Electrical performance and stability of polypyrrole coated PET fibres

Alessio Varesano, 1 Anna Ibarzabal Ferrer, 2 Claudio Tonin 1*

1 CNR-ISMAC, Institute for Macromolecular Studies, C.so Pella 16, 13900 Biella, Italy. Fax: +39-015-8408387; email: c.tonin@bi.ismac.cnr.it.
2 Universitat Politecnica de Catalunya, EUETIT, C/Colom 1, 08222 Terrassa (Barcelona), Spain

(Received: 6 October, 2006; published:20 February, 2007)

Abstract: PET non-wovens were treated with intrinsically electro-conducting polypyrrole (PPy) produced by chemical oxidative in situ polymerization from pyrrole aqueous solution, using Fe3+ or S2O82- as oxidant, and different dopants. The resulting materials have different electrical performances and thermal properties depending on the thickness of the PPy coating, the amount and the type of dopant embedded into the polymer layer, the type of oxidant used and the pH of the polymerization bath. Samples were maintained at different temperatures and humidity with the aim of gathering information about the electrical performance stability in different environmental conditions. Generally, PPy shows conductivity decay when maintained at high temperature, whereas the conductivity slightly decreases when stored for a long time at cold or room temperature. Moreover, the PPy coating enhances the resistance to heat of the PET fibres (i.e. increase in melting temperature).

Introduction

Several methods have been proposed to improve the electrical properties of textiles made of fibres with poor electrical conductivity because of the large number of potential applications that can be successfully developed with conducting textiles in the technical fields (e.g. protective clothing, furnishing textiles, automotive fabrics, building covering, geo-textiles and medical devices). Electrically conducting textiles, including yarns and fabrics, have been produced by weaving thin metal wires, by incorporating conductive fillers (carbon, metal powder or conductive particles) into textile fibres or by coating fibres with thin metal film or conductive polymer [1, 2]. Incorporation of large amounts of conductive fillers results in a deterioration of the mechanical properties of the fibres and processing problems. In situ deposition of intrinsically conducting polymers (ICPs) seems the most promising way to coat fibres with a light and flexible conducting thin film, without changing significantly the mechanical properties of the textile material.

ICPs are doped π-conjugated polymers such as polypyrrole, polyaniline, polythiophene, polyfuran, poly(p-phenylene), poly(phenylenevinylene), poly(3,4-ethylenedioxythiophene) [3]. When ICPs are produced by oxidative polymerization, they contain positive charges on the backbone chain. It is supposed that the charged species are delocalised over portions of several monomer units. The mobility of charged species along the polymer chain is responsible for the electrical conduction. The charges are neutralized by the introduction in the polymer structure of negative charged counter-ions. The counter-ions (also called dopants) play an important role...
in the synthesis of conducting polymers, because they promote the stability of charged complexes [4, 5].

In the case of polypyrrole (PPy), literature depicts a wide range of counter-ions that can be embedded into the polymer structure. The counter-ions are generally organic sulfonate or sulphate [1,6-9] or inorganic ions such as ClO$_4^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$ [1, 6, 10-11] and greatly influence the final properties (e.g. morphology, conductivity and stability) of the whole polymer [1, 6, 8, 12-13].

Along with electrical conductivity, ICPs possess other interesting properties. They can generate heat by Joule effect, give shielding properties against electromagnetic wave interference (EMI) and protect from spark generation due to electrostatic discharge (ESD). Moreover, recent research on ICPs have shown that they also give heat and flame resistance [14-15], corrosion resistance [16-19], biosensor capacity [20], and antibacterial and antifungal properties [21-22] to the substrates.

Notwithstanding these interesting properties, ICPs have not yet encountered a full development for practical applications in spite of the number of works about the stability of their performances [23-30]. The aim of this work is to study the electrical performance stability of electrically conducting non-wovens, made of PET fibres coated with PPy, with different oxidants and dopants, submitted to temperature and moisture simulating mild-duty ambient conditions such as those normally found, for example, inside a car.

**Results and discussion**

**Electrical properties and heat generation**

Tab. 1 reports the details of the PPy deposition conditions and sample labelling. APS is ammonium persulfate, 2,6NDS is sodium 2,6-naphthalenedisulfonate, 2NS is sodium 2-naphthalenesulfonate and 2,6AQDS is sodium 2,6-anthraquinone disulfonate.

Fitting curves were achieved by means of the SigmaPlot (by SPSS Inc.) computer program. A second-order polynomial equation (1) provides the best fit (square correlation coefficients higher than 0.99) to the current versus voltage curves:

\[ I = aV + bV^2 \]  

where \(a\) and \(b\) are constants, \(I\) is the current (mA) and \(V\) is the applied voltage (V).

Temperature versus voltage data is excellently fitted (square correlation coefficients higher than 0.98) by the exponential equation (2):

\[ T = T_0 + ce^{-dV} \]  

where \(c\) and \(d\) are constants, \(T_0\) is the initial temperature of the sample (°C), \(T\) is the measured temperature (°C) and \(V\) is the applied voltage (V).

Fig. 1 shows that the electrical conductivity of the samples increases with increasing monomer concentration. Unfortunately, waste production and treatment cost increase too, therefore, an acceptable compromise should be found for practical application.

In agreement with the most recent literature [31], we found that Fe$^{3+}$ produces highly conducting PPy. As Fig. 1 shows, PPy produced with FeCl$_3$ is more conductive than PPy produced using APS. Nevertheless, APS is easier to handle than FeCl$_3$. In an attempt to increase the electrical conductivity of the PPy produced with APS, H$_2$SO$_4$
was added to the polymerization bath in order to lower the pH. An increase in conductivity was obtained only in the presence of dopant.

**Tab. 1.** Details about the polymerization conditions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Py conc. (g l⁻¹)</th>
<th>Oxidant</th>
<th>Oxidant/Py molar ratio</th>
<th>Dopant</th>
<th>Dopant/Py molar ratio</th>
<th>H₂SO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>F10</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>F5</td>
<td>5</td>
<td>FeCl₃</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>F2</td>
<td>2</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>F05</td>
<td>0.5</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>PS10</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>No</td>
</tr>
<tr>
<td>PS5</td>
<td>5</td>
<td>APS</td>
<td>1.1</td>
<td>-</td>
<td>-</td>
<td>No</td>
</tr>
<tr>
<td>PS2</td>
<td>2</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>F5A1</td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F5A2</td>
<td>5</td>
<td>FeCl₃</td>
<td>2.2</td>
<td>2,6NDS</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>F5A3</td>
<td></td>
<td>FeCl₃</td>
<td>2.2</td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>PS5H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS5A1H</td>
<td>5</td>
<td>APS</td>
<td>1.1</td>
<td>0.1</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>PS5A2H</td>
<td>5</td>
<td>APS</td>
<td>1.1</td>
<td>2,6NDS</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>PS5A3H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>F5B2</td>
<td>5</td>
<td>FeCl₃</td>
<td>2.2</td>
<td>2NS</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>F5C2</td>
<td></td>
<td></td>
<td></td>
<td>2,6AQDS</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>PS5A2</td>
<td>5</td>
<td>APS</td>
<td>1.1</td>
<td>2,6NDS</td>
<td>0.2</td>
<td>No</td>
</tr>
<tr>
<td>PS5B2</td>
<td>5</td>
<td>APS</td>
<td>1.1</td>
<td>2NS</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>PS5B2H</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Yes</td>
</tr>
</tbody>
</table>

Fig. 2 reports the I-V curves of samples produced with different 2,6NDS dopant amount. Nevertheless, an increase of the dopant content in the polymerization solution above the dopant/monomer molar ratio of 0.2, does not increase proportionally the conductivity. Generally, good results were obtained for the dopant/monomer molar ratio 0.2. In particular, the samples F5A2 and F5A3 exhibit similar I-V curves (Fig. 2 a), and PS5A2H is even more conducting than PS5A3H (Fig. 2 b).
Fig. 1. *I*-*V* curves of samples produced using (a) FeCl₃ and (b) APS as oxidants at different concentrations (2, 5 and 10 g l⁻¹).

Fig. 2. *I*-*V* curves of samples produced using (a) FeCl₃ and (b) APS (in acidified bath) as oxidants with 2,6NDS dopant at different dopant/Py molar ratio (0, 0.1, 0.2 and 0.3).

In addition, when FeCl₃ is used as the oxidant (Fig. 3 a), 2,6NDS and 2NS dopants produce a more conducting PPy layer, with respect to 2,6AQDS, but 2,6NDS and 2NS seem to produce the same effect on the conductivity. In fact, F5A2 and F5B2 show the same *I*-*V* curve that is higher than that of F5C2.

Interesting findings were obtained when the APS oxidant was used in acidified bath. As discussed above, the resulting conductivity increased by effect of a low pH only in the presence of dopant in the polymerization bath. As Fig. 3 b reports, PS5 and PS5H show similar *I*-*V* curves. On the contrary, PS5A2H and PS5B2H show *I*-*V* curves higher than those of PS5A2 and PS5B2 respectively. Moreover, samples produced using 2,6NDS dopant show higher conductivity with respect to the samples produced with 2NS dopant.
Fig. 3. *I*-*V* curves of samples produced using (a) FeCl$_3$ and (b) APS (in acidified and non-acidified bath) as oxidants with different dopant (2,6NDS, 2NS and 2,6AQDS) at 0.2 dopant/Py molar ratio.

Passage of current raises the temperature of the sample by Joule heating. Moreover, the conductivity of the ICPs layer increases as the temperature increases, like inorganic semi-conductor materials and on the contrary of metallic conductors. Fig. 4 reports the plots of temperature versus voltage for the F5, F5A2, PS5A2 and PS5A2H samples. As expected, the *T*-*V* curves follow the same succession of the *I*-*V* curves, that is to say that highly conducting samples produced a great amount of heat, reaching higher temperatures. It is worth noting that the temperature exhibits a voltage-dependent exponential growth despite of the third-order function (*T* ∝ *V*)$^3$) expected from the Joule law equation for constant sample resistance.

Fig. 4. Heat generation of the samples by Joule heating (*T*-*V* curves).
SEM analysis

During polymerization, the fibres immersed in the bath are coated with an even adherent polymer layer, directly grown on the fibre surface (in situ) by adsorption of pyrrole monomer and oxidant molecules.

Fig. 5. SEM pictures of PPy coated fibres obtained with (a) FeCl$_3$ and 2,6NDS, (b) APS and 2,6NDS, and (c) APS and 2,6NDS in acidified bath.

On the contrary, the polymer synthesized in the solution bulk assumes the shape of spheres that deposit and accumulate on the fibre surface forming PPy aggregates weakly linked to the fibre itself which are the cause of low rub fastness. The bulk formation of PPy increased with increasing the monomer concentration in the polymerization bath. SEM images reported in Fig. 5 show the surface of PET fibres
coated with an adherent layer of PPy. The pictures show both an even layer of PPy and large aggregates of PPy. The adhesion and the evenness of the PPy layer seem better using FeCl₃ as the oxidant with respect to APS. Detachments of the PPy layer are visible in the samples produced with APS (Fig. 5 b and c from non acidified and acidified solution, respectively), which were not observed on the samples produced with FeCl₃ (Fig. 5 a). Moreover, dopants seem to increase the presence of aggregates with both FeCl₃ and APS as oxidants.

**ATR FT-IR analysis**

Attenuated Total Reflection (ATR) technique is a powerful tool for investigating evenness, thickness and degree of coating because the infrared beam analyses only a thin layer of the fibre surface.

Fig. 6 reports the FT-IR spectrum from 1850 to 600 cm⁻¹ of uncoated PET fibres and the spectra of coated samples produced with increasing monomer concentration. The spectrum of the F05 sample produced with low monomer concentration (0.5 g l⁻¹ of Py) still shows all the absorption bands typical of PET (1712 cm⁻¹ C=O stretching, 1242 cm⁻¹ C–O stretching, 1095 cm⁻¹ C–O–C stretching, 1016 cm⁻¹ C–O–C asymmetric stretching, 723 cm⁻¹ C–H bending). Spectra of the F2 and F5 samples (obtained using 2 and 5 g l⁻¹ of monomer, respectively) show a decrease of the peak intensity of the PET absorption bands, due to superimposition with PPy absorption bands. F10 sample shows the spectrum of the PPy characterized by weak and broad absorption bands at 1530 cm⁻¹ attributed to the C=C stretching, at 1450 cm⁻¹ assigned to C–C stretching, and the bands at 1370 and 1290 cm⁻¹ assigned to C–N vibrations [31-33]; besides, the peaks at 1140 and 1030 cm⁻¹ may be attributed to PPy ring breathing and C–H deformation, respectively [7].

![ATR FT-IR spectra of PPy coated fibres](image)

**Fig. 6.** ATR FT-IR spectra of PPy coated fibres obtained with different concentration of monomer.

Therefore, the progressive disappearance of the peaks attributed to PET suggests an increase of the degree of fibre coating related to the increase of monomer
concentration in the solution. On the other hand, an increase in monomer concentration implies an increase of the PPy formation in the solution bulk as well.

Fig. 7 shows a comparison between FT-IR spectra obtained from 2,6NDS doped PPy, synthesized with both FeCl₃ and APS. No significant differences in the spectra features were observed by changing the condition of polymerization. The strong attenuation of the absorption bands of PET means that a good degree of coating was achieved also using the dopant.

![ATR FT-IR spectra of PPy coated fibres obtained using FeCl₃ and APS (in acidified and non-acidified bath) as oxidants with 2,6NDS dopant.](image)

**Fig. 7.** ATR FT-IR spectra of PPy coated fibres obtained using FeCl₃ and APS (in acidified and non-acidified bath) as oxidants with 2,6NDS dopant.

**DSC analysis**

The substrate used in this work is a non-woven produced with PET/PET core-shell fibres. The core has higher melting point than the shell. The heating runs of DSC thermogram in Fig. 8 a, clearly shows two peaks at 248 and 254 °C related to the fusion of shell and core, respectively. In literature [14], it has been reported that PPy improved the resistance to heat of silk and cotton fibres because of its highly stable chemical structure. By the DSC analysis of PPy coated samples we observe shifts of PET melting points toward higher temperatures. As reported in Fig. 8 a, the thermogram of F2 sample shows a decrease in enthalpy of the above-mentioned peaks corresponding to the PET fusion and the development of two new peaks at 251 and 259 °C. With increasing amounts of PPy deposited on the fibres (F5 and F10 samples), the peaks at 248 and 255 °C become just shoulders and the enthalpy of the peaks at 251 and 259 °C increases. Therefore, treatment with PPy improves the resistance to heat of PET with an increase of the melting temperature.

The thermograms obtained in the cooling runs (Fig. 8 b) change from uncoated to PPy-coated fibres. The thermogram of the PET fibres shows an exothermic peak at 177 °C related to the PET crystallization. The formation of a single broad peak is due to the mixing of the two PET components (core and shell). The thermograms of the PPy-coated fibres show the increasing of PET crystallization temperatures with
increasing the PPy amount. The crystallization temperatures are 196 °C for F2 sample, 198 °C for F5 sample and 204 °C for F10 sample, respectively. The PPy-coated fibres solidify at higher temperature (about 20 °C) with respect to PET fibres. The increase in melting point allows the crystallization process to begin occurring earlier within the cooling process [34]. It seems that the orientation of PET polymer chains in the coated fibres is preserved in the molten state. The formation of a shoulder at about 180 °C in the thermogram of the F10 sample supports the hypothesis of an incomplete mixing of the two PET components during melting.

Fig. 8. DSC thermograms of PPy coated fibres obtained with different concentration of monomer: (a) heating and (b) cooling.

Fig. 9. SEM picture of PPy coated fibres (F5 sample) after a DSC run up to 300 °C in N$_2$.

Moreover, further SEM observations of PPy coated samples after DSC analysis (up to 300 °C in N$_2$) revealed that the morphology of the fibres was practically unchanged, as Fig. 9 shows. Nevertheless, the material became brittle and frail. It seems that the PPy layer preserves the PET coated fibre shape when the fibre bulk melts.
Stability of the electrical properties

The stability of the electrical properties was evaluated by measuring the increase of the resistance ratio $R/R_0$ due to the storing conditions. Several F5, F5A2 and PS5A3H samples were maintained for long time at different conditions: 20 °C and 65 % R.H.; 80 °C and 100 % R.H.; 80 °C and 3 % R.H.; –28 °C and 100 % R.H.

Fig. 10. Logarithmic resistance ratio ($R/R_0$) of samples produced using (a) FeCl₃, (b) FeCl₃ and 2,6NDS, (c) APS (in acidified bath) and 2,6NDS, stored at different environmental conditions.
Fig. 10 shows the resistance ratio vs. time of the samples submitted to the above-mentioned conditions. From these results, it could be understood that temperature is the parameter that had the major influence on the PPy conductivity decay. High temperature leads to a large increase in resistance, whereas the samples stored at low temperature (room temperature and cold environment) exhibit small resistance increase. In Fig. 10a, the F5 sample obtained using FeCl$_3$ without organic dopant, showed high resistance increase (R/R$_0$ = 24.9 after 120 h at 80 °C in wet conditions, and R/R$_0$ = 18.6 in dry conditions). The sample coated with 2,6NDS doped PPy (F5A2 sample) was the most stable, with resistance ratio R/R$_0$ < 10 obtained after 120 h at 80 °C and 100 % R.H. (see Fig. 10b). The PS5A2H showed poor stability to high temperature with the highest values of R/R$_0$ (R/R$_0$ = 47.2 after 120 h in wet conditions and R/R$_0$ = 44.3 after 120 h in dry conditions, respectively), as reported in Fig. 10c. Whereas, the resistance increase measured on all the samples stored at 20 and −28 °C were modest, with values in the range of 1.3-1.8, but not negligible. In particular, the F5, F5A2 and PS5A2H samples after 120 h had average R/R$_0$ values of 1.55, 1.47 and 1.80, respectively, when stored at room temperature (20 °C, 65 % R.H.), and 1.32, 1.42 and 1.76 when stored at −28 °C. In that case, the PPy produced using APS still displayed the worst stability, while the PPy produced with FeCl$_3$ had good stability both with and without 2,6NDS as the dopant.

Conclusions

The electrical conductivity of the samples treated by in situ polymerization of pyrrole increases with increase in monomer concentrations, but waste and cost also increase proportionally. Satisfactory results in terms of electrical conductivity have been obtained with a pyrrole concentration of 5 g l$^{-1}$. The PPy produced with FeCl$_3$ is more conductive than PPy produced using APS, and the use of doping agents (such as 2,6NDS, 2NS and 2,6AQDS) further increases the conductivity. Generally, good results were achieved using dopant/monomer molar ratio of 0.2. When APS is used as the oxidant in acidified bath, in the presence of a dopant, the resulting PPy is more conductive. Moreover, PPy improves the resistance to heat of coated PET fibres shifting the PET melting point toward higher temperatures.

The electrical conducting stability was evaluated measuring the R/R$_0$ resistance ratio of samples stored in different environmental conditions. It was found that the temperature had great influence on the conductivity decay with respect to humidity. In fact, a large increase in resistance was measured on the samples stored at 80 °C in both moist and dry conditions. Whereas, the samples stored at low temperature (room temperature and cold environment) exhibited small resistance increase. The dopant also enhances the stability of the conducting properties, particularly in the case of PPy synthesized with FeCl$_3$ as the oxidant.

Experimental part

Materials

The chemicals used were Pyrrole, 97% (Py, by Fluka) as monomer; Iron (III) chloride hexahydrate, 98% (FeCl$_3$·6H$_2$O, by Fluka) and Ammonium persulfate, 98+% (APS, by Sigma-Aldrich) as oxidants; 2,6-naphthalenedisulfonic acid, disodium salt, 97% (2,6NDS, by Sigma-Aldrich), naphthalenesulfonic acid, sodium salt, 90% (2NS, by Sigma-Aldrich) and 2,6-anthraquinonedisulfonic acid, disodium salt, 97% (2,6AQDS, by Sigma-Aldrich), sulphuric acid, 95-97 % (H$_2$SO$_4$, by Fluka) as pH corrector.
The substrate used was a commercial non-woven mat (45 kg m$^{-3}$) composed of 20 µm poly(ethylene terephthalate) core-shell fibres.

**PPy deposition**

The non-woven mat was cut in squares (7.0 × 7.0 cm) of 0.7 cm thickness. The PPy deposition was carried out by *in situ* chemical oxidative polymerization in aqueous solution. The squares were plunged in a solution containing the oxidant and the dopant (when used), and then the monomer was added to the continuously stirred polymerization bath. After 4 h, the samples were rinsed in water, squeezed, dried and stored in a conditioned laboratory (20 °C, 65 % R.H.) for at least 24 h before testing. For all the samples, the ratio between volume of solution and weight of substrate was fixed at 75 ml g$^{-1}$ and the molar ratios between oxidants and monomer was fixed at 2.2 and 1.1 for FeCl$_3$ and APS, respectively. Polymerizations were carried out varying both the monomer and the dopant concentrations. Moreover, three dopants (2,6NDS, 2NS and 2,6AQDS) were tested using both FeCl$_3$ and APS oxidants. For comparison, some samples were produced at pH 1.4 by adding H$_2$SO$_4$ in the polymerization bath using APS as the oxidant. Tab. 1 reports the details of the polymerization bath conditions and sample labelling.

**Electrical properties and heat generation**

The electrical conductivity of the samples were measured in a conditioned laboratory (20 °C, 65 % R.H.) by means of an electrical circuit consisting of a Metrel potentiometer (0-230 V, 50 Hz), a digital Multimeter Escort 170 and a Supertester 680G ammeter. The sample was connected to the electrical circuit using 8 terminals (alligator clips) for each side. The surface temperature was measured by means of a Raytek Raynger ST infrared thermometer in 9 points on the samples during the electrical tests. The system is very quick to reach steady-state current and temperature as the voltage changes and the values are stable for some minutes.

**Environmental conditions**

The stability of the electro-conducting properties to temperature and humidity was evaluated measuring the electrical resistance ratio $R/R_0$ from the current-voltage curves. Several F5, F5A2 and PS5A3H samples were placed: 1) in a conditioned laboratory at 20 °C and 65 % R.H., 2) over a thermostatic water bath at 80 °C in vapour saturated air (100 % R.H.), 3) in a stove at 80 °C in dry air (3 % R.H.), and 4) in a freezer at -28 °C. The electrical conductivity of the samples was measured every 24 h. All the samples were stored at least 24 h in a conditioned laboratory (20 °C, 65 % R.H.) before the electrical measurements to normalize their moisture content.

**SEM analysis**

Scanning Electron Microscopy (SEM) investigation was performed with a Leica Electron Optics 135 VP SEM, with an acceleration voltage of 15 kV, current probe of 400 pA and working distance of 20 mm. Before SEM observations, the samples were mounted on aluminium specimen stubs with double-sided adhesive tape and sputter-coated with gold in rarefied argon using an Emitech K550 Sputter Coater with a current of 20 mA for 180 s.
**ATR FT-IR analysis**

Infrared (FT-IR) analysis was carried out in a Thermo Nicolet Nexus spectrometer by ATR technique with the Smart Endurance accessory in the range from 4000 to 600 cm\(^{-1}\) with 100 scansions and 4 cm\(^{-1}\) of band resolution.

**DSC analysis**

Differential Scanning Calorimetry (DSC) was performed in a Mettler Toledo DSC 821 calibrated by indium standard. The calorimeter cell was flushed with 100 ml min\(^{-1}\) of nitrogen. About 3 mg of sample were used in each test using aluminium crucibles. The heating runs were performed from 30 °C to 300 °C with a heating rate of 10 °C min\(^{-1}\), the cooling runs from 300°C to 50°C with a cooling rate of 10 °C min\(^{-1}\). Heating and cooling runs were performed consecutively. The data were collected on a computer with the Mettler Toledo STAR\(\text{e}\) System.

**References**