PANI-EB	103.2	24.1
AM80/20	100.7	27.1
AM50/50	94.1	26.8
PMANI-EB	93.6	22.5
PMANI-ES	108.1	20.0

spond to the water absorbed at amine centers ( $13\text{--}22\text{ kJ mol}^{-1}$ ),<sup>25</sup> both for PANI-EB and PMANI-EB as well as for their copolymers. The slight difference between  $E$  values of the homopolymers is due to the methoxyl group (MeO) in PMANI, which as a donor of electron increases the electron density at the nitrogen atom. Thus, the amine N-atoms of PMANI are more basic as compared to those in PANI, and the water molecules are more weakly bonded to them. The weaker the hydrogen bond, the lower the activation energy is.

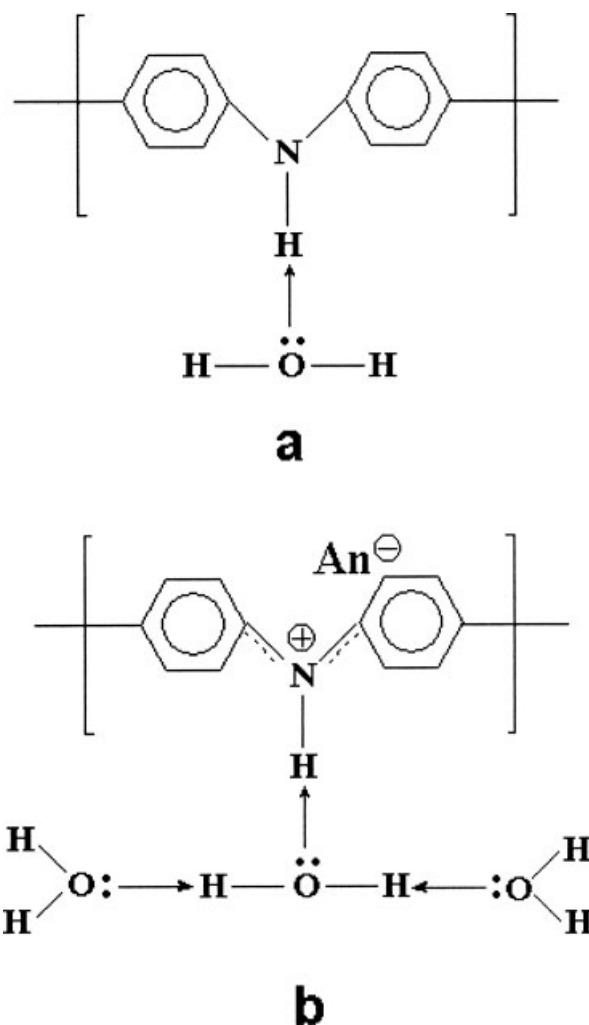
The homo- and copolymers were thermally studied after keeping at identical atmospheric conditions (temperature, humidity, etc.) when they absorbed almost equal quantity of water. On the other hand, higher values of  $E$  for the ANI/MANI copolymers, as compared to the homopolymers, were estimated (Table I). It can be suggested that the existence of methoxyl groups at random sites throughout the copolymer chains<sup>21</sup> changes the conformation of the macromolecules, which may result in hampered evolution of the absorbed water from the copolymers.

It is well known<sup>25</sup> that the emeraldine base (EB) and salt forms of PANI essentially differ by their chemical structures. All nitrogen atoms of PANI-ES are equivalent and belong to the semiquinone configuration (quasi-amine centers). At the same time, nitrogen atoms in PANI-EB are divided into two equal groups of amine or imine structures. Thus, the interaction between water molecules and nitrogen centers of PANI-EB and PANI-ES must be different. Matveeva et al.<sup>25</sup> assumed that each ANI core of PANI-EB holds one water molecule [Scheme 1(a)], whereas each ANI core of PANI-ES holds nearly three hydrogen-bonded water molecule [Scheme 1(b)]. Hence, the absorbed by PANI-ES water can more easily leave the system, and thus it is reasonable to expect similar interaction between the PMANI chains and water molecules. It is seen in Table I that the value of  $E$  for PMANI-ES is lower than that for PMANI-EB.

It is known that the dedoping of PANI polymerized in the presence of mineral acids results in an amorphous EB.<sup>27–29</sup> That is why a relaxation transition (at about  $56^\circ\text{C}$ ) can be registered during its heating in the calorimetric chamber. Undoped PMANI is also amorphous, as evidenced by X-ray diffraction.<sup>30,31</sup> We found by DSC that its  $T_g$  is much higher than the  $T_g$  of PANI-EB ( $\sim 105^\circ\text{C}$ ).

In our previous article<sup>21</sup> the formation of ANI/MANI copolymers was proved by using FTIR, electronic, and NMR spectroscopy, as well as solubility tests. Another evidence that the final products are real copolymers rather than mixtures of homopolymers is the registration of single  $T_g$  located between the  $T_g$  of PANI-EB and  $T_g$  of PMANI-EB recorded at first heating (after water removing) during the DSC study (Table II).

As it was mentioned in the Experimental part, mass loss for the homopolymers in a base form was determined after each heating/cooling cycle, up to gradu-



**Scheme 1** Possible water absorbed structures on amine center in (a) PANI-EB and (b) PANI-ES.

ally increasing final heating temperature. The evolution of absorbed water is registered up to about  $120$  and  $150^\circ\text{C}$  for PANI-EB (Fig. 2, curve 1) and PMANI-EB (Fig. 2, curve 2), respectively. Afterward, mass losses on heating of about  $0.5\text{ wt } \%$  and about  $1\text{ wt } \%$  in the temperature ranges from  $150\text{--}170^\circ\text{C}$  to  $220\text{--}250^\circ\text{C}$ , respectively, are calculated for PANI-EB (Fig. 2, curve 1). We accept the statements of other authors<sup>28,31</sup> that they result from the evolution of non-polymerized ANI and its oligomeric products, respectively. The nonpolymerized MANI (of about  $3\text{ wt } \%$ ) has been evolved between  $200$  and  $270^\circ\text{C}$  (Fig. 2, curve 2). At temperatures exceeding  $330^\circ\text{C}$  and  $300^\circ\text{C}$  for PANI-EB and PMANI-EB, respectively, changes in polymer mass are observed again (Fig. 2). Thus, as seen from Figure 1, the exothermal effect registered over  $300^\circ\text{C}$  for the copolymers and for PMANI-EB itself might be due to the progress of the decomposition of the already crosslinked polymers. It is seen that up to  $400^\circ\text{C}$  (final temperature studied) PANI-EB is thermally more stable than PMANI-EB (Fig. 2).

**TABLE II**  
**Relaxation Transition Temperature Determined Upon Heating of Undoped ( $T_g^{\text{IH}}$ ) and of Crosslinked ( $T_g^{\text{IHH}}$ ) Polymers and Exothermal Effect Temperatures ( $T_{\text{min1}}$  and  $T_{\text{min2}}$ )**

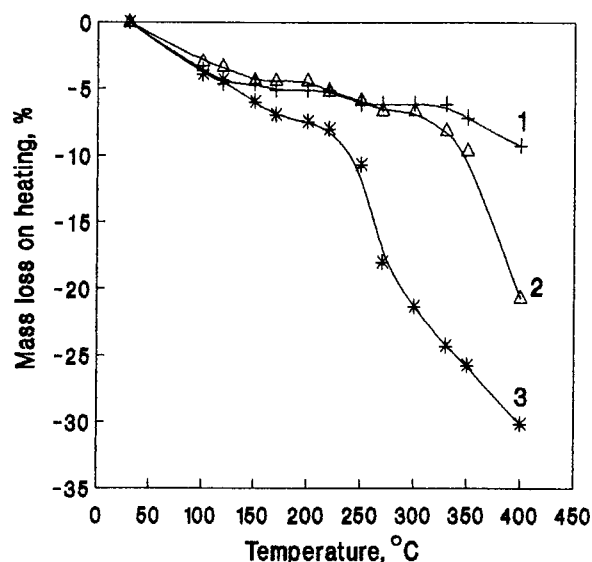
Sample	$T_g^{\text{IH}}$ (°C)	$T_{g1}^{\text{IHH}}$ (°C)	$T_{g2}^{\text{IHH}}$ (°C)	$T_{\text{min1}}$ (°C)	$T_{\text{min2}}$ (°C)
PANI	55.8	58.3	177	226.4	302.7
AM80/20	59.1	88.6	213	230.0	286.4
AM50/50	81.8	109.4	272	235.4	280.9
PMANI	105.3		221.7	240.9	275.4
PANI (insoluble in chloroform)		88.2	189	291.8	–
AM50/50 (insoluble in chloroform)		90.3	176	220.3	–
PMANI (insoluble in acetone)		173.3	224.2	–	–

As was already mentioned, an intensive broad exothermal effect in a wide temperature range was registered in Figure 1. It suggests overlapping of many exo- and endothermal processes taking place at temperature exceeding 150°C (evolution of nonreacted initial substances and low-molecular-weight reaction products, reorganization, crosslinking, postpolymerization, etc.). It is also seen that the maximum heating temperature of the powdered PANI-EB (350°C) is not high enough for completion of the total exothermal process. Moreover, the curves of the homo- and copolymers reveal two clearly separated minima at temperatures  $T_{\text{min1}}$  and  $T_{\text{min2}}$ . It can be assumed that the processes of crosslinking and postpolymerization of residual monomers in the systems might be responsible for these two effects at  $T_{\text{min1}}$  and  $T_{\text{min2}}$ , respectively, based on the following considerations.

It is known<sup>22–24,27</sup> that a crosslinking process between PANI-EB macromolecules occurs upon heating over 150°C. It was supposed that this process proceeds at the imine nitrogen atom, resulting in a two-dimensional polymer structure of phenazine type.<sup>6,32–37</sup> In our previous article,<sup>26</sup> it was found that the exothermal effect at temperature about  $T_{\text{min1}}$  corresponds to the formation of PANI-EB network.

A slight difference in the pattern of the curves 1 and 4 in Figure 1 for PANI and PMANI, respectively, at about 200°C have been observed, small minima being recorded for both homopolymers. This is the temperature range after evolution of the residual ANI (Fig. 2, curve 1), wherein the rigid-rod PANI chains have become more mobile and can reorganize.<sup>26</sup> Then the increased mobility and the reorganization facilitates both the removal of ANI oligomers (dimers, trimers, etc.) and the crosslinking process in the same temperature range (220–250°C). For PMANI (Fig. 1, curve 4), the reorganization proceeds before the evolution of MANI and its oligomers (200–270°C) as seen in Figure 2, curve 2. Probably they act as “plasticizers” in the system. Then the PMANI macromolecules form a network in the same temperature range simultaneously, with the evolution of residual MANI and its oligomers. Some of them left the system, and another participated in the crosslinking process.

The effect at temperature  $T_{\text{min2}}$  was registered for the first time for PANI-EB.<sup>26</sup> Its nature needs further investigations, but most probably it can be related to a postpolymerization process suggested in previous articles.<sup>38,39</sup> As seen in Figure 1, it is well manifested for PANI-EB and becomes less pronounced for PMANI-EB. From the values in Table II, it can be noticed that  $T_{\text{min1}}$  slightly rises and  $T_{\text{min2}}$  decreases with increasing content of MANI units in the polymers studied. At the crosslinking stage, postpolymerization and evolution of MANI and its oligomers take place almost simultaneously, the temperature range of the total exothermal process gets narrower with increasing content of MANI units (Fig. 1, curves 2–4). It has been found that ANIs with electron-donating substituents (such as MeO, EtO, etc.) are more reactive than the unsubstituted ANI in the oxidative polymerization reaction because of the lower oxidation potential. Synthesis in the presence of two different monomers has shown preferential polymerization of the monomer with lower oxidation potential.<sup>16,19,20</sup> Thus, a smaller amount of MANI oligomers and nonpolymerized monomer than



**Figure 2** Mass loss determined on heating up to gradually rising programmed temperature and subsequent quenching of 1, PANI-EB, 2, PMANI-EB, and 3, PMANI-ES, versus final heating temperature.

ANI and its low molecular products are involved in the polymer systems. On the other hand, the presence of MeO substituent can introduce some nonplanar conformations, reducing intermolecular interactions and enhancing flexibility. Thus, the crosslinking of PMANI chains has been facilitated, and the process proceeds to a greater extent in PANI, whose rod-like macromolecules are more rigid and less flexible, than in PMANI chains. This results in less intensive, crosslinking effect observed in broader temperature range for PANI-EB. The postpolymerization effect noticed for PANI-EB, however, is more remarkable than that for PMANI-EB. That is why, we suppose that mainly ANI and its oligomers are responsible for the postpolymerization (Fig. 1, curves 1 and 2), since a minimum for this process is almost unnoticeable in curves 3 and 4.

We have recently found<sup>26,40</sup> that two relaxation transitions can be recorded by DSC on second heating of PANI-EB next to the first heating up to 350°C. The  $T_g$  values obtained upon second heating of the samples are presented in Table II. As the crosslinking process has not been completed (Fig. 1, curve 1), we can suppose that the lower  $T_g$  ( $T_{g1}$ ) (about 58°C) might be due to the motion of polymer chains noncrosslinked during the first heating. The higher  $T_g$  ( $T_{g2}$ ) (about 177°C) can be assigned to the cooperative motion of the segments of PANI-EB network. On the contrary, only single  $T_g$  of PMANI has been registered (about 222°C) at second heating in the calorimetric chamber that might be due only to the crosslinked PMANI-EB chains. As is seen from Figure 1 curves 2 and 3, the crosslinking process for both copolymers AM80/20 and AM50/50 has also been completed on heating up to 300°C. In our previous article,<sup>21</sup> it was found that undoped copolymers contain neither PANI-EB nor PMANI-EB homopolymers. Two relaxation transitions, however, have been observed for both samples. Hence, we can conclude that they are not related to noncrosslinked and crosslinked copolymers, but to crosslinked fractions enriched of ANI and MANI units, respectively.  $T_{g2}$  of AM50/50 (272°C), however, is higher than  $T_g$  of the PMANI-EB homopolymer (222°C) after crosslinking (Table II). It is seen that the decomposition onset for PMANI is about 290°C (Fig. 1, curve 4), whereas it is not observed for PANI (Fig. 1, curve 1) in the temperature range studied (up to 350°C). The decomposition over about 290°C of the PMANI-EB network formed at first heating proceeds to the highest extent. Maybe, this network involves segments of partially decomposed macromolecules that facilitate the mobility of the system, and thus result in decreasing  $T_g$  of PMANI-EB.

We suppose that the segments of copolymers enriched of MANI units are more crosslinked, and the fractions enriched of ANI units continue to polymerize on heating in the respective temperature region. Because of the dense and rigid PANI network formed, ANI oligomers can not easily leave the system and predominantly polymerize. In conclusion, it can be stated that the postpoly-

merization process appears to be a reason for the small mass loss determined for PANI-EB, and thus for the higher thermal stability of PANI-EB as compared to PMANI-EB (Fig. 2, curves 1 and 2).

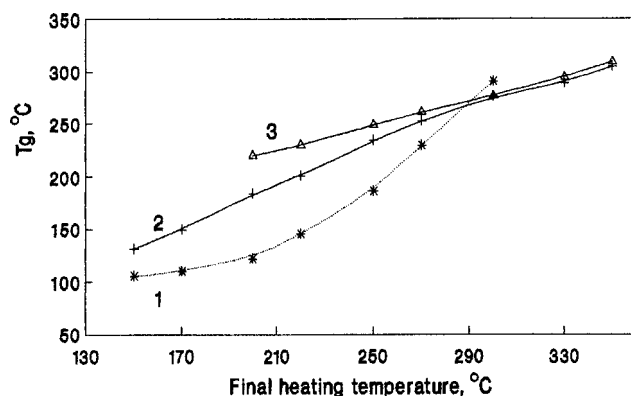
To confirm that the residual monomers and oligomers affect the thermal transition processes, monomer- and oligomer-free samples of PANI-EB and the copolymer AM50/50 were obtained by extraction with chloroform, while the analogous PMANI-EB sample was prepared by extraction with acetone, since it is completely soluble in chloroform. DSC traces of the insoluble (oligomer-free) samples were recorded under the same heating conditions as the initial polymers, the results being given in Table II.

It is seen that in all insoluble fractions  $T_{\min 2}$  has not been registered, i.e., the peak of postpolymerization process has not been found, because of the lack of unreacted monomers and oligomers. The maximum temperature of crosslinking and the two glass transition temperatures of the insoluble-in-chloroform crosslinked PANI increase significantly as compared to the initial one. It is reasonable, since it does not contain low molecular products acting as a plasticizer. On the contrary, the  $T_g$  of the insoluble in acetone-crosslinked PMANI is much lower as compared to the original sample. This confirms our assumption that MANI oligomers take part in the crosslinking process, and when they are absent a looser network is formed, with lower  $T_g$  being determined. Since PMANI homopolymer is completely soluble in chloroform, there is no chance for the chloroform insoluble fraction to contain AM50/50 copolymer. If PANI homopolymer is present in this oligomer-free copolymer system, the crosslinking temperature of the copolymer has to be higher than the crosslinking temperature of the net insoluble in chloroform PANI. However, in our case, the crosslinking temperature is lower than that of the initial copolymer, which is an evidence proving the lack of PANI homopolymer in the AM50/50. Therefore, it can be concluded that the residual monomers and oligomers are taking part in the postpolymerization and crosslinking, thus influencing the relaxation transitions of the polymers studied.

$T_g$  of PANI-EB, PMANI-EB, and PMANI-ES after each heating run up to gradually rising temperatures were also determined (Fig. 3). The higher the final temperature, the greater the degree of crosslinking and the higher the  $T_g$ . The crosslinking of PANI-EB macromolecules proceeds simultaneously with the evolution of residual ANI (up to about 170°C). The network formed is loose, and  $T_g$  rises very slowly (Fig. 3, curve 1). Afterward, the curve slope gets very steep due to the denser network obtained. Then competitive processes of decomposition and postpolymerization take place at temperatures exceeding 300°C (Fig. 1, curve 1 and Fig. 2, curve 1) and  $T_g$  cannot already be registered.

Two linear parts of curve 2 in Figure 3 (PMANI-EB) intersected at 270°C can be observed. The crosslinking up to 270°C proceeds gradually and simultaneously





**Figure 3** Relaxation transition temperatures of 1, PANI-EB, 2, PMANI-EB, and 3, PMANI-ES, determined on heating up to gradually rising programmed temperature and subsequent quenching versus final heating temperature.

with the removal of the nonpolymerized MANI. The decomposition starting over this temperature results in macromolecular segments taking part in the network formation. This second linear part of the curve almost coincides with the trend of PMANI-ES (Fig. 3, curve 3).  $T_g$  of PMANI-ES can be recorded only after water and counteranion release (over 220°C). As seen in Figure 2 curve 3, initially absorbed water and a counterion ( $\text{HSO}_4^-$ )<sup>27</sup> have been evolved from PMANI-ES (up to about 220°C), but the temperature ranges of this evolution cannot be well distinguished.

## CONCLUSIONS

The activation energy of the water release in the temperature range up to about 150°C was estimated for the first time for PMANI. The results obtained indicate that the possible absorbed water structures in PANI given by Matveeva et al.<sup>25</sup> are applicable also for PMANI.

A dependence between the irreversible chemical processes (crosslinking, postpolymerization, and decomposition) proceeding upon heating in inert atmosphere of undoped and crosslinked homo- and copolymers of ANI and MANI in emeraldine oxidation state and  $T_g$  was established.

We suppose that mainly ANI oligomers might be responsible for the postpolymerization process observed on heating of undoped homo- and copolymers studied. It can be stated that the proceeding of this process appears to be a reason for the greater thermal stability of PANI-EB as compared to PMANI-EB.

## References

- Pron, A.; Rannou, P. *Prog Polym Sci* 2002, 27, 135.
- Pud, A.; Ogurtsov, N.; Korzhenko, A.; Shapoval, G. *Prog Polym Sci* 2003, 28, 1701.
- MacDiarmid, A. G.; Chiang, J. C.; Richiter, A. F.; Epstein, A. J. *Synth Met* 1987, 18, 285.
- Genies, E. M.; Boyle, A.; Lapkowski, M.; Tsintavis, C. *Synth Met* 1990, 36, 139.
- Luzny, W.; Banka, E. *Macromolecules* 2000, 33, 425.
- Rannou, P.; Nechtschein, M.; Travers, J. P.; Berner, D.; Wolter, A.; Djurado, D. *Synth Met* 1999, 101, 734.
- Tsocheva, D.; Tsanov, T.; Terlemezyan, L.; Vassilev, S. *J Therm Anal Calorim* 2001, 63, 133.
- Haba, Y.; Segal, E.; Narkis, M.; Titelman, G. I.; Sigemann, A. *Synth Met* 2000, 110, 189.
- Cao, Y.; Smith, P.; Heeger, A. J. *Synth Met* 1992, 48, 91.
- Zheng, W.-Y.; Levon, K.; Taka, T.; Laakso, J.; Oesterholm, J.-E. *J Polym Sci Part B: Polym Phys* 1995, 33, 1289.
- Tsanov, T.; Mokreva, P.; Tsocheva, D.; Terlemezyan, L. *J Macromol Sci Polym Rev* 2004, 44, 311.
- Tsocheva, D.; Terlemezyan, L. *J Therm Anal Calorim* 2004, 75, 739.
- Tsocheva, D.; Terlemezyan, L. *J Therm Anal Calorim* 2005, 81, 3.
- Huang, M.-R.; Li, X.-G.; Yang, Y.-L.; Wang, X.-S.; Yan, D. *J Appl Polym Sci* 2001, 81, 1838.
- Savitha, P.; Sathyanarayana, D. N. *Polym Int* 2004, 53, 106.
- Piza, M. A.; Constantino, C. J. L.; Venancio, E. C.; Matosso, L. H. C. *Polymer* 2003, 44, 5663.
- Yeh, J.-M.; Chen, C.-L.; Chen, Y.-C.; Ma, C.-Y.; Lee, K.-R. *Polymer* 2002, 43, 2729.
- Pandey, S. S.; Annapoorni, S.; Malhotra, B. D. *Macromolecules* 1993, 26, 3190.
- Liao, Y.-S.; Angelopoulos, M.; Levon, K. *J Polym Sci Part A: Polym Chem* 1995, 33, 2725.
- Rehan, H. H.; Al-Mazroa, S. H.; Al-Fawzan, F. F. *Polym Int* 2003, 52, 918.
- Mokreva, P.; Tsocheva, D.; Ivanova, G.; Terlemezyan, L. *J Appl Polym Sci* 2006, 99, 75.
- Wei, Y.; Jang, G.-W.; Hsuesh, K. F.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Polym Mater Sci Eng* 1989, 61, 916.
- Wei, Y.; Jang, G.-W.; Hsuesh, K. F.; Scherr, E. M.; MacDiarmid, A. G.; Epstein, A. J. *Polymer* 1992, 33, 314.
- Chen, S.-A.; Lee, H. T. *Macromolecules* 1993, 26, 3254.
- Matveeva, E. S.; Diaz Calleja, R.; Parkhutik, V. P. *Synth Met* 1995, 72, 105.
- Tsocheva, D.; Zlatkov, T.; Terlemezyan, L. *J Therm Anal Calorim* 1998, 53, 895.
- Boyle, A.; Penneau, J. F.; Genies, E.; Riekel, C. *J Polym Sci Part B: Polym Phys* 1992, 30, 265.
- Tsubakihara, H.; Okamura, H.; Yoshimura, H.; Hayashi, K.; Okada, K.; Sakamoto, A. *Kobunshi Ronbunshu* 1994, 51, 759.
- Yue, J.; Epstein, A. J.; Zhong, Z.; Gallagher, P. K.; MacDiarmid, A. G. *Synth Met* 1991, 41–43, 765.
- Mattoso, L. H. C.; Malmonge, L. F. *Polymer* 1999, 40, 513.
- Malmonge, L. F.; Matosso, L. H. C. *Polymer* 2000, 41, 8387.
- Scherr, E. M.; MacDiarmid, A. G.; Manohar, S. K.; Masters, J. G.; Sun, Y.; Tang, X.; Druy, M. A.; Glatkowski, P. J.; Cajipe, V. B.; Fischer, J. E.; Cromack, K. R.; Jozefowicz, M. E.; Ginder, J. M.; McCall, R. P.; Epstein, A. J. *Synth Met* 1991, 41–43, 735.
- Lee, Y. M.; Kim, J. H.; Kang, J. S.; Ha, S. Y. *Macromolecules* 2000, 33, 7431.
- Rodrigue, D.; Rigga, J.; Verbist, J. J. *J Chim Phys* 1992, 89, 1209.
- Milton, A. J.; Monkman, A. P. *Synth Met* 1993, 57, 3571.
- Conklin, J. A.; Huang, S.-C.; Huang, S.-M.; Wen, T.; Kaner, R. *Macromolecules* 1995, 28, 6522.
- Oka, O.; Kiyohara, O.; Morita, S.; Yoshino, K. *Synth Met* 1993, 55, 999.
- Kobryanskii, V. M.; Arnautov, S. A.; Motyakin, M. V. *Vysokomol Soedin* 1995, 37, 35.
- Kulkarni, V. *Thermochim Acta* 1991, 188, 265.
- Tsocheva, D.; Zlatkov, T.; Terlemezyan, L. *J Therm Anal Calorim* 2000, 59, 721.