Polymer 41 (2000) 8387–8391

polymer

www.elsevier.nl/locate/polymer

Thermal analysis of conductive blends of PVDF and poly(*o*-methoxyaniline)

L.F. Malmonge[a,b], L.H.C. Mattoso[c,*]

[a]*Instituto de Química de São Carlos, USP, São Carlos, 13560-970, SP, Brazil*
[b]*Depto. Física e Química, UNESP, Ilha Solteira, 15385-000, SP, Brazil*
[c]*Centro Nacional de Pesquisa e Desenvolvimento de Instrumentação Agropecuária, CNPDIA/EMBRAPA, C.P. 741, São Carlos, 13560-970, SP, Brazil*

Received 4 February 1999; received in revised form 8 February 2000; accepted 12 February 2000

Abstract

The thermal behavior of blends of poly(vinylidene fluoride), or PVDF, and poly(*o*-methoxyaniline) doped with toluene sulfonic acid was studied by thermogravimetic analysis, electrical conductivity measurements, differential scanning calorimetry, X-ray diffraction and scanning electron microscopy. Blends with thermal and electrical conductivity stabler than the conductive polymer alone were obtained. Nevertheless, degradation occurs after a long period of time (500 h) at high temperatures. The possible association of the conductivity decay with dopant loss, degradation and structural and morphological changes of the blend is discussed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Conducting polymers; Polyanilines; Blends

1. Introduction

The thermal analysis of a polymer is crucial to define its performance during application. For conducting polymers [1–3], in particular, the deterioration of conductivity at temperatures above room temperature is a key factor to determine its potential application. It is also important to elucidate the changes in the polymer structure promoted by the temperature treatment. This is particularly important for polyanilines and their derivatives [4–6], since this class of polymers is doped by protonic acids which are more or less volatile depending upon their characteristics, such as molecular weight. In our previous work [7–9], we have shown that the temperature at which polyaniline blends are prepared also affects the structure and properties of the materials produced.

One of the advantages of making a blend of conducting polymers [10–13] and high performance commercial polymers is to increase the performance of the former. Since the discovery of polyacetylene [14] a lot of concern has been raised about the environmental and thermal stability of this new class of polymers. Although several other polymers [3,4,15,16] have achieved much better environmental stability than polyacetylene, their thermal behavior is still a big concern in the conducting polymer field [17–22]. In this sense, poly(vinylidene fluoride) (PVDF) has been widely used as a thermally stable polymer which holds great promise for blending with conducting polymers [23–25].

In this work, the thermal behavior and electrical conductivity stability of blends of PVDF and poly(*o*-methoxyaniline) (POMA) doped with toluene sulfonic acid (TSA) will be focused on and studied by thermogravimetic analysis (TGA), electrical conductivity measurements, differential scanning calorimetry (DSC), X-ray diffraction and scanning electron microscopy (SEM).

2. Experimental

2.1. Polymer synthesis

POMA was chemically synthesized with ammonium peroxydisulfate in aqueous 1.0 M HCl at 0°C, as described elsewhere [26,27]. Deprotonation was performed with 0.1 M ammonium hydroxide for 16 h at room temperature to yield the polymer in the emeraldine base form (EB). The resulting polymer was then dried under dynamic vacuum for 24 h at room temperature. PVDF—Foraflon 4000 HD—was purchased from Atochem and used as received.

---

* Corresponding author. Tel.: + 55-162-742477; fax: + 55-162-725958.

E-mail address: mattoso@cnpdia.embrapa.br (L.H.C. Mattoso).

PII: S0032-3861(00)00182-8

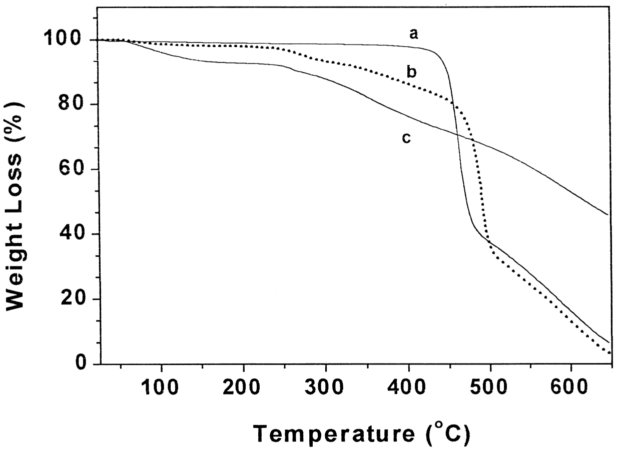

Fig. 1. Thermogravimetric analysis of: (a) PVDF; (b) PVDF/POMA (75/25)-TSA blend; and (c) POMA-TSA.

2.2. Blend preparation

Stock solutions of the conducting polymer (2% w/v) and PVDF (10% w/v) in dimethylacetamide (DMA) were prepared separately. For the preparation of doped POMA blends [27], protonic doping of POMA–EB dissolved in DMA was carried out by addition of TSA in order to have a 50% doping level. No detectable insoluble fraction was noticed upon filtering the solutions. Films (15–30 μm thick) were prepared by casting the blend solutions at the composition PVDF/POMA = 75/25 on a pre-heated glass slide, placed in an oven (50°C) with air circulation. Solvent evaporation was complete after ca. 1 h at 50°C.

2.3. Characterization

Thermal analysis was done in a DSC Du Pont model 2000 at a scan rate of 10°C/min in a nitrogen atmosphere. TGA was performed in a Netzch TG 209 instrument at the same conditions of DSC analysis (10°C/min and nitrogen atmosphere). Electrical conductivity was measured by the standard four-probe method. X-ray diffraction patterns were taken on a Rigaku RU-200B diffractometer, using Cu Kα radiation and a Ni filter. SEM was performed in a ZEISS DSM 960 computerized microscope operated between 10 and 20 kV on samples containing a thin layer (ca. 15 nm) of gold sputter coating.

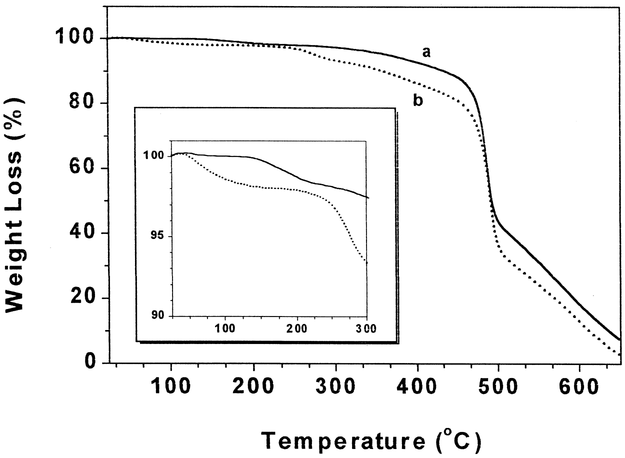

Fig. 2. Thermogravimetric analysis of the PVDF/POMA (75/25) blend: (a) undoped; and (b) doped with TSA. The inset shows the same data in a shorter temperature range.

3. Results and discussion

It was interesting to observe that the characteristics of a high performance polymer such as PVDF can be combined with the properties of a conducting polymer by solution blending. In Fig. 1, one observes that PVDF is very stable till temperatures as high as 400°C, after which it begins to degrade leading to the formation of hydrogen fluoride in an appreciable quantity along with the monomer and small amounts of $C_4H_3F_3$, as reported elsewhere [25]. The conducting polymer, on the other hand, presents considerable weight losses at much lower temperatures than for PVDF in a three-step process. The first step, starting practically from room temperature and going up to ≈ 130°C, corresponds to the expulsion of water molecules from the polymer matrix, although the coevolution of other species such as free acid, oxidant and solvent were not ruled out by other authors [21,28]. The second step, commencing at about 220°C up to ≈ 270°C, is associated with the elimination of the dopant and degradation reactions. This is consistent with the boiling point of the dopant (241.6°C), as well as other studies [17–22], which observed water and dopant losses for polyaniline and derivatives doped with different types of acidic dopants (HCl, H_2SO_4, H_3PO_4, HCOOH, TSA, etc.). Although in our case the doping process was not done in aqueous solution, a strong water adsorption process occurs due to the hydrophilic characteristic of TSA. The third step, commencing at 270°C, is associated with the degradation of the polymer chain structure, in agreement with the literature [21,28].

The thermal stability of PVDF can be combined with the electrical properties of the conductive material. The weight losses observed in POMA doped with TSA (e.g. 3.8% at 100°C, 6.5% at 150°C and 7.3% at 200°C) are diminished in the blend (0.7, 1.2 and 1.3%, respectively), more than would be expected for the amount of POMA-TSA (25%) present in the blend (1, 1.6 and 1.8%, respectively) (Fig. 1). Moreover, the onset temperature for the three weight losses described above occurs usually in a temperature between 5 and 10°C lower for the pure POMA than for the blend. Even though these differences are relatively close to the experimental error of the measurement, this result is important since it shows that the 25% blend combines electrical conductivity close to the pure POMA (10^{-3} S/cm) with a lower weight loss upon heating, due probably to a shielding effect of the surrounding continuous PVDF matrix, which apparently decreases the diffusion and loss of the dopant. Since the

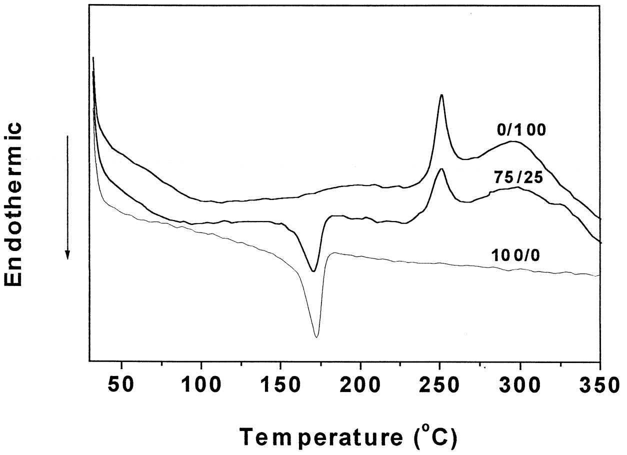

Fig. 3. DSC thermograms of PVDF/POMA-TSA blends with different compositions, as indicated.

melting temperature of PVDF is around 170°C, such stability is more than that necessary for practical use. An evidence that the dopant is associated with the weight losses of the conducting polymer in the blend is presented in Fig. 2, where one observes that the stability of the undoped blend is considerably higher than that of the doped one.

The DSC analysis gives further insight into the thermal behavior of the blends as illustrated in Figs. 3 and 4. Although the samples had been dried before the DSC analysis, one observes the presence of a broad endothermic band around 100°C for both the POMA and the blend doped with TSA, which is associated with absorbed water, consistent with the TGA analysis. Such a band does not appear if a first run from 30 to 130°C is carried out prior to this scan. Another well-defined endothermic peak is also observed for the blend and pure PVDF (Fig. 3), which is assigned to the fusion of the crystalline PVDF phase. It is important to note that the addition of 25% of such a conducting polymer in this blend did not destroy the crystalline structure of the PVDF. The decrease in the heat of fusion observed in the blend, as compared to pure PVDF, is in agreement with the decrease of the relative amount of PVDF in the blend, as has been shown previously [27]. Such an observation is also consistent with the X-ray diffraction analysis which is presented later. Furthermore, for the doped blend and POMA (Fig. 3) two exothermic peaks at ≈ 250 and 300°C can be observed in the DSC analysis, associated with degradation reactions of the polymer chain and dopant structures, such as crosslinking, loss of conjugation, oxidation, decomposition and other reactions including a possible chemical reaction between the dopant and the polymer, as reported in the literature [20–22]. For the undoped blend (Fig. 4) the peak at ≈ 300°C is not observed due to the absence of the dopant. It is known from the literature [17,20–22] that POMA, as well as polyaniline and other derivatives in general, do not present a fusion temperature since they degrade before any fusion can be detected, although crystallinity can be present in some of them.

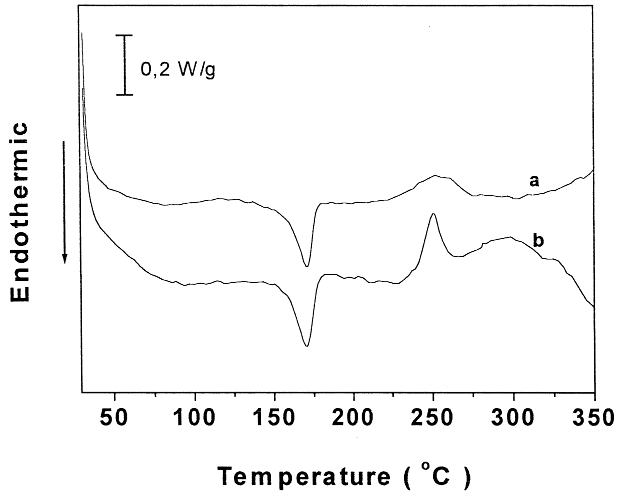

Fig. 4. DSC thermograms of PVDF/POMA blends: (a) undoped; and (b) doped with TSA.

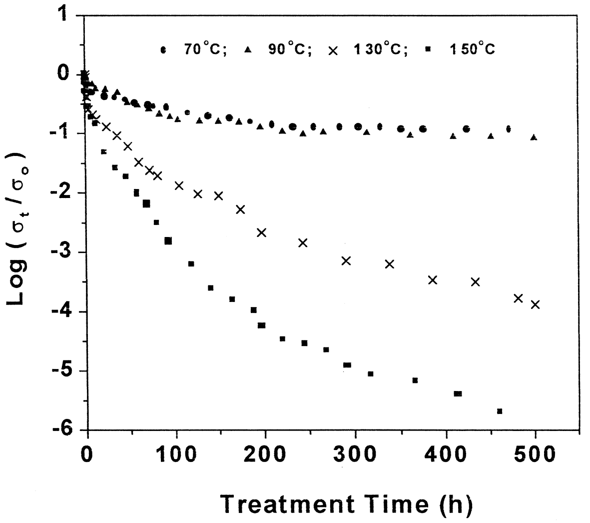

Fig. 5. Normalized electrical conductivity of PVDF/POMA (75/25)-TSA blends as a function of treatment time for several temperatures, as indicated (initial conductivity $\sigma_0 \cong 10^{-3}$ S/cm; σ_t = conductivity after treatment).

The thermal stability of the electrical conductivity of the PVDF/POMA blend was investigated at several temperatures as illustrated in Fig. 5. It can be seen that the conductivity is quite stable at temperatures between 70 and 90°C for the time scale studied (500 h), with only a small decay in the first hours of treatment, due probably to the elimination of residual solvent and/or water, which may contribute to an increase in the charge carrier mobility and consequently, the conductivity. Studies in the literature have shown [19,29], for instance, that small amounts of water lead to an increase in the conductivity of polyanilines due to a decrease in the apparent separation of the metallic islands and/or the height of the barrier between them, making tunneling much more favorable. It should be pointed out that at room temperature the conductivity of these blends have been stable for three years [7]. On the other hand, for temperatures as high as 130

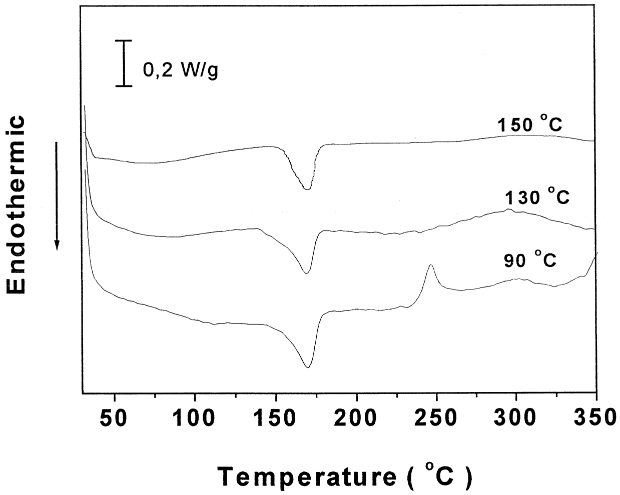

Fig. 6. DSC thermograms of PVDF/POMA (75/25)-TSA blends exposed to 500 h of thermal treatment at different temperatures, as indicated.

and 150°C the conductivity decreases continuously from 10^{-3} to 10^{-7} and 10^{-9} S/cm, respectively. Among the possible causes for this behavior are dopant loss, degradation reactions, and structural and morphological changes. In order to evaluate these effects, the treated samples were further analyzed, as will be shown.

The thermal analysis by DSC of the treated samples (Fig. 6) indicates that the exothermic peaks associated with degradation tend to disappear as the treatment temperature increases. At 90°C, where quite a stable conductivity is still obtained, no significant decrease in the exothermic peaks is observed. However, after 500 h at 130°C the exothermic peak at 250°C disappears, indicating that a degradation reaction has already taken place during the long treatment. Furthermore, after 500 h at 150°C both exotherms are not seen any more, consistent with the degradation under this treatment. These degradation reactions are confirmed by the fact that these samples become insoluble and remarkably less conductive under this treatment, an indication of cross-linking. As reported in the literature [18] degradation by

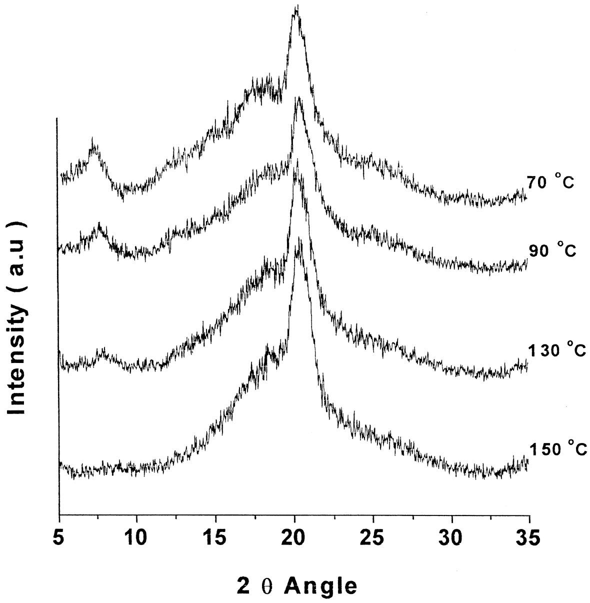

Fig. 7. X-ray diffraction patterns of PVDF/POMA (75/25)-TSA blends exposed to 500 h of thermal treatment at different temperatures, as indicated.

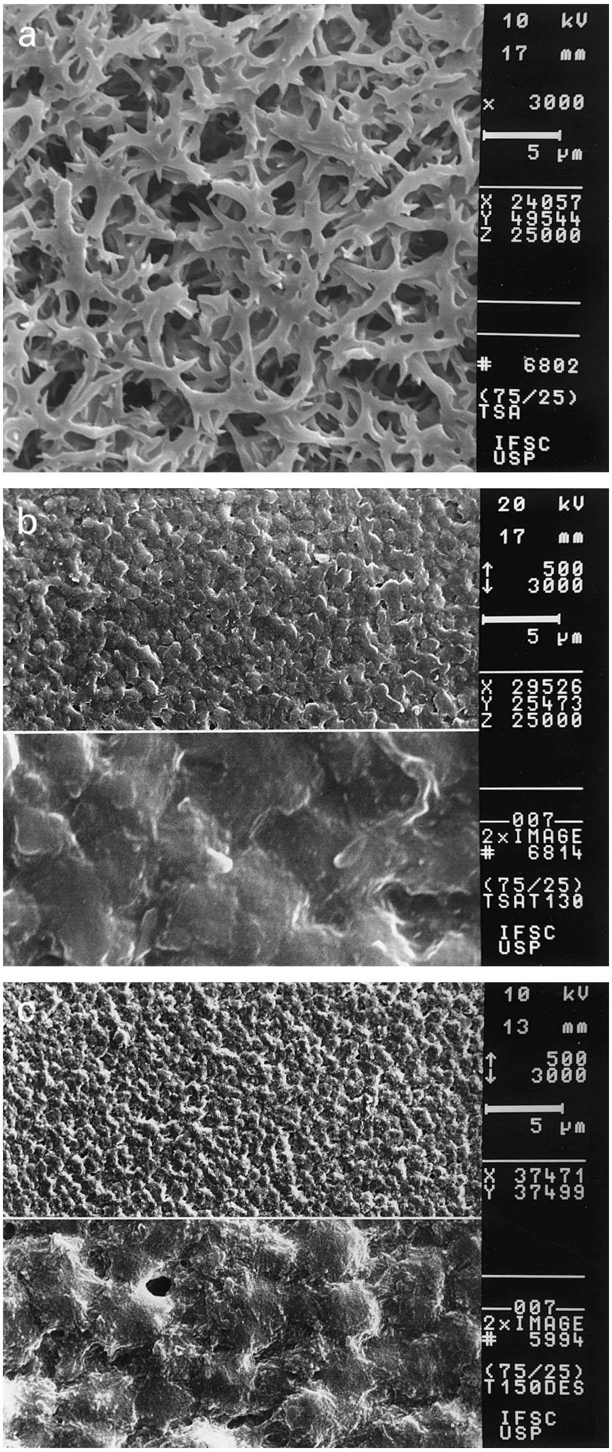

Fig. 8. SEM images of PVDF/POMA (75/25)-TSA blends exposed to 500 h of thermal treatment at different temperatures: (a) no thermal treatment; (b) 130°C; and (c) 150°C.

crosslinking reactions in polyanilines occurs in the double bonds of the imine nitrogens, decreasing the number of nitrogens available for further protonation and doping. As a consequence the conductivity obtained, in our case, for the sample treated at 150°C after redoping was significantly lower than that obtained for untreated samples. It should be pointed out that it was not possible to perform similar stability studies for unblended POMA films since they would not stand the thermal treatment, cracking very easily after a few hours. Nevertheless, the conductivity values obtained in the initial hours were below those presented for the blend, usually about one order of magnitude lower. Therefore, one important advantage of these blends is that the films are flexible and exhibit high tenacity, unlike the POMA films which were very brittle due to the stiff, conjugated and aromatic nature of the polyaniline backbone.

As has been previously pointed out [27], the X-ray analysis of Fig. 7 shows that the ordered regions, corresponding to the diffraction peak at $2\theta = 7^\circ$, which is associated with the conductive doped POMA in the blend, decreases as the treatment temperature increases. No significant difference in $2\theta = 20^\circ$ was noticed upon treatment, associated with β-phase PVDF, consistent with the results described in the DSC analysis. In a previous work [27] it has been shown that the diffraction patterns of crystalline phases of PVDF can be maintained in the blend even for the addition of up to 50% of doped POMA. Additionally, the SEM analysis (Fig. 8) shows that the interconnected fibrillar morphology associated with the formation of conductive pathways of doped POMA within the blend is destroyed at temperatures above 130°C, which might also contribute to the conductivity decrease upon thermal treatment.

4. Conclusions

The thermal analysis indicates a three-step weight loss for POMA-TSA associated with the expulsion of water molecules from the polymer matrix, the elimination of the dopant, and degradation reactions of the dopant and the polymer chain structure, in agreement with the literature. Blends with thermal and electrical conductivity stability better than the conductive polymer alone were obtained. Nevertheless, degradation occurs over a long period of time (500 h) at high temperatures. The conductivity decay is associated with dopant loss, degradation reactions and structural and morphological changes of the blend.

Acknowledgements

The financial support given by CNPq, FAPESP and CAPES (Brazil) is gratefully acknowledged.

References

[1] Wessling B. In: Skotheim TA, Elsenbaumer RL, Reynolds JR, editors. Handbook of conducting polymers, 2nd ed.. New York: Marcel Dekker, 1998, p. 467.
[2] Menon R, Yoon CO, Moses D, Heeger AJ. In: Skotheim TA, Elsenbaumer RL, Reynolds JR, editors. Handbook of conducting polymers, 2nd ed.. New York: Marcel Dekker, 1998. p. 27.
[3] Pud AA. Synth Met 1994;66:1.
[4] MacDiarmid AG, Chiang JC, Richter AF, Epstein AJ. Synth Met 1987;18:285.
[5] Genies EM, Boyle A, Lapkowski M, Tsintavis C. Synth Met 1990;36:139.
[6] Chan HSO, Gan LM, Hor TSA, Seow SH, Zhang LH. Thermochim Acta 1993;225:75.
[7] Malmonge LF. PhD thesis, Universidade de São Paulo, São Carlos, Brazil, 1996.
[8] Malmonge LF, Mattoso LHC. Polímeros: Ciência e Tecnologia 1998;VIII(3):72.
[9] Mattoso LHC, Malmonge LF, Mantovani GL, MacDiarmid AG. Curr Trends Polym Sci 1998;3:99.
[10] Cao Y, Smith P, Heeger AJ. Synth Met 1993;32:263.
[11] Virtaen E, Laakso J, Ruohonen H, Vakiparta K, Jarvinen H, Jussila M, Passiniemi P, Osterholm J-E. Synth Met 1997;84:113.
[12] Laska J, Zak K, Pron A. Synth Met 1997;84:117.
[13] Fu Y, Weiss RA. Synth Met 1997;84:103.
[14] Chiang CK, Fischer CR, Park YW, Heeger AJ, Shirakawa H, Louis EJ, Grau SC, MacDiarmid AG. Phys Rev Lett 1977;39:1098.
[15] Roncali J. Chem Rev 1992;92:711.
[16] Child AD, Kuhn HH. International Conference on Science and Technology of Synthetic Metals, 1996, Utah, USA.
[17] Gupta MC, Umare SS. Macromolecules 1992;25:138.
[18] Wei Y, Hsueh KF. J Polym Sci Polym Chem 1989;27:4351.
[19] Javadi HHS, Zuo F, Angelopoulos M, MacDiarmid AG, Epstein AJ. Mol Cryst Liq Cryst 1988;160:225.
[20] Amano K, Ishikawa H, Kobayashi A, Satoh M, Hasegawa E. Synth Met 1994;62:229.
[21] Palaniappan S, Narayana BH. J Polym Sci Polym Chem 1994;32:2431.
[22] Rannou P, Nechtschein M. International Conference on Science and Technology of Synthetic Metals, 1996, Utah, USA.
[23] Gregório Jr. R, Cestari M, Nociti NCPS, Mendonça J Á, Lucas AA. In: Salamone JC, editor. The encyclopedia of polymeric materials, CRC Press, 1996, p. 7128.
[24] Lovinger AJ. In: Basset DC, editor. Developments in crystalline polymers—1, London: Applied Science, 1982.
[25] Zulfiqar S, Zulfiqar M, Rizvi M, Munir A, McNeill IC. Polym Degrad Stabil 1994;43:423.
[26] Mattoso LHC, Faria RM, Bulhoes LOS, MacDiarmid AG. J Polym Sci Polym Chem 1994;32:2147.
[27] Mattoso LHC, Malmonge LF. Polymer 1999;40:513.
[28] Chan HSO, Ho PKH, Khor E, Tan MM, Tan KL, Tan BTG, Lim YK. Synth Met 1989;31:321.
[29] Angelopoulos M, Ray A, MacDiarmid AG, Epstein AJ. Synth Met 1987;21:21.