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In-situ production of electrically conductive fibres in polyaniline-SBS blends

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Blending of electro-conductive monofilaments with more traditional insulating materials is a promising approach for the production of composites for applications in static dissipative packaging and in industrial textiles. Accordingly, we report on a favourable method for manufacturing these kinds of material which involves generating the fibres *in-situ*, that is, during the actual forming process. Electrically conductive polyaniline (PANI) was thermally blended with polystyrene-polybutadiene-polystyrene (SBS) at different weight compositions. The resultant blends were capillary extruded in order to induce a drawing process in the dispersed phase (PANI) of the blend and hence, the *in-situ* formation of PANI fibres within the above mentioned polymeric matrix. Microscopic analysis on the extrudates revealed that PANI was deformed during the process to produce elongated structures, i.e. ellipsoids or even short fibres, in the blends. Electrical measurements were performed and it was found that blending SBS with no more than 20 weight percent of PANI could produce an electrically conductive composite with a good level of conductivity. The relationship between the volume conductivity and content of PANI in the PANI-SBS blends, was found to be characteristic of a percolation system, with a threshold as low as 5 weight percent of PANI.

1. Introduction

Polymers and polymer-based composite materials with electro-conductive properties, respectively, are materials with potential applications in energy storage [1], antistatic packaging [2], electro-optical devices [3, 4], welding of plastics [5], etc. New materials are being offered in every area and novel products are constantly being introduced. Among these new materials, composites made of electro-conductive monofilaments and insulating polymers are nowadays being used for electrostatic discharge protection and in the textile, carpet and packaging industries [6]. One promising approach for the manufacture of this kind of material, is to generate the electrically conductive fibres *in-situ*, that is, during the actual forming of the component.

Polyaniline (PANI) is one of the most promising conductive polymers due to its excellent chemical stability combined with relatively high levels of conductivity [7, 8]. The electrically conductive form of PANI (emeraldine salt), obtained when the neat polymer is doped with a specific functionalized protonic acid, is soluble in particular common solvents and also can be used to prepare melt processable blends with a low percolation limit [6, 9–11].

For the *in-situ* production of electrically conductive fibres, it is necessary to consider two areas of research activity. The first is related to the study of the rheological properties and microstructure of extruded specimens of two-component blends. This has been the subject of extensive investigation and it has been shown that under appropriate conditions, the dispersed phase can deform during processing to produce elongated structures, i.e. ellipsoids or even short fibres. Evidence of fibrillation in the flow of polymer blends is widespread in studies which are concerned with the microstructure and rheological properties of melt processed blends of polymers. For example, studies performed by Folkes *et al.* [12] concerning the microstructure of extruded samples of SBS block copolymer-polystyrene blends, revealed that the homopolymer polystyrene formed a separate phase, which in some cases was in the form of well-developed fibrils aligned parallel to the extrusion direction. Similar micro-morphoplogy was observed by Ehtaiatkar *et al.* [13] in extruded specimens of SBS block copolymer-polyethylene blends. In this work, the careful control of the blending process and subsequent extrusion led the dispersed polyethylene to form well-developed fibres aligned parallel to the extrusion direction. Ehtaiatkar and co-workers concluded that these fibres were produced primarily as a result of the elongational flow field pertaining at the die entrance and by the lowering of the surface energy of the polyethylene by the block copolymer matrix. The second area of research to be considered is the production of electrically conductive fibres, especially those based on PANI. Gel and solution spinning methods are techniques that have been well developed in the past. Among these techniques, Andreatta and Smith [14] report on the production of continuous monofilaments of electro-conducting PANI at room temperature by extruding a solution of PANI-dodecyl-benzene sulfonic acid (DBSA) in xylene through a spinneret into an acetone bath. Andreatta and Smith [14] also report on the production of polyblend fibres of PANI and ultra high molecular weight polyethylene (UHMW-PE) by a spinning technique. A solution of PANI-DBSA in decaline was combined with an UHMW-PE-decaline solution and the resultant mixture was transferred to a miniature twin screw extruder for blending and processing. The resulting viscous solution was extruded through a spinneret into an acetone bath that cooled and gelled the monofilaments. On the other hand, Virtanen *et al.* [6] give an account of the production of conducting PANI-polypropylene fibres in industrial scale processing equipment. The as-spun and subsequently oriented fibres showed a unique morphology with a phase separated continuous conductive PANI-network embedded in the polypropylene matrix. Chacko *et al.* [15] also report on the production of conducting PANI by means of a solution spinning method. The fibre generation was accomplished using an in-house pilot scale wet spinning unit. Finally, the work that Mattes *et al.* [16] carried out involved the generation of emeraldine base (the non-conducting form of PANI) fibres using a gel-inhibitor, following a spinning procedure. The as-spun fibres were subjected to a further drawing process and, afterwards, were immersed in an acidic solution for doping. They were removed from the doping solution and then dried. These fibres exhibited good mechanical strength and high electrical conductivities.

Consequently, our main objective was to establish the feasibility of producing electrically conductive PANI fibres, fully aligned within a suitable polymer matrix, using a straightforward and suitable technique, so as to form an anisotropically conducting composite.

2. Materials

Electrically conductive melt processable PANI complex, provided by NESTE Oy Chemicals, was used as received. According to the supplier, the approximate composition of the PANI complex is 25% of emeraldine salt and 75% of an organometallic zinc compound. SBS copolymer, Shell Cariflex TR1102 (Kraton 102), was used as a polymer matrix.

3. Experimental

3.1. Blends preparation

Blends consisting of PANI and SBS were prepared by melt mixing in a Brabender, PLE 330. PANI-SBS blends with 5, 10, 15, 20, 35 and 50 weight percent (wt%) of PANI, respectively, were prepared at 15 rpm for 5 min. The blending temperature used was 130°C. For conductivity measurements, flat plaques of about 1 mm thickness were prepared by compression moulding.

3.2. Blends extrusion

Each PANI-SBS blend was capillary extruded using a Davenport extrusion rheometer and a capillary die with a length (L) and radius (R) of 35 and 0.8 mm, respectively. The extrusion temperature and the piston drive speed were 120°C and 1.25 mm/min (wall shear rate of 14.77 s^{-1}), respectively.

3.3. Thermogravimetric analysis

The thermal stability of PANI within the range of temperatures from 40 to 740°C, was investigated using a Perkin-Elmer TGS-2 thermogravimetric analyser (TGA). The analysis was carried out at a rate of 10°C/min under a nitrogen atmosphere.

3.4. X-ray diffraction

X-ray diffraction experiments were carried out on PANI with a Philips 1050 Goniometer X-ray diffractometer, using Ni filtered Cu K_α radiation with $\lambda = 0.15406$ nm. The diffractometer was operated at 36 kV and 26 mA. The diffraction pattern of powdered PANI was obtained by scanning this in an interval of $2\theta = 6$ to 80 degrees at a rate of 0.02 degree/s.

3.5. Infrared spectroscopy

The Fourier transform infrared (FTIR) spectrum of PANI was measured at room temperature with a Nicolet 710 FT-IR spectrometer in a spectral range of 4000 to 400 cm^{-1}. The specimens for analysis were prepared by grinding powered PANI with KBr powder and then pressing the mixture into a tablet. The number of scans and the resolution of the measurements were 150 and 4 cm^{-1}, respectively.

3.6. Rheometry

The rheological behaviour of PANI and SBS was investigated using a Davenport extrusion rheometer. A capillary die with an L of 35 mm and an R of 0.8 mm was used. Apparent viscosity-wall shear rate relationships were calculated at different temperatures for each material. The rheological behaviour of PANI and SBS was analysed at 80, 100, 120 and 150°C, respectively.

3.7. Conductivity measurements

Electrical measurements were carried out using a Keithley 614 electrometer for measuring the electrical resistance of the samples. The volume conductivity was evaluated for five to ten specimens using mercury as electrical probes. Electrical resistance readings were taken from the electrometer after 5 min of sample electrification.

The conductivity evaluation for PANI was carried out on the as-received cylindrical shaped pellets.

For the PANI-SBS blends, the volume conductivity was evaluated for specimens obtained from the respective compression moulded plaques. Specimens of about 2.5 mm length, 2.0 mm width and 1.00 mm thickness were tested. At this stage of the work, no conductivity measurements have been performed on the extrudates.

3.8. Morphological characterisation

The microstructure of the extrudates was initially examined using transmission light microscopy. For this, thin sections were cut parallel to the extrusion direction using a microtome. The direction of cutting, however, was oblique to the axis of the extrudate to eliminate any possibility of cutting artefacts. The sections were examined using a Reichart Microstar 110 optical microscope.

4. Results and discussion

4.1. Characterisation of PANI

Fig. 1 is a TGA thermogram of PANI that shows a small weight loss (about 3%) below 260°C, presumably due to the loss of water. It is also shown that, between 260 and 540°C, PANI undergoes a considerable weight loss (about 68%). This weight loss is attributed to dopant loss. Degradation of the polymer is observed above 540°C. This result served to indicate an upper limit temperature for the processing of PANI in order to avoid the loss of its intrinsic properties.

The X-ray diffraction pattern of PANI is presented in Fig. 2. Four main reflections can be found at 2θ of about 9°, 17.4°, 19° and 47°. However, the intensity of the reflection at 2θ of 47° is very low. These results indicate that the degree of crystallinity in PANI is relatively low.

Fig. 3 shows the X-ray diffraction pattern of a yellow powder found after pyrolysing PANI. The relative intensities of the main reflections found in this figure coincide with those of zinc oxide (ZnO). These results confirm the presence of the element zinc (Zn), originally present as part of the organometallic zinc compound.

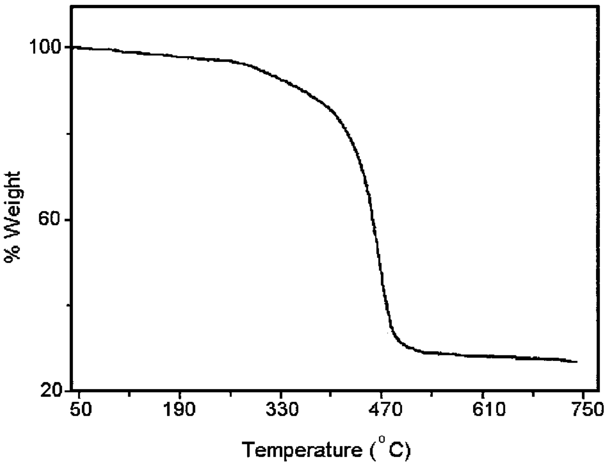

Figure 1 TGA thermogram of polyaniline.

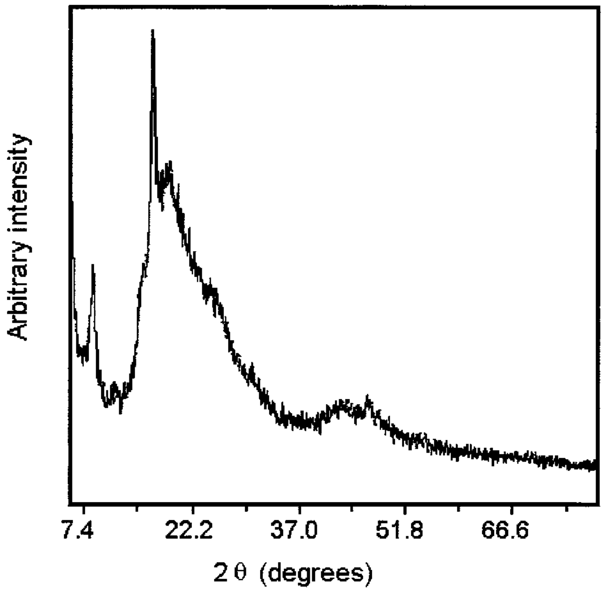

Figure 2 X-ray diffraction pattern of PANI.

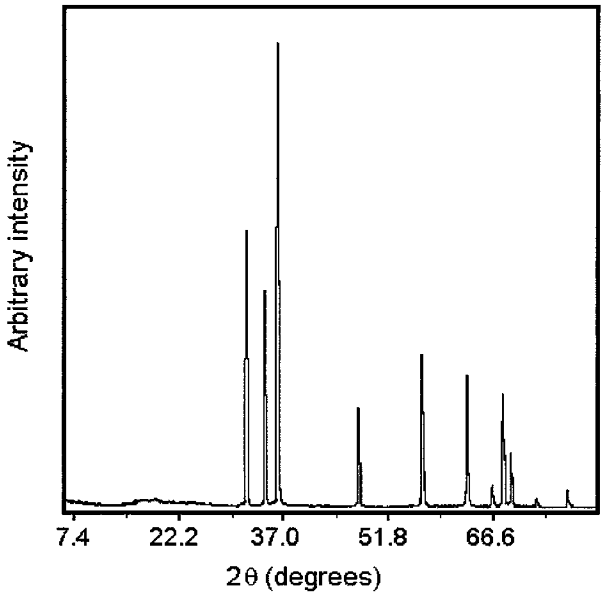

Figure 3 X-ray diffraction pattern of the pyrolysed PANI.

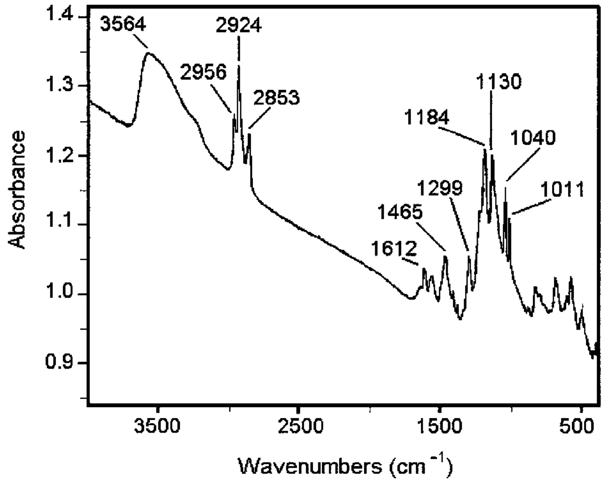

Figure 4 FTIR spectra of PANI.

Fig. 4 shows the FTIR spectra of PANI. The intensities of the main absorption peaks are assigned as follow: C-H bending for para-substituted benzene rings at 1011 and 1040 cm^{-1}. The absorption peaks at 1130 and 1184 cm^{-1} can be considered as characteristic absorptions of the doping band since these two peaks are characteristic of $\text{-SO}_2\text{-}$ stretching for sulfonic salts. C-N stretching vibration is assigned at 1299 cm^{-1} since this kind of vibration is found in the 1350–1280 cm^{-1} band. The deformation of benzene and quinone rings are assigned at 1465 and 1612 cm^{-1}. The absorption peaks at 2853 and 2924 cm^{-1} correspond to $\text{-CH}_2\text{-}$ stretching vibrations whereas the absorption at 2956 cm^{-1} is assigned to $\text{CH}_3\text{-}$ stretching vibrations. The OH band at 3564 cm^{-1} exists because of residual water. There are no features in the spectra between 1700 and 2800 cm^{-1} because no functional groups of PANI show vibration absorption peaks in this region. These results indicate that the doping agent used to yield electrically conductive PANI is a sulfonic acid with benzene rings, probably dodecyl-benzene sulfonic acid, which is commonly used as a protonating acid for PANI [17, 18]. Also, the presence of the element Zn in the pyrolysed PANI,

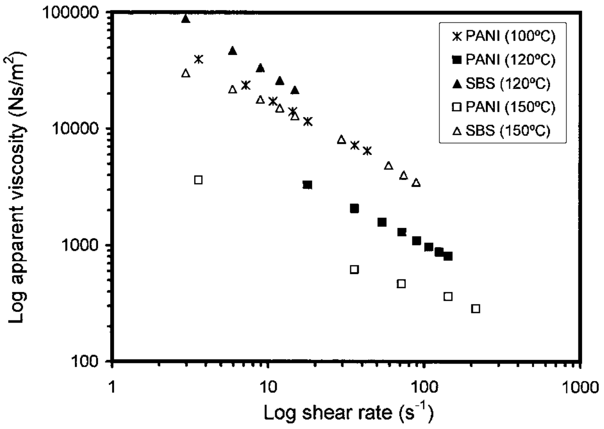

Figure 5 Apparent viscosity-wall shear rate relationships for PANI and SBS at different temperatures.

suggests that possibly a Zn salt of DBSA was also used as plasticizer.

The evaluated average volume conductivity of the PANI pellets was 2.57×10^{-3} S/cm and this compares with the value of 10^{-4} S/cm reported by NESTE Oy Chemicals.

4.2. Rheometry

Apparent viscosity-wall shear rate relationships for PANI and SBS at different temperatures are shown in Fig. 5. The results presented indicate that the viscosity of SBS is higher than that of PANI at comparable extrusion temperatures. These results suggest that the SBS phase could act as a carrier for the dispersed PANI particles, and hence promote *in-situ* fibre formation of PANI in the blends.

4.3. PANI-SBS blends

The average volume conductivity versus PANI content for compression moulded PANI-SBS blends is presented in Fig. 6. The percolation threshold occurs at about 5 wt% of PANI. The blend with 10 wt% of PANI is already conductive (4.48×10^{-6} S/cm), which represents an abrupt increase of about four orders of magnitude in the percolation region. Beyond the percolation point, the conductivity level gradually increases with the PANI content, reaching an average conductivity of 2.10×10^{-4} S/cm for the blend with 20 wt% of PANI. This degree of conductivity is of the same order of magnitude as that of the maximum level observed for the blend with 50 wt% of PANI (7.61×10^{-4} S/cm). Moreover, these conductivity values are very close to those of the neat electrically conductive PANI in the form of pellets (the difference is less than one order of magnitude), depicted in Fig. 6 as 100 wt% of PANI. These results suggest that blending SBS with no more than 20 wt% of PANI could produce an electrically conductive composite with a reasonably good level of conductivity (when compared with the conductivity of PANI).

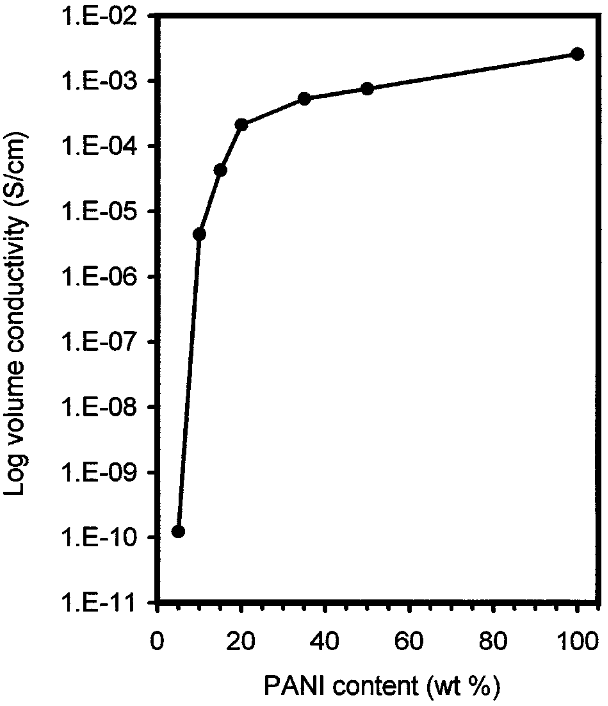

Figure 6 Volume conductivity of PANI-SBS blends as a function of PANI weight percent.

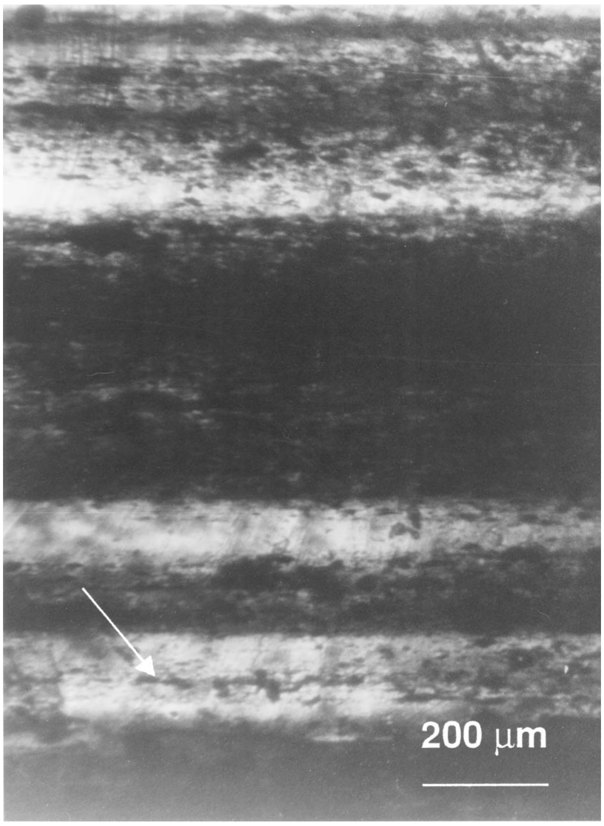

Figure 7 Optical micrograph of the extruded PANI-SBS blend with 10 wt% of PANI. The arrow indicates typical elongated structures in PANI.

The light microscopy analysis of the extruded blends revealed the formation of elongated structures (or even short fibrils) of PANI, aligned parallel to the extrusion direction, as indicated by the arrow in Fig. 7. In Fig. 7, which corresponds to the extruded blend with a PANI content of 10 wt%, the polyaniline phase is represented by the dark regions, whereas the white regions correspond to the SBS phase.

The microstructure detailed above arises from a combination of critical factors. Of primary importance is the development of elongational flow at the capillary entrance which enables the dispersed phase to be locally stretched. However, the dispersed phase will only be effectively elongated if there is sufficient shear stress transfer from the matrix. This requires a matrix polymer that has a high viscosity and yet whose processing temperature allows for a "processing window" to be established for the blend. Earlier work [12, 13] also demonstrates the beneficial effects of using a block copolymer as matrix in that it stabilizes the drawing process occurring in the dispersed phase. As a result of these considerations, we are now optimising the extrusion process to generate a larger concentration of elongated structures throughout the whole body of the extrudate. Parameters to be investigated will include temperature and rate of extrusion. This should result in an enhancement of the level of conductivity along the extrusion direction, thus producing an anisotropically conducting composite.

5. Conclusions

The microstructure of extruded specimens of PANI-SBS blends has been studied using light microscopy. By controlling the blending process and subsequent capillary extrusion, it was found that some elongated structures of PANI were formed and aligned parallel to the extrusion direction. These structures, in the form of short fibrils, are presumably produced as a result of the elongational flow taking place at the die entrance and by lowering of the surface energy of the PANI by the SBS.

The relationship between the volume conductivity and content of PANI in the PANI-SBS blends was found to be characteristic of a percolation system, with a threshold as low as 5 wt% of PANI. The results suggested that blending SBS with no more than 20 wt% of PANI could produce an electrically conductive composite with a reasonably good level of conductivity.

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References

1. E. DALAS, *J. Mater. Sci.* **27** (1992) 453.
2. J. ANAND, S. PALANIAPPAN and D. N. SATHYANARAYANA, *Prog. Polym. Sci.* **23** (1998) 993.
3. E. HARLEY, T. GULAKHMEDOVA, I. RUBINOVICH and G. AIZENSHTEIN, *Adv. Mater.* **8** (1996) 994.
4. Y. CAO, G. M. TREACY, P. SMITH and A. J. HEEGER, *Synth. Met.* **55–57** (1993) 3526.
5. C. Y. WU and A. BENATAR, *Polym. Eng. Sci.* **37** (1997) 738.
6. E. VIRTANEN, J. LAAKSO, H. RUOHONEN, K. VÄKIPARTA, H. JÄRVINEN, M. JUSSILA, P. PASSINIEMI and J. E. ÖSTERHOLM, *Synth. Met.* **84** (1997) 113.
7. J. C. CHIANG and A. G. MACDIARMID, *ibid.* **13** (1986) 193.
8. F. LUX, *Polymer* **35** (1994) 2915.
9. V. JOUSSEAUME, M. MORSIL, A. BONNET, O. TESSON and S. LEFRANT, *J. Appl. Polym. Sci.* **67** (1998) 1205.
10. L. W. SHACKLETTE, C. C. HAN and M. H. LULY, *Synth. Met.* **57** (1993) 3532.
11. M. ZILBERMAN, A. SIEGMANN and M. NARKIS, *J. Macromol. Sci.-Phys.* **B37** (1998) 301.
12. M. J. FOLKES and P. W. REIP, *Polymer* **27** (1986) 377.
13. F. EHTAIATKAR, M. J. FOLKES and S. C. STEADMAN, *J. Mater. Sci.* **24** (1989) 2808.
14. A. ANDREATTA and P. SMITH, *Synth. Met.* **55–57** (1993) 1017.
15. A. P. CHACKO, S. S. HARDAKER and R. V. GREGORY, *Abstracts of Papers of the Amer. Chem. Soc.* **214** (1997) 276.
16. B. R. MATTES, H. L. WANG, D. YANG, Y. T. ZHU, W. R. BLUMENTHAL and M. F. HUNDLEY, *Synth. Met.* **84** (1997) 45.
17. S. J. DAVIES, T. G. RYAN, C. J. WILDE and G. BEYER, *ibid.* **69** (1995) 209.
18. W. P. HSU and K. S. HO, *J. Appl. Polym. Sci.* **66** (1997) 2095.

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