

## CALORIMETRIC INVESTIGATIONS OF HIGH DENSITY POLYETHYLENE/POLYANILINE COMPOSITES

D. Tsocheva\* and L. Terlemezyan

Institute of Polymers, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. 103A, 1113 Sofia, Bulgaria

Electrically conductive composites containing high density polyethylene (HDPE) and polyaniline (PANI) - dodecylbenzenesulfonic acid (DBSA) complex were prepared *in situ* by bulk oxidative polymerization of aniline (ANI) in presence of DBSA. Their thermal behaviour and crystallinity parameters were studied for the first time by using differential scanning calorimetry (DSC). It was found that the presence of the conductive complex does not affect the crystalline structure of the matrix polymer neither during *in situ* polymerization of ANI in powdered HDPE nor upon heating of HDPE/PANI.DBSA composite up to 180°C followed by fast cooling.

**Keywords:** composite, crystallinity parameters, differential scanning calorimetry, high density polyethylene, polyaniline

### Introduction

There are two basic approaches to the preparation of electroactive polymer composites consisting of a conventional thermoplastic polymer and an electrically conductive polymer, such as polyaniline (PANI):

- Oxidative polymerization of aniline (ANI) *in situ* in the presence of another (soluble or non-soluble) polymer in acidic aqueous or organic medium [1–6]; and
- Dispersing or ‘dissolving’ PANI in a solution or in a melt of another polymer [7, 8]. For protonation of this preliminary synthesized PANI may be used so called functionalized protonic acids such as dodecylbenzenesulfonic acid (DBSA) [9–15] which makes PANI ‘compatible’ with polymers of similar molecular structure (e.g. polyolefins) [14–18].

Recently it was reported on *in situ* solvent-free bulk polymerization of ANI in presence of DBSA in a matrix of high density polyethylene (HDPE) of normal molecular mass [19] and ultra-high-molecular-mass polyethylene (UHMMPE) [20]. It was suggested that more perfect conductive pathways have been formed in bulk-polymerized blends, as compared to solution or melt blending, due to polymerizing of small ANI molecules in polyethylene (PE) matrix rather, than by interpenetrating of PANI and PE chains. In the case of HDPE/PANI composite [19], on increasing content of the conductive constituent density of the conductive network becomes higher. However, formation of a denser and more ordered conductive network in UHMMPE/PANI composites of higher PANI content

during processing is hampered due to the extremely high melt viscosity of the matrix [20].

There are only a few papers concerning the supramolecular structure of PANI-polyolefine blends. A loose particulate surface morphology of PANI/polypropylene (PP) composite films formed of preliminary synthesized PANI doped with HCl and PP has been observed [16]. According to Cao *et al.* [14], the PANI main chains reveal a relatively high degree of orientation in oriented PE matrix. In another study [21], an unusual interpenetrating network morphology is formed in films of UHMMPE-PANI composite prepared in solution. It is also known that thermal analysis methods are useful in studying PANI and its blends with conventional polymers [22–25].

Our previous structural investigations by using differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD) and thermogravimetry (TG) concern conductive composites of DBSA doped PANI with poly(ethylene-co-vinylacetate) (EVA) [26, 27] and UHMMPE [28] prepared by *in situ* oxidative polymerization of ANI in the matrix polymer. It was found that during the polymerization of ANI at ambient temperature, mixed crystals of PANI.DBSA complex and EVA can be formed [26, 27]. When ANI was polymerized in the presence of UHMMPE, PANI.DBSA complex formed crystallizes separately in the amorphous phase of UHMMPE partially destroying PE crystals [28].

In this paper we will present structural investigations by using DSC of electrically conductive HDPE/PANI.DBSA composites prepared *in situ* by bulk oxidative polymerization of ANI in presence of

\* Author for correspondence: tsocheva@polymer.bas.bg

DBSA. To the best of our knowledge, for the first time the thermal behaviour and crystallinity parameters of such composites were determined.

## Experimental

### Preparation of the composites

HDPE/PANI.DBSA composites were prepared in situ by adding equimolar amounts of DBSA (Tokyo Kasei), ANI and ammonium peroxydisulfate (both Fluka) into powdered HDPE (Neftochim, Bulgaria), followed by bulk polymerization of ANI at room temperature for 4 h with subsequent drying in vacuum at 50°C [19]. A set of composites containing 0.7–20 mass% of net PANI based on the mass of HDPE/PANI blend has been obtained.

For the sake of comparison, UHMMPE/PANI.DBSA composite containing 5 mass% of net PANI was also prepared under similar polymerization conditions, following the procedure described previously [28].

### Thermal treatment

Powdered composites containing 0.7–5 mass% PANI were processed in a melt-index-apparatus (Priborostroi, Russia) for 10 min at 140°C, 5 kg. The strands extruded were allowed to cool to room temperature in air. The processing temperature was chosen to be ca. 10°C higher than the melting peak maximum of HDPE (128.9°C) and also several degrees higher than the end of HDPE melting (ca. 135°C) measured by DSC.

### DSC

Thermal behaviour of melt crystallized HDPE and composites containing PANI.DBSA complex before and after processing in the melt-index-apparatus, were performed on a Perkin Elmer DSC 7 differential scanning calorimeter in nitrogen atmosphere in the temperature range of –40–180°C and heating rate of 10°C min<sup>-1</sup>. The samples were reheated two or three times after quenching at a rate of 200°C min<sup>-1</sup>. The instrument was calibrated by using indium and lead as standards. Samples of about 10 mg were sealed in standard aluminum pans with holes.

### Calculations

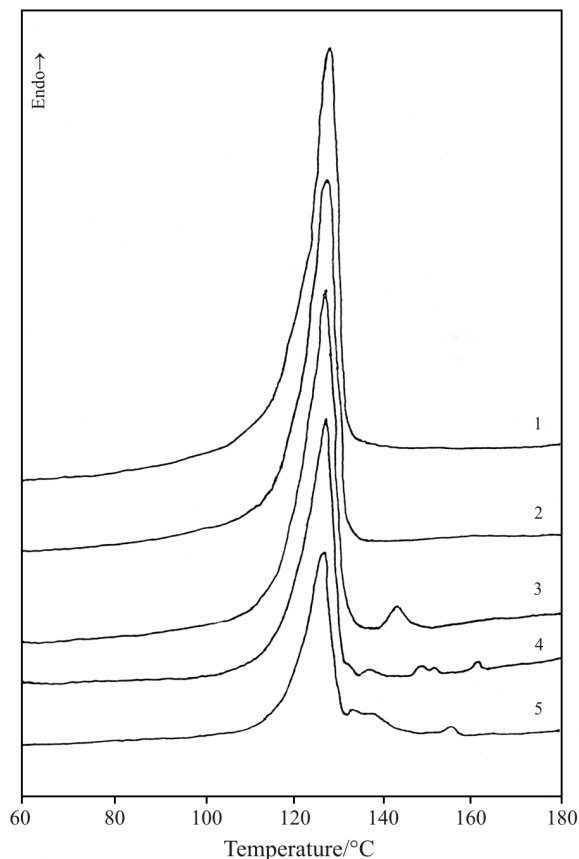
The crystallographic parameters of the samples (the crystallinity degree ( $X_c$ ), average thickness of the crystalline lamellae ( $l_c$ ), amorphous phase ( $l_a$ ) and long period ( $L$ )) were calculated (based on DSC re-

sults) using the equations shown for similar UHMMPE/PANI.DBSA composites in our previous work [28].

The heat of fusion ( $\Delta H$ ) of the HDPE crystals in the composites was calculated by the relationship:  $\Delta H = \Delta H_{\text{total}} W$ , where  $\Delta H_{\text{total}}$  is the sample enthalpy found by DSC and  $W$  is the mass fraction of HDPE in the composite.

## Results and discussion

As seen from DSC trace 1 in Fig. 1, the neat HDPE has a monomodal melting transition in a narrow temperature range, reflecting its original crystalline structure. HDPE chosen for our experiments reveals a moderate crystallinity (ca. 60%), thus it has a large amount of amorphous phase (ca. 40%). In the case at hand, the amount of the amorphous phase is of great importance. It was suggested [28] that PANI macromolecules obtained during in situ preparation of UHMMPE/PANI.DBSA composites can be distributed in the amorphous regions of the matrix polymer forming an electrically conductive network.



**Fig. 1** DSC traces of HDPE/PANI.DBSA composites with different PANI content, registered upon heating up to 180°C at a heating rate of 10°C min<sup>-1</sup> (1–0 %, 2–1.5%, 3–5%, 4–10% and 5–20%)

**Table 1** Thermodynamical and crystallographic parameters of the HDPE in powdery HDPE/PANI.DBSA composites obtained at heating up to 180°C with a heating rate of 10°C min<sup>-1</sup>

PANI/ mass%	$T_m/^\circ\text{C}$	$\Delta H^{\text{sample}}/$ $\text{J g}^{-1}$	PE/%	$\Delta H^{\text{PE}}/$ $\text{J g}^{-1}$	$X_c^{\text{PE}}/\%$	$l_c^{\text{PE}}/\text{nm}$	$L^{\text{PE}}/\text{nm}$	$l_a^{\text{PE}}/\text{nm}$
0	128.9	170.9	100.0	170.9	59.1	5.6	9.5	3.9
0.7	127.6	166.8	95.5	144.6	50.0	5.2	10.4	5.2
1.5	128.7	158.7	90.8	144.1	49.8	5.6	11.2	5.6
5.0	128.7	136.1	74.9	98.5	34.1	5.6	16.4	10.8
10.0	128.4	117.5	65.8	69.3	24.0	5.5	22.9	17.4
20.0	127.6	106.7	49.0	52.3	18.1	5.2	28.7	23.5

$T_m$  – melting temperature of HDPE;  $H^{\text{sample}}$  – heat of fusion of the sample; PE – content of HDPE in the sample;  $H^{\text{PE}}$  – heat of fusion of the HDPE;  $X_c^{\text{PE}}$  – crystallinity degree;  $l_c^{\text{PE}}$  – average size of the HDPE crystalline lamellae;  $L^{\text{PE}}$  – long period;  $l_a^{\text{PE}}$  – average size of the HDPE amorphous phase,

On the DSC traces 3–5 (Fig. 1) of the composites containing more than 1.5 mass% of PANI, melting peaks at temperature above the melting range of HDPE are observed. We relate them to the melting of the crystallites of PANI.DBSA complex evidenced previously by WAXD and DSC studies [29]. As seen in Table 1,  $X_c$  of HDPE in the composites decreases with increasing the PANI content up to 20 mass%, whereas the values of  $T_m$  and  $l_c$  remain almost constant regardless of the presence of PANI.DBSA complex. Consequently, in situ preparation of the PANI.DBSA complex in HDPE matrix does not affect the size and the perfectness of PE crystalline lamella, in contrast to in situ preparation of the PANI.DBSA complex in the matrix of UHMMPE [28] where the PE crystalline phase has been partially destroyed. It is due to the variety of the more defective crystalline structures in UHMMPE.

As seen in Table 2, during the second heating in the calorimetric chamber,  $T_m$  and  $l_c$  also do not essentially change on melting of the quenched samples.  $X_c$  of the matrix polymer - neat and in the composites is slightly lower, because of the high cooling rate of the melts.

The crystallographic parameters of PE in powdered HDPE/PANI.DBSA and UHMMPE/PANI.DBSA composites both containing 5 mass%

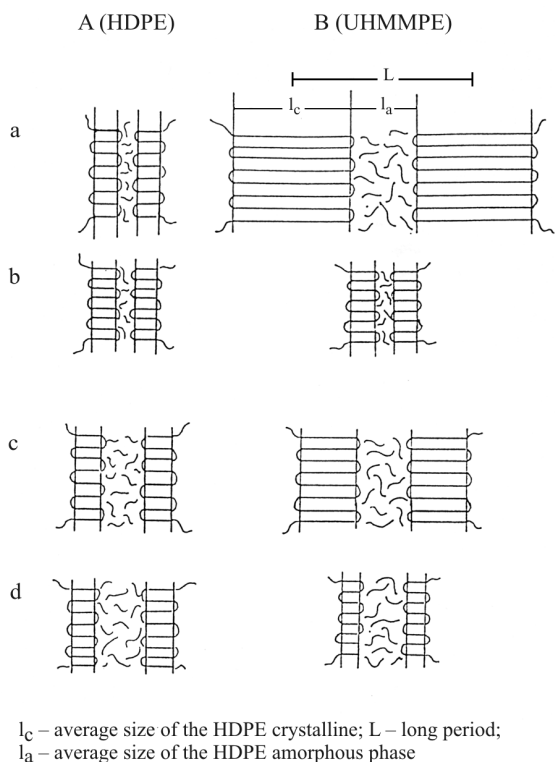
PANI prepared under similar conditions were compared. Due to the different molecular mass of the two polyethylenes (both having  $X_c$  of about 60%) their original structure undergoes different changes during in situ polymerization of ANI in presence of DBSA and upon subsequent melt crystallization. Models of the crystalline morphology of the neat matrix PE polymers and PE/PANI.DBSA composites before and after melting are presented in Fig. 2. It is seen that neither in situ polymerization of ANI in powdered HDPE nor the heating of HDPE/PANI.DBSA composite up to 180°C followed by fast cooling affect substantially the crystalline structure of HDPE in contrast to UHMMPE.

Our previous investigations showed that crosslinking process between PANI macromolecules in an inert atmosphere proceeds both upon dynamic heating over 150°C [30] and annealing at 80°C for 30 min [31]. We also found that on manyfold heating up to 180°C with scanning rate of 10°C min<sup>-1</sup> and subsequent fast cooling, PANI.DBSA complex crystallizes forming a number of crystalline phases [32]. On each subsequent heating cycle they become smaller decreasing their melting temperature and gradually disappear. We tried to follow what happened with PANI.DBSA complex upon manyfold heating and subsequent quenching when it was prepared in situ in

**Table 2** Thermodynamical and crystallographic parameters of the HDPE in powdery HDPE/PANI.DBSA composites obtained at heating up to 180°C with a heating rate of 10°C min<sup>-1</sup> after first heating run under the same conditions and subsequent cooling with a rate of 200°C min<sup>-1</sup>

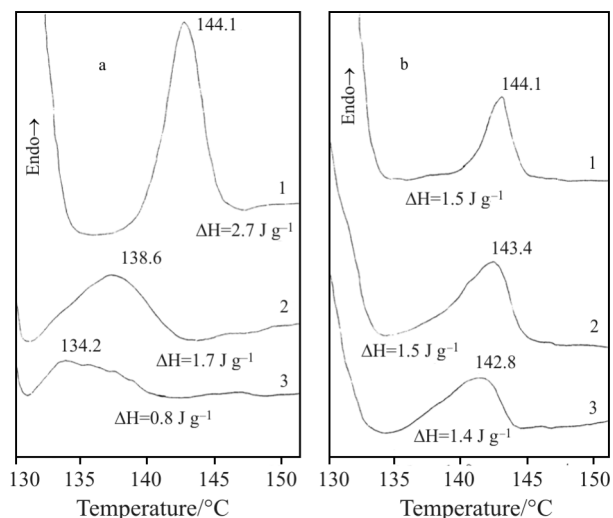
PANI/ mass%	$T_m/^\circ\text{C}$	$\Delta H^{\text{sample}}/$ $\text{J g}^{-1}$	PE/%	$\Delta H^{\text{PE}}/$ $\text{J g}^{-1}$	$X_c^{\text{PE}}/\%$	$l_c^{\text{PE}}/\text{nm}$	$L^{\text{PE}}/\text{nm}$	$l_a^{\text{PE}}/\text{nm}$
0	128.2	164.8	100.0	164.8	57.0	5.4	9.4	4.0
0.7	128.4	158.2	95.5	137.1	47.4	5.5	11.6	6.1
1.5	127.9	149.9	90.8	136.1	47.1	5.3	11.2	5.9
5.0	128.0	121.8	74.9	88.1	30.5	5.3	17.4	12.1
10.0	127.9	107.2	65.8	63.2	21.9	5.3	24.2	18.9
20.0	126.9	90.4	49.0	44.3	15.3	5.0	32.7	27.7

All parameters as in Table 1



**Fig. 2** Comparative scheme of morphological changes in HDPE (A) and UHMPE (B) as a result of in situ polymerization of ANI and melt crystallization; (a – neat PE, b – neat PE after melt crystallization, c – PE/PANI.DBSA composite containing 5 mass% PANI, and d – PE/PANI.DBSA composite containing 5 mass% PANI after melt crystallization)

the matrix of HDPE. It was established that the melting behaviour of the PANI.DBSA complex in the composite containing 5 mass% of PANI during the second and third heating of HDPE/PANI.DBSA composite is similar to the behaviour of the neat complex, as found in our previous study [32]. Of course, when the complex has been formed in the PE matrix its  $\Delta H$  becomes much smaller – about  $2.7 \text{ J g}^{-1}$  ( $\Delta H$  of the neat PANI.DBSA complex, registered at first heating, is about  $12.5 \text{ J g}^{-1}$ ). As seen in Fig. 3a (traces 2 and 3, respectively) both  $T_m$  and  $\Delta H$  of the PANI.DBSA complex drastically drop. It can be supposed that during the consecutive heating and cooling cycles the melted PANI.DBSA complex is not able to recrystallize entirely and the crystallites obtained be-



**Fig. 3** DSC traces of HDPE/PANI.DBSA composites containing 5 mass% PANI (a – as received and b – after thermal treatment in melt-index-apparatus) registered upon heating up to  $180^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  (traces a-1 and b-1, respectively) and after melt crystallization (traces a-2 and b-2 during the second run, and traces a-3 and b-3 during the third run, respectively)

come smaller and less perfect due to both the high cooling rate and the presence of HDPE matrix.

After recrystallization of the crystalline structure of neat HDPE during annealing of the melt in the melt-index-apparatus at  $140^\circ\text{C}$  for 10 min followed by extrusion and slow resolidification down to ambient temperature, again perfect PE crystals were formed. As seen from Table 3,  $T_m$ ,  $X_c$  and  $l_c$  of the recrystallized HDPE are even higher as compared to the corresponding values for the as prepared powdery samples given in Table 1. This is true also for the crystallographic parameters of HDPE in HDPE/PANI.DBSA composites containing very small amount of PANI (less than 5 mass%), when the values become equal (compare Tables 1 and 3).

As mentioned in the Experimental part, the annealing temperature ( $140^\circ\text{C}$ ) was chosen to be higher than the end of HDPE melting range. However, it is lower than the melting peak of PANI.DBSA complex ( $144^\circ\text{C}$ ). Hence, the complex can not melt during the annealing, but the temperature and the time for thermal treatment are high enough for crosslinking to pro-

**Table 3** Thermodynamical and crystallographic parameters of HDPE in the HDPE/PANI.DBSA composites after thermal treatment in a melt-index apparatus at  $140^\circ\text{C}$  for 10 min obtained at heating up to  $180^\circ\text{C}$  with a heating rate of  $10^\circ\text{C min}^{-1}$

PANI/mass%	$T_m/^\circ\text{C}$	$\Delta H^{\text{PE}}/\text{J g}^{-1}$	$X_c^{\text{PE}}/\%$	$l_c^{\text{PE}}/\text{nm}$	$L^{\text{PE}}/\text{nm}$	$l_a^{\text{PE}}/\text{nm}$
0	129.8	201.3	96.6	5.9	8.5	2.6
0.7	129.6	153.7	53.2	5.9	11.0	5.1
1.5	129.2	144.5	50.0	5.7	11.5	5.8
5.0	128.8	98.3	34.0	5.6	16.5	10.9

All parameters as in Table 1



ceed between a part of PANI molecules [31]. The crosslinked macromolecules can not order any more, that is why the heat of fusion is strongly reduced (Fig. 3b, trace 1) as compared with the thermally non-treated composite (Fig. 3a, trace 1).

It was found from our previous DSC and WAXD studies of PANI.DBSA complex [29] that three types of crystalline regions are formed in PANI-DBSA system: (1) free (non-bonded) DBSA molecules ordered between fixed dodecylalkyl tails electrostatically bonded to PANI chains; (2) fixed adjacent DBSA alkyl tails electrostatically bonded to PANI chains; and (3) ordered free (non-bonded) DBSA molecules. It was also found [32] that PANI.DBSA complex reveals crystallinity even after heating up to 270°C, when the free DBSA present in the system has been removed [27]. Therefore, the largest and most stable PANI.DBSA crystallites might be of the above mentioned type (2) formed without free acid participation. In the case at hand, the crosslinking during thermal treatment at 140°C of PANI main chains can 'fix' the supramolecular crystalline structure. The as-received PANI.DBSA crystallites formed during the composite preparation and, according to us being of type (2), have not been affected during annealing and  $T_m$  has the same value of 144°C (Fig. 3b, trace 1). The thermodynamical parameters upon the following heating and subsequent fast cooling cycles (Fig. 3b, traces 2 and 3) do not change. The same PANI.DBSA crystallites are formed between the crosslinking points due to a 'memory effect' of the melt and hindered flexibility of the molecules.

In our previous paper [19] it was established that HDPE/PANI blends possess also remarkable stability of electrical conductivity upon the multiple thermal treatment as used in the present work. Upon second and third heating cycle in the melt-index-apparatus, the conductivity did not decrease. Hence, it can be assumed that a correlation between the composition, conductivity and thermodynamical parameters occurs. PANI amount of 5 mass% seems to be optimal in respect to the crystalline structure. Lower PANI content does not result in ordered structure (Fig. 1, trace 2) and higher one leads to obtain a variety of unstable crystalline phases and to a dense crosslinking network after annealing in melt-index-apparatus.

In conclusion, it can be stated that thermal studies of HDPE/PANI.DBSA composites prepared in situ by oxidative bulk-polymerization of ANI in HDPE of normal molecular mass were performed by using DSC and presented for the first time. Conductive PANI.DBSA complex included in HDPE does not change the size of the crystalline lamellae of the matrix polymer neither during the preparation process, nor upon heating. Stabilization of the supramo-

lecular structure of the composite containing 5 mass% PANI upon thermal treatment at 140°C was found.

## Acknowledgements

The authors acknowledge the financial support provided by the Bulgarian Ministry of Education and Science (Grant No. X-905).

## References

- 1 P. Banerjee, S. N. Battacharyya and B. M. Mandal, *Langmuir*, 11 (1995) 2414.
- 2 S. P. Armes and M. Aldissi, *Mat. Res. Soc. Symp. Proc.*, 173 (1989) 311.
- 3 S. P. Armes, M. Aldissi, S. F. Agnew and S. Gottesfeld, *Langmuir*, 6 (1990) 1745.
- 4 C. DeArmitt and S. P. Armes, *J. Colloid Interface Sci.*, 150 (1992) 134.
- 5 J.-M. Liu, L. Sun, J.-H. Hwang and S.-Ch. Yang, *Mat. Res. Soc. Symp. Proc.*, 247 (1992) 601.
- 6 F. Ruckenstein and S. H. Yang, *Synth. Met.*, 53 (1993) 283.
- 7 P. Banerjee and B. M. Mandal, *Macromolecules*, 28 (1995) 3940.
- 8 M. Angelopoulos, G. E. Asturias, E. Ermer, S. P. Ray, E. M. Scherr and A. G. MacDiarmid, *Mol. Cryst. Liq. Cryst.*, 160 (1988) 151.
- 9 Y. Cao, P. Smith and A. J. Heeger, *Synth. Met.*, 55-57 (1993) 3514.
- 10 Y. Cao, G. M. Treacy, P. Smith and A. J. Heeger, *Appl. Phys. Lett.*, 60 (1992) 2711.
- 11 Y. Cao, N. Colaneri, A. J. Heeger and P. Smith, *Appl. Phys. Lett.*, 65 (1994) 2001.
- 12 Y. Cao, J. Qui and P. Smith, *Synth. Met.*, 69 (1995) 187.
- 13 J.-E. Oosterholm, Y. Cao, F. Klavetter and P. Smith, *Polymer*, 35 (1994) 2902.
- 14 Y. Cao, P. Smith and A. J. Heeger, *Synth. Met.*, 48 (1992) 91.
- 15 Y. Haba, E. Segal, M. Narkis, G. I. Titelman and A. Sigemann, *Synth. Met.*, 111 (2000) 189.
- 16 J. Yang, Ch. Zhao, D. Cui, J. Hou, M. Wan and M. Xu, *J. Appl. Polym. Sci.*, 56 (1995) 831.
- 17 S. Y. Oh, H. C. Koh, J. W. Choi, H. W. Rhee and H. S. Kim, *Polym. J.*, 29 (1997) 404.
- 18 W. Zheng, K. Levon, T. Taka, J. Laakso and J.-E. Oosterholm, *J. Polym. Sci., Part B: Polym. Physics*, 33 (1995) 1289.
- 19 L. Terlemezyan and P. Mokreva, *Intern. J. Polym. Mater.*, 51 (2002) 23.
- 20 L. Terlemezyan, M. Radenkov, P. Mokreva, Ph. Radenkov and A. Atanasov, *J. Polym. Mater.*, 20 (2003) 213.
- 21 A. Andreatta and P. Smith, *Synth. Met.*, 55 (1993) 1017.
- 22 H. Yan, N. Sada and N. Toshima, *J. Therm. Anal. Cal.*, 69 (2002) 881.
- 23 K. Pielichowski, *J. Therm. Anal. Cal.*, 54 (1998) 171.
- 24 J. Pielichowski, *J. Therm. Anal. Cal.*, 53 (1998) 633.
- 25 R. F. de Farias and L. M. Nunes, *J. Therm. Anal. Cal.*, 70 (2002) 559.

- 26 D. Tsocheva, T. Tsanov and L. Terlemezyan, *J. Therm. Anal. Cal.*, 66 (2001) 415.
- 27 D. Tsocheva, T. Tsanov and L. Terlemezyan, *J. Therm. Anal. Cal.*, 68 (2002) 159.
- 28 D. Tsocheva and L. Terlemezyan, *J. Therm. Anal. Cal.*, 75 (2004) 739.
- 29 D. Tsocheva, T. Tsanov, L. Terlemezyan and S. Vassilev, *J. Therm. Anal. Cal.*, 63 (2001) 133.
- 30 D. Tsocheva, T. Zlatkov and L. Terlemezyan, *J. Therm. Anal. Cal.*, 53 (1998) 895.
- 31 D. Tsocheva, T. Zlatkov and L. Terlemezyan, *J. Therm. Anal. Cal.*, 59 (2000) 721.
- 32 D. Tsocheva and L. Terlemezyan, unpublished data.

---

Received: February 13, 2004

In revised form: February 14, 200

---

DOI: 10.1007/s10973-005-6344-1