Journal of Thermal Analysis and Calorimetry, Vol. 68 (2002) 159–168

AGEING OF CONDUCTIVE POLYANILINE/ POLY(ETHYLENE-CO-VINYLACETATE) COMPOSITES STUDIED BY THERMAL METHODS

D. Tsocheva[1], *T. Tsanov*[2] *and L. Terlemezyan*[1]

[1]Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
[2]University of National and World Economy, Department of Commodity Science, Studentsky grad Ch. Botev, 1100 Sofia, Bulgaria

(Received July 12, 2001; in revised form October 10, 2001)

Abstract

The long-term environmental ageing of conductive composite films containing ethylene-co-vinylacetate (EVA) copolymer and a complex of polyaniline (PANI) and dodecylbenzenesulfonic acid (DBSA) was studied by using differential scanning calorimetry (DSC). We assume that both phase separation and crosslinking of PANI main chains occur in the systems. On the other hand, the competition between PANI–DBSA complex self-organization and crystallization of EVA matrix result in structural changes and formation of continuous conductive network, responsible for significantly increased (ca five orders of magnitude) electrical conductivity of the aged films.

Keywords: ageing, crystallinity, differential scanning calorimetry, ethylene-co-vinylacetate copolymer, glass transition, polyaniline

Introduction

The disadvantages of the intrinsically conductive polyaniline (PANI) such as insolubility, infusibility and hence non-processability often hinder its potential applications. Several methods were used to overcome these disadvantages including N- and ring-substitution of aniline by aliphatic large radicals, or preparation of blends/composites with conventional thermoplastic polymers – polyethylene, polypropylene, poly(methylmethacrylate) etc. [1–5]. In order to increase the mobility of the rigid-rod PANI chains and to improve the compatibility and miscibility of PANI with matrix polymers, PANI has been doped with functionalised protonic acids, which usually serves as a surfactant, such as camphorsulfonic acid (CSA) [6–11], dodecylbenzenesulfonic acid (DBSA) [2, 12–15] or other acids with long alkyl chains [16–19]. The bulky non-polar hydrophobic tail of the dopant renders PANI in a conducting form more soluble in non-polar or weakly polar organic solvents and facilitates the processing of PANI by using conventional techniques [20–23]. The glass transition temperature (T_g) of these complexes, e.g. PANI-DBSA, is low enough for optimal processing with thermoplastic polymers such as ethyl-

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

ene-co-vinylacetate (EVA) copolymer [24] which offers excellent ozone and weather resistance as well as good mechanical properties.

It is of great importance to study the interactions between the three constituents in the PANI–DBSA/EVA composites, their supermolecular structure and thermal stability. During processing and storage such composites can be exposed to elevated temperature and changes in their structure can take place (chain defects, crosslinking, etc.). Such structural changes are responsible for relaxation and phase transitions, and deviations in the electrical conductivity of the composites.

It has been found that thermal treatment of PANI–emeraldine base (EB) leads to non-reversible chemical crosslinking reactions between the macromolecules resulting in a two-dimensional polymer structure of phenasine type [25–29]. By using differential scanning calorimetry (DSC) we have recently found [30] that the crosslinking process in PANI–EB films proceeds both upon short-time heating of the polymer over 80°C or during a long-term (1 year) storage of the films at room temperature. It was also found [30] that relaxation transitions can be recorded only for crosslinked PANI–EB and registration of T_g upon the first heating of aged PANI–EB appeared to be an evidence for crosslinking taking place under ambient conditions.

Thermal ageing in various conducting PANI composites protonated with hydrochloric acid and containing polymers with sulfonic groups has been also investigated [31]. It has been found that the presence of sulfonic groups retards the ageing process and the electrical conductivity decreases with ageing time (from 0 to 300 h at 70°C).

In the present investigation we report a DSC study of long-term (up to four years) environmental ageing of PANI–DBSA/EVA composite films of various content of the conductive polymer (from 0 to 17.5 mass%) to explore the structural changes, responsible for the thermal stability and electrical conductivity variations of the composites.

Experimental

Reagent-grade aniline, xylene and ammonium peroxydisulfate (APDS) were purchased from Fluka. EVA copolymer containing 11 mol% of vinyl acetate units (Elvax 210, DuPont) and DBSA (Tokyo Kasei) were commercial products, used as received.

Aqueous dispersion of PANI–DBSA complex was prepared by oxidative polymerization of aniline in the presence of DBSA in aqueous media, using APDS as an oxidant according to the procedure described previously [32].

PANI–DBSA/EVA composites were prepared by mixing appropriate amount of thus obtained aqueous dispersion of PANI–DBSA complex with 1% xylene solution of EVA. They were formulated based on different content of the net PANI in the composites, varying from 0.25 up to 17.5% by the mass of EVA/PANI blend (Table 1). After stirring for 2 h at room temperature, free standing films of the composites were cast in Petri-dishes and the solvents were evaporated in vacuum. The thickness of the films was ca 120 μm. The samples were not kept under any special conditions, i.e. they were exposed to the ambient atmosphere (20–25°C, ca 80% humidity).

Table 1 Thermodynamical characteristics of the composites studied

PANI/ mass%	Before ageing					After 1 year					After 4 years
	T_{m1}/°C	T_{m2}/°C	T_{m3}/°C	T_g/°C	ΔH_m/J g^{-1}	T_{m1}/°C	T_{m2}/°C	T_{m3}/°C	T_g/°C	ΔH_m/J g^{-1}	T_g/°C
0	34.5	48.9	63.5	–25.0	15.9	41.0	52.0	65.0	–24.5	16.0	–24.3
2	35.7	47.9	62.3	–21.6	25.9	48.5	51.6	64.5	–11.0	33.9	–6.4
5	35.0	49.6	63.8	–19.0	41.0	57.0	62.1	72.0	–8.0	77.4	0
7.5	35.5	55.0	66.3	–17.3	44.4	–	–	–	–	–	–
10	36.5	57.5	69.0	–15.5	39.7	57.6	63.1	73.5	–7.2	88.2	–
17.5	37.5	58.0	70.0	–10.7	34.4	58.0	66.2	76.0	–2.9	78.3	16.0
100	–	–	–	65.0	–	–	–	–	73.0	–	92.0

$T_{m1,\ m2,\ m3}$ – melting temperatures for EVA copolymer; T_g – glass transition temperature for PANI = DBSA complex; ΔH – heat of fusion for EVA melting

Thermal studies of the films as received and aged for one and four years under environmental conditions 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^{-1}. The instrument was calibrated by using indium and lead as standards. Samples of about 10 mg were sealed in standard aluminum pans with holes.

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

Results and discussion

As mentioned above, a crosslinking process proceeds in PANI–EB upon a long-term storage under ambient conditions [30]. The greater the number of crosslinks, the higher the T_g of the films cast. In our previous paper [24] it was shown by using DSC that only single T_g of PANI–DBSA/EVA composites appeared upon heating. It gradually increases according to classical Fox's equation [33] that correlates the T_g of a miscible blend system with its composition (Fig. 1, curves 1 and 2). This is an evidence for the miscibility and compatibility of PANI and EVA copolymer. As seen from the results presented in Table 1 and Fig. 1, T_g of the EVA copolymer does not change within the ageing period and the T_g of PANI–DBSA complex and of all the composites studied rise after ageing and the corresponding values do not obey the Fox's equation. Moreover, the longer the ageing period, the higher the T_g. Furthermore, the crosslinking process proceeds at the highest extent in samples of low PANI content (Fig. 1, curves 3 and 4) as inferred from the faster rise of T_g with increasing PANI content. As it is seen from Table 1 the increase of T_g after one-year ageing of

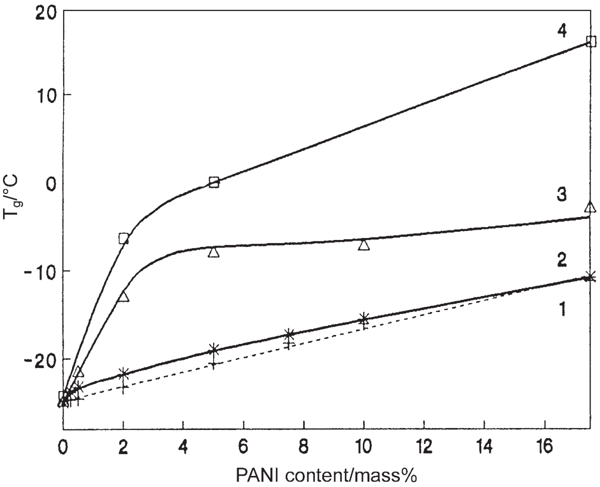

Fig. 1 T_g of PANI-DBSA/EVA composite films *vs*. PANI content; 1 – estimated according Fox's equation; 2 – as-received; 3 – after one-year ageing; 4 – after four-year ageing

the neat PANI-DBSA complex as well as of PANI-DBSA/EVA composites containing more than 10 mass% of PANI, is approximately the same (ca 8°C higher than the corresponding T_g before ageing). An additional rise of about 19°C is observed for the same systems after environmental four-year ageing. Thus, it can be supposed that the crosslinking degree of PANI in the neat complex and in the composites of higher (more than 10 mass%) PANI content is similar and the EVA copolymer matrix do not affect this process.

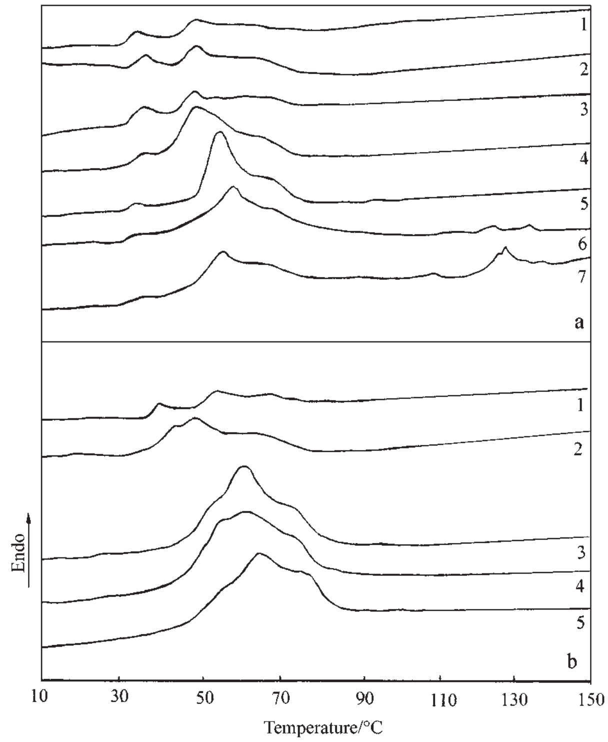

Fig. 2 DSC curves of PANI-DBSA/EVA composite films with different PANI content, registered upon heating up to 180°C at a heating rate of 10°C min^{-1}; (a – as-received: 1 – 0 mass%; 2 – 0.25 mass%; 3 – 2 mass%; 4 – 5 mass%; 5 – 7.5 mass%; 6 – 10 mass% and 7 – 17.5 mass%; b – after one-year ageing: 1 – 0 mass%; 2 – 2 mass%; 3 – 5 mass%; 4 – 10 mass% and 5 – 17.5 mass%)

It was recently found [34] that the conductivity behaviour of PANI–DBSA/EVA composites is variable and dynamic during storage. The electrical conductivity of the films of low PANI content (up to 2.5 mass%) was found to increase by several orders of magnitude over a period of eight months. Phase separation in composite films, resulting in formation of PANI enriched and PANI deficient areas was established during storage of these composites [35]. It was assumed that a process of flocculation of PANI particles occurs, resulting in additional conductive pathway formation, giving rise to significantly enhanced conductivity of the composites [36]. As it is shown above, at the same time a crosslinking process between PANI main chains takes place, resulting in a continuous increase of T_g in spite of the presence of EVA copolymer matrix, particularly in composites containing more than 10 mass% of PANI. Consequently, it can be stated that both phase separation and PANI chains crosslinking are responsible to the formation of continuous conductive network and increased electrical conductivity of aged PANI–DBSA/EVA conductive films.

DSC traces of PANI–DBSA/EVA composites with PANI content from 0 to 17.5 mass% before and after one-year ageing are illustrated on Fig. 2 (Fig. 2a and Fig. 2b, respectively). A broad multimodal melting peak at 30–90°C for all samples is observed. It has been previously established by differential thermal analysis (DTA) that two or three melting peaks appear upon heating the neat EVA copolymer, reflecting the original structure of the samples [37]. The lowest temperature peak (T_{m1}) is assigned to the melting of fringed micellar crystals, and the others (T_{m2} and T_{m3}), to the melting of more perfect chain-folded crystals due to the compositional and configurational heterogeneity in the EVA copolymer [38]. In our recent DSC study [24] we have shown that similar multiple peaks appear also upon heating of PANI-DBSA/EVA composites. Now it is seen (Fig. 2) that in EVA melting range the general shape of the traces for corresponding PANI containing samples prior to and after one-year ageing are similar. However, the following differences were observed: (i) the melting temperature of the aged films is shifted up to higher values (Table 1); (ii) transformation of the peak at T_{m1} into a shoulder for the composites of low PANI content (up to 5 mass%); and (iii) more pronounced peak at T_{m3} for all samples after ageing (Fig. 2). Due to the partial superposition of the melting peaks at T_{m1}, T_{m2} and T_{m3}, the heat of fusion (ΔH_m) for EVA melting was analyzed by determining the total broad area of the multimodal peak.

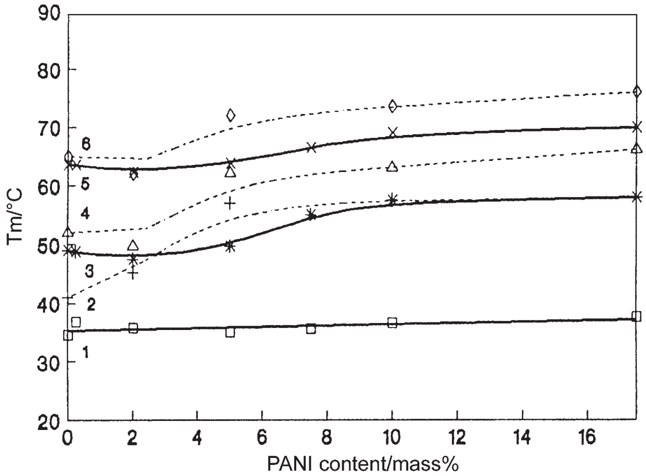

Fig. 3 Dependence of T_m of PANI-DBSA/EVA composite films on PANI content (1–T_{m1}, as received; 2 – T_{m1}, aged for one year; 3 – T_{m2} as received; 4 – T_{m2}, aged for one year; 5 – T_{m3}, as received; 6 – T_{m3}, aged for one year)

As seen from Fig. 3, curve 1, T_{m1} values of as received composites are almost equal at various PANI content, i.e. EVA and PANI do not form mixed fringed micellar crystals during the film formation. PANI–DBSA complex and 'free' DBSA molecules are uniformly dispersed in the nonpolar EVA copolymer matrix [34]. The intensity of the peaks at T_{m1}, however, decreases with increasing PANI content and they become more diffuse (Fig. 2a). This means that the presence of PANI–DBSA in PANI–DBSA/EVA composites hinders the fringed micellar crystallization and the higher the PANI content the lower the content of such EVA crystals. As mentioned above, after one-year ageing the peak at T_{m1} is transformed into a shoulder for the composites of low PANI content (up to 5 mass%) (Fig. 2b). It can be supposed that during the phase separation and crosslinking of PANI chains a part of the unstable fringed micellar EVA crystals are destroyed and involved into the amorphous phase. On the other hand, they have higher melting temperature than the corresponding crystals before ageing, i.e. these crystals become more perfect. Maybe it is due to the flocculation of PANI particles, thus reducing their hindering effect on EVA fringed micellar crystallization, particularly at PANI content up to ca 5 mass% (Fig. 3, curve 2).

As seen from Fig. 3, curves 3 and 5, T_{m2} and T_{m3} corresponding to the melting of less and more ordered EVA chain-folded crystals [37], respectively, registered during the heating of PANI–DBSA/EVA composites, initially slightly decrease and then enhance with increasing PANI content. It is also seen that the intensity of these peaks rises up to PANI content of 7.5 mass% (Fig. 2a), resulting in higher heat of fusion

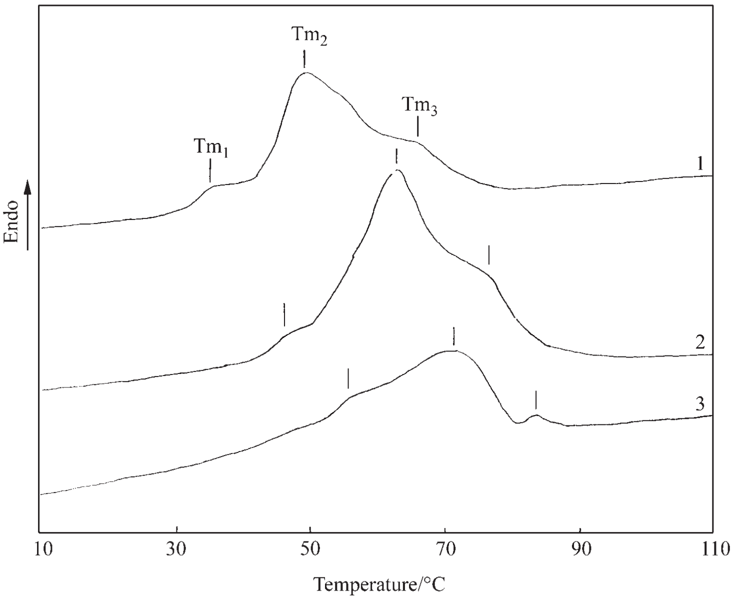

Fig. 4 DSC curves of PANI–DBSA/EVA composite film with PANI content of 5.0 mass% registered upon heating up to 180°C at a heating rate of 10°C min^{-1}; (1 – as-received; 2 – after one-year ageing; 3 – after four-year ageing)

(Table 1). In our previous paper [24] we suggested that PANI affects EVA crystallization as follows:

1. Up to 2 mass% of PANI: The crystalline EVA structures become more defective by mixing with more amorphous PANI. Thus, T_{m2} and T_{m3} slightly decrease on increasing PANI content (Fig. 3, curves 3 and 5). On the other hand, ΔH_m increases (Table 1) due to the ordering of 'free' DBSA long alkyl chains present in the composites.

2. Between 2 and 10 mass% of PANI: The maximum value of ΔH_m is at 7.5 mass% of PANI (Table 1). The degree of crystallinity rises due to thickening of EVA chain-folded crystalline lamellae with participation of alkyl chains of both 'free' and electrostatically bounded DBSA molecules. The melting of these mixed crystals is retarded resulting in a shift of T_{m2} and T_{m3} to higher values (Fig. 3, curves 3 and 5).

3. Over 10 mass% of PANI: T_{m2} and T_{m3} do not change (Fig. 3, curves 3 and 5) and ΔH_m decreases on increasing PANI content (Table 1). Phase separation occurs and PANI–DBSA complex forms its own crystals (Fig. 2a, traces 6 and 7), thus, the peak intensity and ΔH_m appear to be lower.

After one-year ageing the same effects are observed on increasing PANI content. However, due to the above mentioned flocculation process resulting in formation of PANI enriched (more amorphous) and PANI deficient (more crystalline) areas, the melting temperature of EVA chain-folded crystals and their ΔH_m are shifted to higher values (Table 1, Fig. 3, curves 4 and 6).

In our previous paper [24] we considered that more stable chain-folded crystals were melted at T_{m3}. It is seen from Fig. 4 that the endothermal effect at T_{m3} becomes more pronounced during the ageing of the PANI–DBSA/EVA composite containing 5 mass% of PANI. Besides, in contrast to the initial composites, PANI–DBSA com-

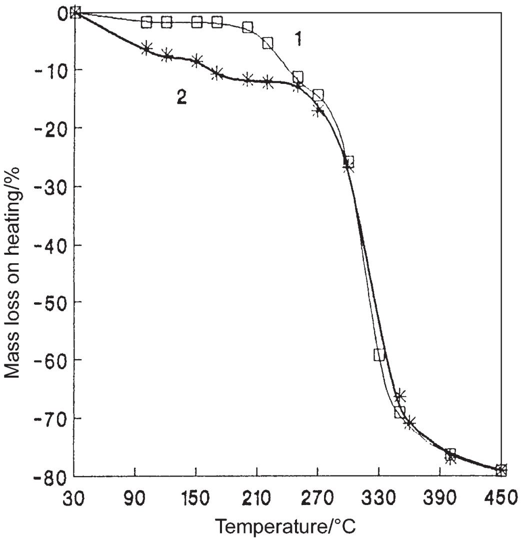

Fig. 5 Mass loss on heating of PANI–DBSA complex *vs*. temperature; TG data (1 – as received; 2 – after four-year ageing)

plex in aged films even of highest PANI contents does not crystalline separately (Fig. 2b). We assume that the peak at T_{m3} is due to the melting of mixed EVA and PANI–DBSA crystals.

TG results show that PANI–DBSA complex (Fig. 5, curve 1) is thermally stable up to approximately 200°C, only absorbed water (ca 2 mass%) being removed. DBSA bounded electrostatically as a counterion has been evolved above 270°C. The ‘free’ DBSA is uniformly distributed in the system, being ordered between fixed DBSA alkyl tails or forming its own crystals [39]. After long-term storage the physical bonds between the ‘free’ DBSA molecules and PANI chains weaken, they can move more easily and ‘free’ DBSA starts to evolve from the system upon heating together with the absorbed water (Fig. 5, curve 2). Electrostatically bounded DBSA, however, remains stable up to ca 270°C. Upon heating after four-year ageing period they evaporated from the PANI–DBSA/EVA composites before melting of the crystals, thus resulting in decreased heat of fusion (Fig. 4).

From the present DSC and TG results obtained for PANI–DBSA/EVA composite films of net PANI content up to 17.5 mass% we can suggest that both phase separation and crosslinking of PANI main chains proceed during the long-term environmental ageing. On the other hand, a competition between PANI–DBSA complex self-organization and crystallization of EVA matrix occurs in the composites studied. Besides, the structural changes and formation of an additional continuous conductive network taking place during the ageing result in substantial increase (ca five orders of magnitude) of electrical conductivity of the films measured previously [34–36].

* * *

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

References

1 M. Wan and M. Xu, J. Appl. Polym. Sci., 56 (1995) 831.
2 C. Y. Yang, Y. Cao, P. Smith and A. J. Heeger, Synth. Met., 53 (1993) 293.
3 S.-A. Chen and W. –G. Fang, Macromolecules, 24 (1991) 1242.
4 M. L. Cerrada, J. M. Perena, P. Benavente and E. Perez, Polymer, 41 (2000) 6655.
5 A. R. Hopkins and J. R. Reynolds, Macromolecules, 33 (2000) 5221.
6 Y. N. Xia, A. G. MacDiarmid and A. J. Epstein, Macromolecules, 27 (1994) 7212.
7 Y. Cao and P. Smith, Polymer, 34 (1993) 3139.
8 Y. N. Xia, J. M. Wiesinger and A. G. MacDiarmid, Chem. Mater., 7 (1995) 443.
9 J. P. Pouget, Z. Oblakowsky, Y. Nogami, P. A. Albouy, M. Laridiani, E. J. Oh, Y. Min, A. G. MacDiarmid, J. Tsukamoto, T. Ishiguro and A. J. Epstein, Synth. Met., 65 (1994) 131.
10 W. Luzny and E. Banka, Macromolecules, 33 (2000) 425.
11 P. Rannou, M. Nechtschein, J. P. Travers, D. Berner, A. Wolter and D. Djurado, Synth. Met., 101 (1999) 734.
12 Y. Cao, J. Qui and P. Smith, Synth. Met., 69 (1995) 187.
13 J.-E. Oesterholm, Y. Cao, F. Klavetter and P. Smith, Polymer, 35 (1994) 2902.

14 A. J. Heeger, Synth. Met., 57 (1993) 3471.

15 Y. Haba, E. Segal, M. Narkis, G. I. Titelman and A. Sigemann, Synth. Met., 111 (2000) 189.

16 C. H. Ong, S. H. Goh and H. S. O. Chan, Polymer Bull., 39 (1997) 627.

17 S. Palaniappan, J. Polym. Sci.: Part A: Polym. Chem., 33 (1995) 2443.

18 D. Li, Y. Jiang, C. Li, Z. Wu, X. Chen and Y. Li, Polymer, 40 (1999) 7065.

19 S. A. Chen and H. T. Lee, Macromolecules, 28 (1995) 2858.

20 J. W. Chevalier, J. Y. Bergeron and L. H. Dao, Macromolecules, 25 (1992) 3325.

21 Y. Chen, E. T. Kang, K. G. Neoh and K. L. Tan, Polymer, 41 (2000) 3279.

22 Y. Cao, P. Smith and A. J. Heeger, Synth. Met., 48 (1992) 91.

23 G. I. Titelman, M. Zilberman, A. Siegmann, Y. Haba and M. Narkis, J. Appl. Polym. Sci., 66 (1997) 2199.

24 D. Tsocheva, T. Tsanov and L. Terlemezyan, J. Therm. Anal. Cal., 66 (2001) 415.

25 J. A. Conklin, S.-C. Huang, S.-M. Huang, T. Wen and R. Kaner, Macromolecules, 28 (1995) 6522.

26 E. M. Scherr, A. G. MacDiarmid, S. K. Manohar, J. G. Masters, Y. Sun, X. Tang, M. A. Druy, P. J. Glatkowski, V. B. Cajipe, J. E. Fischer, K. R. Cromack, M. E. Jozefowicz, J. M. Ginder, R. P. McCall and A. J. Epstein, Synth. Met., 41–43 (1991) 735.

27 B. Lubentsow, O. Timofeeva, S. Saratovskikh, V. Krinichenyi, A. Pelekh, V. Dmirenko and M. Khidekel, Synth. Met., 41–43 (1991) 765.

28 D. Rodrigue, J. Rigga and J. J. Verbist, J. Chim. Phys., 89 (1992) 1209.

29 O. Oka, O. Kiyohara, S. Morita and K. Yoshino, Synth. Met., 55 (1993) 999.

30 D. Tsocheva, T. Zlatkov and L. Terlemezyan, J. Therm. Anal. Cal., 59 (2000) 721.

31 E. Dalas, S. Sakkopoulos and E. Vitoratos, Synth. Met., 114 (1990) 365.

32 T. Tsanov, P. Mokreva and L. Terlemezyan, Polymer, 38 (1997) 743.

33 T. G. Fox, Bull. Am. Phys. Soc., 1 (1956) 123.

34 T. Tsanov and L. Terlemezyan, Polymers and Polymer Composites, 5 (1997) 483.

35 T. Tsanov and L. Terlemezyan, Polymers and Polymer Composites, 6 (1998) 39.

36 T. Tsanov, N. Gospodinova, P. Mokreva and L. Terlemezyan, Polymers and Polymer Composites, 6 (1998) 447.

37 N. Okui and T. Kawai, Makromol. Chem., 154 (1972) 161.

38 Y. Mori, H. Sumi, T. Hirabayashi, Y. Inai and K. Yokota, Macromolecules, 27 (1994) 1051.

39 D. Tsocheva, T. Tsanov, L. Terlemezyan and S. Vassilev, J. Therm. Anal. Cal., 63 (2001) 133.