

## DSC AND FTIR STUDY OF THE GAMMA RADIATION EFFECT ON *cis*-1,4-POLYISOPRENE

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The effect of  $\gamma$ -radiation on the *cis*-1,4-polyisoprene in the presence of oxygen is investigated by ATR-FTIR technique and non-isothermal DSC measurements. FTIR measurements have shown that the formation of hydroperoxides, ketones, alcohols and/or ethers is apparent already at lower, 20–50 kGy, doses of  $\gamma$ -radiation and it increases significantly with the exposure time. Besides, lactones, anhydrides, peresters, carboxylic acids, and esters are formed, too. Spectral changes in the region of C=C conjugated double bonds indicate a formation of shorter polyene structures and aromatic rings. Kinetic parameters describing the temperature dependence of the induction period have been obtained from DSC measurements using the isoconversional method. Residual stabilities have been calculated in order to characterize the gamma radiation effect on polyisoprene thermooxidative stability. Both methods proved that doses lower than 50 kGy do not cause severe changes in polymer properties.

**Keywords:** degradation, DSC, FTIR, gamma radiation, oxidation, polyisoprene

### Introduction

Polymer products undergo degradation, which is mainly caused by oxygen, ozone, heat and dynamic stress. Radiation is also responsible for the polymer degradation, oligomer formation and chain cross-linking. Understanding the  $\gamma$ -radiation-oxidation process is technologically important, since polymers, when irradiated, are mostly exposed also to air during and/or after irradiation. Radiation doses applied in practice are usually in the range of several tens of kGy used in sterilization or during the polymer lifetime in nuclear power plants [1, 2].

Diene elastomers are known to be very sensitive to oxidative ageing. One of the major differences between elastomers and polyolefins consists in the presence of a large number of C=C bonds in the former. These are a part of the regular structural units of the polymer and not defect structures as in polyolefins. Sensitivity of elastomers to radiation results from the presence of C=C bonds which easily undergo radical attack followed by hydrogen abstraction on the carbon atom in  $\alpha$ -position to the double bond [3, 4].

Using  $^{17}\text{O}$  NMR, in  $\gamma$ -irradiated polyisoprene Alam *et al.* found oxidation products such as alcohols, ethers, unsaturated ethers, ketones, aldehydes, water and small amounts of carboxylic acids and esters [5]. Similar oxidation products are formed in the case of photochemical oxidation of polyisoprene – hydroperoxides, alcohols, ketones, aldehydes, epo-

xides and carboxylic acids were detected by IR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR [6, 7].

The oxidation is an exothermic process; hence DSC can be employed for its study. In most cases, the oxidation processes occurring in the condensed phase exhibit an induction period (IP) which is the stage preceding the main process, where apparently no chemical reaction takes place. At the end of the IP there is often a sudden change of material characteristics, so the length of the IP is frequently considered to be a measure of the material stability. In this study, the influence of  $\gamma$ -radiation on the thermooxidative stability of polyisoprene has been examined. The chemical changes induced by  $\gamma$ -radiation and oxidation of polyisoprene have been investigated using FTIR (FTIR – Fourier transform infrared) spectroscopy in order to characterize the samples used in DSC measurements and for the correlation of spectral changes with obtained DSC results.

### Experimental

Thin, 0.2–0.3 mm, *cis*-1,4-polyisoprene films were placed in a  $^{60}\text{Co}$  gamma ray source with dose rate 0.26 kGy  $\text{h}^{-1}$ . The samples were irradiated at room temperature for 3–49 days.

Samples used in DSC measurements have been characterized using FTIR spectroscopy. The attenuated total reflectance (ATR) infrared spectra of

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non-irradiated and  $\gamma$ -irradiated polyisoprene samples in the region 4000–400  $\text{cm}^{-1}$  were recorded using the Nicolet model NEXUS 470 FTIR spectrometer at room temperature. The nominal resolution of spectra was 4  $\text{cm}^{-1}$  and the number of scans 128.

The calorimeter Perkin Elmer DSC-7 was employed to study the thermooxidative stability of the samples. The temperature scale was calibrated to the melting points of In, Sn and Zn, the enthalpy calibration has been carried out to the heat of fusion of In. The samples of 2–4 mg were placed in crimped standard aluminium pans, where the lid of each pan was perforated by ten pinholes. Heating rates were 1, 3, 5, 7 and 10  $\text{K min}^{-1}$ . The purge gas forming the reaction atmosphere was oxygen. The starting temperature of oxidation was determined as the onset temperature of the oxidation peak.

## Results and discussion

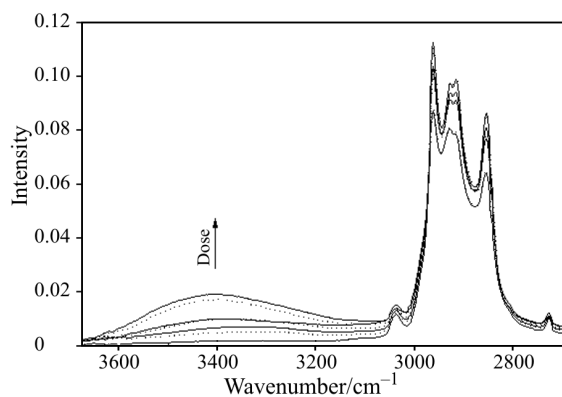
### FTIR spectra measurements

Gamma radiation in the presence of air leads to significant changes in the IR spectra of the exposed polyisoprene films. Broad increase in absorption caused by polymer oxidation can be found in the C=O, O–H, and C–O stretching vibration domains. Besides, subtraction spectra enable the observation of several further maxima/minima and shoulders. Significant changes appeared in the region of conjugated double bonds (Table 1), too.

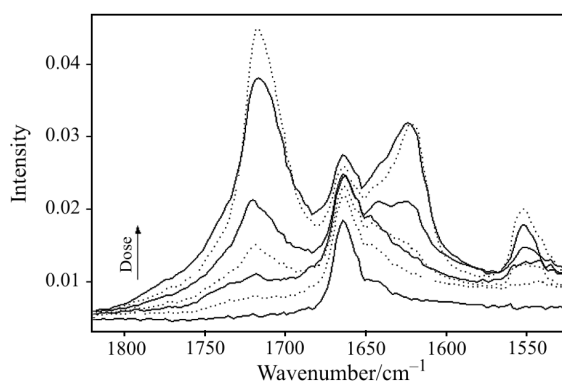
The hydroxyl region, 3600–3100  $\text{cm}^{-1}$ , reveals broad absorption band with the maximum shifting from 3290 to 3400  $\text{cm}^{-1}$  (Fig. 1). Several oxidation products contribute to this band, i.e. alcohols (band at

**Table 1** Main spectral changes observed in  $\gamma$ -irradiated polyisoprene

Wavenumber/ $\text{cm}^{-1}$	Absorbing species
Hydroxyl region 3400–3290	hydroperoxides, alcohols, water
C=O stretching region	
1791	peresters
1780	anhydrides
1772	$\gamma$ -lactones
1740	esters
1722–1717	methylketones, $\alpha,\beta$ -unsaturated esters, carboxylic acids
1697	$\alpha,\beta$ -unsaturated carboxylic acids
1680	$\alpha,\beta$ -unsaturated ketones
C=C stretching region 1650–1450	vinylethers, C=C conjugated with C=O, polyenes, polyenals, aromatic rings, 4-membered-ring cycloenes



**Fig. 1** ATR FTIR spectra of  $\gamma$ -irradiated (doses 0, 47, 87, 133, 144, 188, and 309 kGy) polyisoprene samples: 3675–2675  $\text{cm}^{-1}$  region



**Fig. 2** ATR FTIR spectra of  $\gamma$ -irradiated (doses 0, 47, 87, 133, 144, 188, and 309 kGy) polyisoprene samples: 1820–1520  $\text{cm}^{-1}$  region

3430–3440  $\text{cm}^{-1}$  [7, 8]), hydroperoxides (3325  $\text{cm}^{-1}$  [7]) and water [9].

In the carbonyl region, Fig. 2, the peak at 1722  $\text{cm}^{-1}$  dominates. This peak shifts to 1717  $\text{cm}^{-1}$  with the increasing radiation dose. Gonon *et al.* [7] have observed this shift in photooxidized polyisoprene, too. Peak at 1722  $\text{cm}^{-1}$  corresponds to methyl ketones and  $\alpha,\beta$ -unsaturated esters [7]. Carboxylic acids exhibit an absorption peak in this region, i. e. at 1718  $\text{cm}^{-1}$  [7, 8]. A broad shoulder in IR spectra at 1740  $\text{cm}^{-1}$  is caused by C=O stretching of esters, which also absorb, together with  $\gamma$ -lactones, at 1160  $\text{cm}^{-1}$  [7, 9] (C–O stretching, peak appears in subtraction spectra). In photooxidized polybutadiene, at weak conversion degree,  $\alpha,\beta$ -unsaturated carboxylic acids absorbing at 1697  $\text{cm}^{-1}$  are formed [10]. Subtractions between two successive spectra in the case of  $\gamma$ -radiation doses not exceeding 87 kGy confirm the occurrence of the weak band located at 1697  $\text{cm}^{-1}$  corresponding to  $\alpha,\beta$ -unsaturated carboxylic acids. In the 1770–1800  $\text{cm}^{-1}$  region three types of structures absorb, i.e. unsaturated anhydrides,  $\gamma$ -lactones, and peresters [7, 8, 10]. The shoulder at

1772  $\text{cm}^{-1}$  can be ascribed to lactones with a five-membered-ring [7, 8, 11]. The peak at 1772  $\text{cm}^{-1}$  is clearly visible in the subtraction spectra in the case of  $\gamma$ -radiation doses lower than 142 kGy. The subtraction spectra also clearly show the peresters peak at 1791  $\text{cm}^{-1}$ . In the photooxidized polybutadiene, peresters were identified at 1789  $\text{cm}^{-1}$  [10]. A band corresponding to anhydrides (1780  $\text{cm}^{-1}$  [10]) is present in the subtraction spectra of the samples irradiated by 87 kGy dose or lower. At the highest, 309 kGy dose, a decrease in absorbance at 1717  $\text{cm}^{-1}$  and significant broadening of this band occurred. As indicated by the band located at 1680  $\text{cm}^{-1}$  [7, 10],  $\alpha,\beta$ -unsaturated ketones are also formed in a higher extent. The overall area of the carbonyl band remains unchanged for the samples irradiated with the two highest doses.

During the oxidation of polyisoprene, saturated ethers may be also formed [5]. In IR spectra ethers and secondary alcohols absorb in the same regions, i. e. at 1141 and 1109  $\text{cm}^{-1}$  [9]. These two bands are present in the subtraction spectra. Another new band in subtraction spectra appeared at 1060  $\text{cm}^{-1}$ , which corresponds to  $\alpha,\beta$ -unsaturated alcohols [12]. Unsaturated ethers have been found using  $^{17}\text{O}$  NMR technique, too. Band at 1620 and shoulder at 1640  $\text{cm}^{-1}$  can be attributed to unsaturated ethers (vinyl-ethers) [11]. They are detected for the samples irradiated with doses 142 kGy and higher. In this region (1600–1620  $\text{cm}^{-1}$ ) the band corresponding to the valence vibration of the C=C conjugated with C=O bond or to the vibration of the C=C bonds of conjugated vinyls (polyenes) can also be located [12, 13].

Due to the formation of oxidation products, the bands related to  $\text{CH}_2$ ,  $\text{CH}_3$ , =C–H and C=C vibrations decrease.  $\text{CH}_2$  deformation band at 1447  $\text{cm}^{-1}$ ,  $\text{CH}_3$  asymmetric deformation at 1375  $\text{cm}^{-1}$ , and =C–H wagging at 835  $\text{cm}^{-1}$  show a significant decrease in the subtraction spectra. Decrease in absorption at 1663  $\text{cm}^{-1}$  is related to the loss of C=C bonds in 1,4-*cis* units [7]. 1,4-*cis* units also absorb at 835  $\text{cm}^{-1}$  [14]. We have observed the decrease in absorption in this region. Besides the oxidation of the C=C bonds in 1,4-*cis* units, *cis-trans* isomerization can take place. This was observed in thermally degraded polyisoprene [14]. The band at 2960  $\text{cm}^{-1}$  related to methyl groups decreases especially at the two highest doses 188 and 309 kGy (Fig. 1). The broadening of this band indicates changes in the polymer backbone.

Oxidative degradation and  $\gamma$ -irradiation of polymers can also induce chain scissions and formation of cross-links [3, 15]. Authors of the polyisoprene photodegradation studies [4, 6–8, 16] did not report appearance of new bands related to these processes in

the conjugated double bonds region of photodegraded polyisoprenes IR spectra. In thermally degraded *cis*-1,4-polyisoprene there have been identified dipentene (DL-limonene), two isomeric forms of dimethylvinylcyclohexene, isoprene, and some aromatic compounds formed via the Diels-Alder reactions [14, 17, 18]. Cataldo reported that during thermal degradation of 1,4-*cis*-polyisoprene, also chains with conjugated C=C bonds are formed (Scheme 1 in [18]). Changes corresponding to similar processes are also present in the region 1620–1450  $\text{cm}^{-1}$  of the  $\gamma$ -irradiated polyisoprene spectra, where no oxidation product absorbs.

Polyenes and polyenals show several bands in the 1500–1650  $\text{cm}^{-1}$  range [19]. Benzene C=C stretching vibrations bands are located between 1600–1450  $\text{cm}^{-1}$ ; hydrogen bond can cause the reduction of the stretching vibration frequency [20].

The subtraction spectra reveal the occurrence of the broad band with significant increase in absorption at 1620, 1553 and 1470  $\text{cm}^{-1}$ . This band can be assigned to aromates and shorter polyene structures. Absorption at 1620  $\text{cm}^{-1}$  remains the same (the maximum is slightly shifted to higher wavenumbers) for two highest doses, absorption at 1553  $\text{cm}^{-1}$  was lowered in the case of the sample irradiated with the highest dose (Fig. 2). It implies that formed species are subject of consecutive reactions.

It can be concluded that  $\gamma$ -radiation induces serious changes in polyisoprene backbone – chain scissions and various consecutive reactions take place. These changes are noticeable in the 1620–1450  $\text{cm}^{-1}$  region that indicates the occurrence of the polyene sequences and aromatic rings. Contrary to the chain scission reactions, formation of cross-links is difficult to detect using IR spectroscopy due to the overlap of many bands in the region of C–C stretching vibrations.

FTIR spectra measurements served to characterize the chemical changes induced by  $\gamma$ -radiation in PI samples measured by non-isothermal DSC in order to determine thermooxidative stability of the samples. Doses exceeding 50 kGy caused serious modification of the polymer structure, so the corresponding samples cannot be considered pure polyisoprene. The FTIR spectra also showed that the sample irradiated with 309 kGy dose represents degraded PI, i. e. the mixture of the products of oxidation, chain-scission and various consecutive processes. These changes significantly altered the appearance of the sample, it was discolored and lost its elasticity.

#### DSC measurements

The thermooxidative stability of the obtained irradiated PI samples has been studied by the non-isother-

mal DSC method. Isoconversional method has been used for the treatment of the experimental results [21]. Dependence of the induction period on temperature can be expressed by an Arrhenius-like relationship [21]

$$t_i = A \exp[B/T] \quad (1)$$

where  $A$  and  $B$  are constants and  $T$  is the absolute temperature. In the case of linear increase of temperature, the parameters  $A$  and  $B$  in Eq. (1) can be obtained from Eq. (2) [21]

$$\beta = \int_0^{T_i} \frac{dT}{A \exp[B/T]} \quad (2)$$

where  $T_i$  is the oxidation onset temperature (OOT) and  $\beta$  stands for the heating rate. The kinetic parameters  $A$  and  $B$  were obtained using Eq. (2) by minimizing the sum of squares between the experimental and calculated values of the OOT using the simplex method [22]. The integration indicated in Eq. (2) has been carried out by the Simpson method. The values of  $A$  and  $B$  for all samples are listed in Table 2. The agreement between the calculated and experimental values of the onset oxidation temperatures for individual heating rates is demonstrated in Fig. 3.

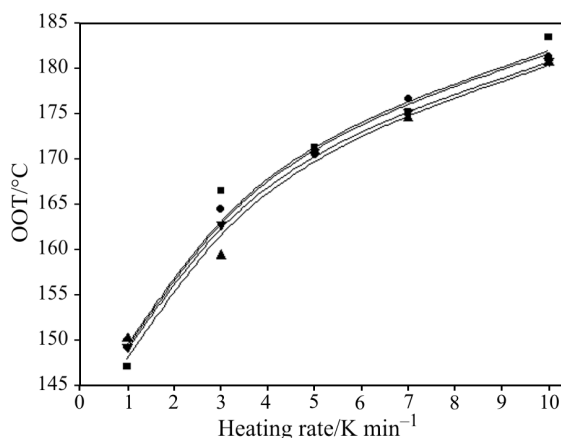
**Table 2** Kinetic parameters  $A$  and  $B$  for individual samples

Sample	$A/\text{min}$	$B/\text{K}$
PI-0 kGy	$7.3 \cdot 10^{-12}$	11900
PI-20 kGy	$8.9 \cdot 10^{-13}$	12800
PI-40 kGy	$8.1 \cdot 10^{-13}$	12800
PI-47 kGy	$4.5 \cdot 10^{-13}$	13100
PI-67kGy	$9.1 \cdot 10^{-13}$	12700
PI-94kGy	$9.2 \cdot 10^{-13}$	12600
PI-142 kGy	$1.0 \cdot 10^{-13}$	13200
PI-309 kGy	$1.7 \cdot 10^{-16}$	14400

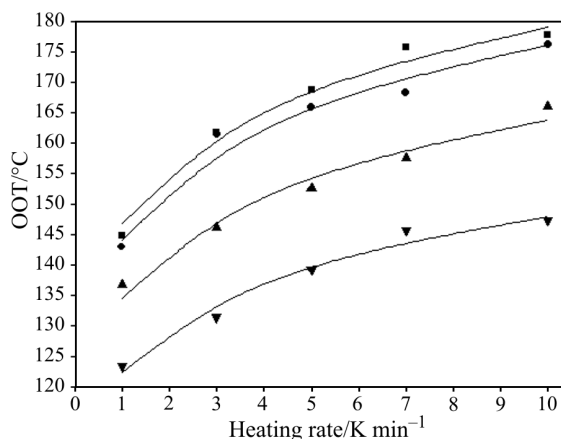
In order to characterize the  $\gamma$ -radiation effect on PI rubber, residual stabilities have been chosen as the criterion. The concept of the residual and depleted stabilities has been introduced and discussed in more detail in [21], where it was shown that the sum of both stabilities is equal to one. For an isothermal process, the residual stability,  $R$ , can be expressed as [21]

$$R = t_i/t_{i0} \quad (3)$$

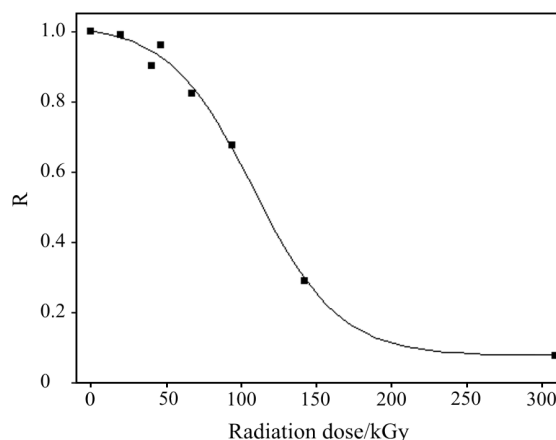
where  $t_i$  is the length of the IP of the sample after the  $\gamma$ -radiation stress and  $t_{i0}$  is the length of the IP of the non-irradiated sample. The values of the residual stability have been calculated using Eq. (3) and the dependence of  $R$  on the radiation dose is plotted in Fig. 4. It can be seen that the dependence exhibits an S-curve shape. The most significant decrease in  $R$  oc-



**Fig. 3a** Agreement between the experimental and the calculated values of the onset oxidation temperatures for various radiation doses: ■ – 0 kGy, ● – 20 kGy, ▲ – 40 kGy, ▼ – 47 kGy



**Fig. 3b** Agreement between the experimental and the calculated values of the onset oxidation temperatures for various radiation doses: ■ – 67 kGy, ● – 94 kGy, ▲ – 142 kGy, ▼ – 309 kGy



**Fig. 4** Dependence of the residual stability,  $R$ , on the  $\gamma$ -radiation dose calculated for 150°C



curs in the 70 to 150 kGy dose range. The dependence also shows that up to 50 kGy only 10% of the polyisoprene thermooxidative stability is depleted. For the doses higher than ca 150 kGy, the *R* values do not significantly decrease and their values range from 20 to 5%. At the highest, 309 kGy dose, practically whole stability of PI is depleted, since the measured sample consisted of PI oxidative degradation products, as it has been shown by FTIR results.

## Conclusions

Degradation of  $\gamma$ -irradiated PI rubber has been studied by ATR FTIR and non-isothermal DSC techniques.

The IR spectra of  $\gamma$ -irradiated polyisoprene confirmed the formation of the various oxidation products, i. e. ketones, alcohols, hydroperoxides, ethers and small amounts of lactones, anhydrides, peresters, carboxylic acids and esters. Significant changes in IR spectra induced by chain scission and cyclization reactions are evident in the 1620–1450  $\text{cm}^{-1}$  region. These processes run simultaneously with the oxidation of polyisoprene. On the basis of the measured spectra we assume the formation of shorter polyene sequences and aromatic rings. FTIR measurements show that doses lower than 50 kGy do not cause serious changes in polymer structure if we consider the development of the bands in carbonyl and conjugated C=C bonds regions. This result is in good accordance with DSC measurements which also confirmed that up to 50 kGy only 10% of the polyisoprene thermooxidative stability is depleted. On the other hand, 309 kGy dose caused such a serious chemical modification of the original PI, that this sample in fact represents the mixture of various PI degradation products. This finding corresponds very well with the almost zero value of the sample residual stability.

From DSC data both kinetic parameters characterizing temperature dependence of the IP and residual stabilities have been calculated. The extinction of residual stabilities with radiation dose can be described with a sigmoidal curve. The most significant decrease in residual stability occurs in the dose range from 70 to 150 kGy.

DSC and FTIR techniques represent powerful and complementary tools for the study of radiation induced oxidation and thermooxidative stability of polyisoprene rubber.

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## References

- 1 M. Pentimalli, D. Capitani, A. Ferrando, D. Ferri, P. Ragni and A. L. Segre, *Polymer*, 41 (2000) 2871.
- 2 M. Polovka, V. Brezová, A. Staško, M. Mazúr, M. Suhaj and P. Šimko, *Radiat. Phys. Chem.*, 75 (2006) 309.
- 3 F. Gugumus, *Oxidation inhibition in organic materials*, Vol. 1, Boca Raton, CRC Press, 1990.
- 4 P. O. Bussière, J. L. Gardette, J. Lacoste and M. Baba, *Polym. Degrad. Stab.*, 88 (2005) 182.
- 5 T. M. Alam, M. Celina, R. A. Assink, R. L. Clough and K. T. Gillen, *Radiat. Phys. Chem.*, 60 (2001) 121.
- 6 J. F. Rodrigues and M. A. De Paoli, *Eur. Polym. J.*, 21 (1985) 15.
- 7 L. Gonnon and J. L. Gardette, *Polymer*, 41 (2000) 1669.
- 8 A. Rivaton, S. Cambon and J. L. Gardette, *Nucl. Instrum. Methods Phys. Res. B*, 227 (2005) 343.
- 9 N. B. Colthup, L. H. Daly and S. E. Wiberley, *Introduction to Infrared and Raman spectroscopy*, 3<sup>rd</sup> Ed., London, Academic Press, 1990.
- 10 M. Piton and A. Rivaton, *Polym. Degrad. Stab.*, 53 (1996) 343.
- 11 G. A. George, M. Celina, A. M. Vassalo and P. A. Cole-Clark, *Polym. Degrad. Stab.*, 48 (1995) 199.
- 12 O. S. Roshchupkina, L. I. Tkachenko and O. N. Efimov, *Synth. Met.*, 90 (1997) 89.
- 13 N. S. Allen, A. Barcelona, M. Edge, A. Wilkinson, C. G. Merchan and V. R. S. Quiteria, *Polym. Degrad. Stab.*, 86 (2004) 11.
- 14 O. Chiantore, M. Guaita, M. Lazari, N. Hadjichristidis and M. Pitsikalis, *Polym. Degrad. Stab.*, 49 (1995) 385.
- 15 A. Bhattacharya, *Prog. Polym. Sci.*, 25 (2000) 371.
- 16 K. A. M. dos Santos, P. A. Z. Suarez and J. C. Rubim, *Polym. Degrad. Stab.*, 2005, in press.
- 17 F. Chen and J. Qian, *Fuel*, 81 (2002) 2071.
- 18 F. Cataldo, *J. Anal. Appl. Pyrol.*, 44 (1998) 121.
- 19 M. Del Zoppo, A. Bianco and G. Zerbi, *Synth. Met.*, 139 (2003) 881.
- 20 Y. Du, H. Wang and S. Chen, *J. Mol. Catal. A*, 179 (2002) 253.
- 21 P. Šimon and Ľ. Kolman, *J. Therm. Anal. Cal.*, 64 (2001) 813.
- 22 J. A. Nelder and R. Mead, *Computer J.*, 7 (1965) 308.

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