Influence of Curing Protocol of Benzoxazine Monomer based on Aromatic Diamines against the Degradation Behaviour of the Resulted Polybenzoxazines

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Two curing protocols were used to polymerize a difunctional benzoxazine monomer based on 4,4'-diamino diphenyl methane. The thermal degradation behaviour of both resulted materials (named PBZ_190 and PBZ_250) was investigated by thermogravimetric analysis coupled with mass spectrometry (TGA/MS), Fourier transform infrared spectroscopy (FT-IR) and X-Ray photoelectron spectroscopy (XPS). The dependence of activation energy on conversion was established using Kissinger-Akahira-Sunose isocoversional method. Degradation of PBZ_250 starts at lower temperatures compared with PBZ_190 but its residual char is higher than for PBZ_190. The degradation of PBZ_250 exhibits a lower activation energy at conversion $\alpha < 0.3$, and higher values than PBZ_190 for $\alpha > 0.3$.

Keywords: polybenzoxazine, degradation kinetics, thermogravimetric analysis (TGA)

Benzoxazines were first synthesized in 1944 by Cope and Holly [1]. These monomers were the base for the synthesis of a new class of phenolic materials in 1994 when Ishida and Ning obtained crosslinked materials with high glass transition temperature by the thermal polymerization of di-functional benzoxazines [2]. Since then, different phenols or amines were used in order to develop new benzoxazine compounds which lead to polybenzoxazines with high performances [3].

Aromatic diamine based benzoxazines lead to polybenzoxazines with high thermal properties compared to those obtained from aliphatic diamines [4,5]. Several methods were proposed for the synthesis of these monomers like for example the use of different solvents [5,6] or a three steps procedure starting from hydroxy-formaldehyde, diamine and formaldehyde [7].

Understanding the degradation mechanism of polybenzoxazine resins is an important issue. Polybenzoxazines obtained from mono amines based benzoxazines have been extensively studied. Their degradation mechanism was investigated by TGA, FT-IR, GC-MS, TG-MS or pyrolysis mass spectrometry [8-10]. Benzoxazines monomers based on aromatic diamines require high curing temperatures like 220°C [11,12], 230 °C [5] or 250°C [6] depending of the benzoxazine monomer. For some benzoxazine monomers it was shown that higher glass transition temperature is obtained when the final curing temperature was increased [7].

This paper aims to investigate for the first time the thermal degradation behavior of a polybenzoxazine obtained from an aromatic diamine based benzoxazine. The influence of two monomers curing protocols on the polybenzoxazine thermostability was established by TG-MS and FT-IR. The dependence of activation energy on conversion for both samples was established using Kissinger-Akahira-Sunose isoconversional method. The residual char at various sintering temperatures was investigated by FT-IR and XPS.

Experimental part

Materials and methods

A difunctional benzoxazine monomer, bis [6-benziloxy-3,4-dihydro-2H-1,3-benzoxazinyl] diphenyl methane was employed for the synthesis of the polybenzoxazine used for the degradation studies (fig. 1). The monomer was previously synthesized from 4-benzyloxyphenol, diaminodiphenylmethane and formaldehyde solution and fully characterized [4].

Two step-curing procedures were used for the benzoxazine monomer polymerization. The first structure, named PBZ_250 was obtained by gradually heating the benzoxazine monomer 2.5 h at 160 °C, 1 h at each of the following temperatures 170, 180, 190, 200, 230°C, respectively 0.5 h at 250°C [4]. The second one, named PBZ_190, was synthesized by heating the monomer 2h at 170 °C and 2h at 190 °C [13].

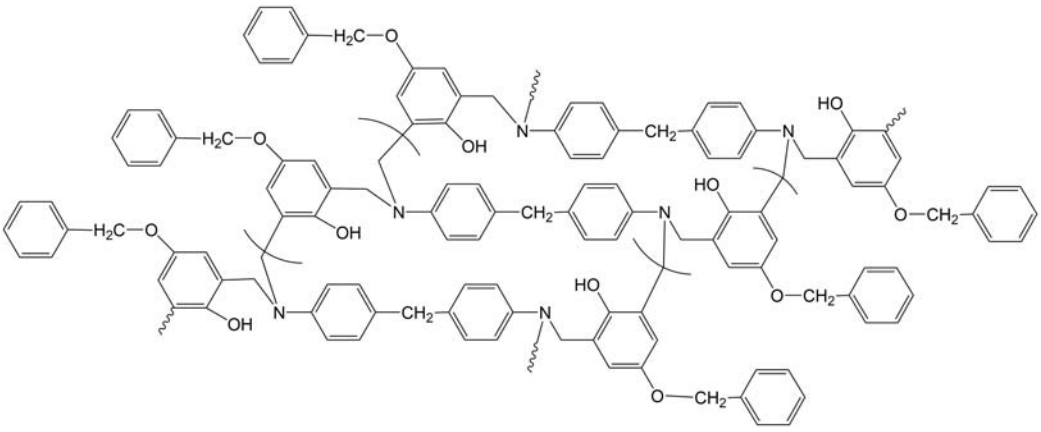

Fig. 1. Theoretical structure of poly(bis [6-benziloxy-3,4-dihydro-2H-1,3-benzoxazinyl] diphenyl methane)

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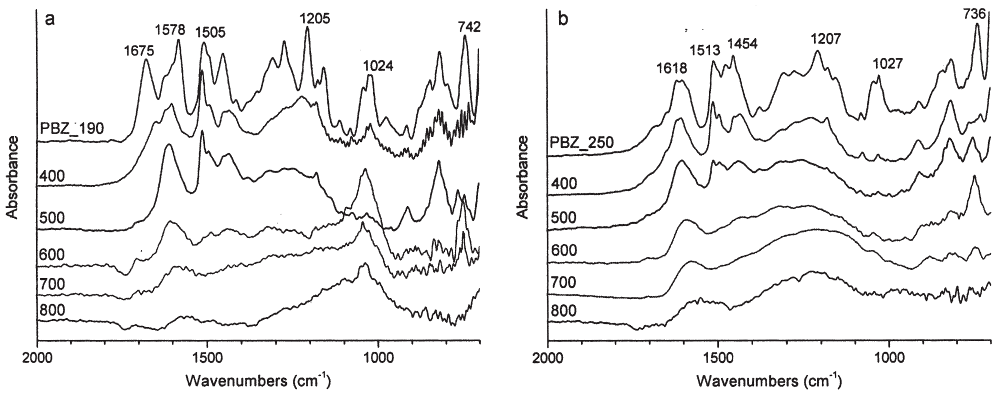

Fig. 2. FT-IR spectra of residual char of a) PBZ_190 and b) PBZ_250 at different sintering temperatures

Table 1
SURFACE COMPOSITION DETERMINED BY XPS

	%C	%N	%O
PBZ_250	78.2	6.6	15.2
Char at 800 °C PBZ_250	94.4	2.9	2.7
PBZ_190	81.7	3.6	14.7
Char at 800 °C PBZ_190	92.6	4.2	3.2

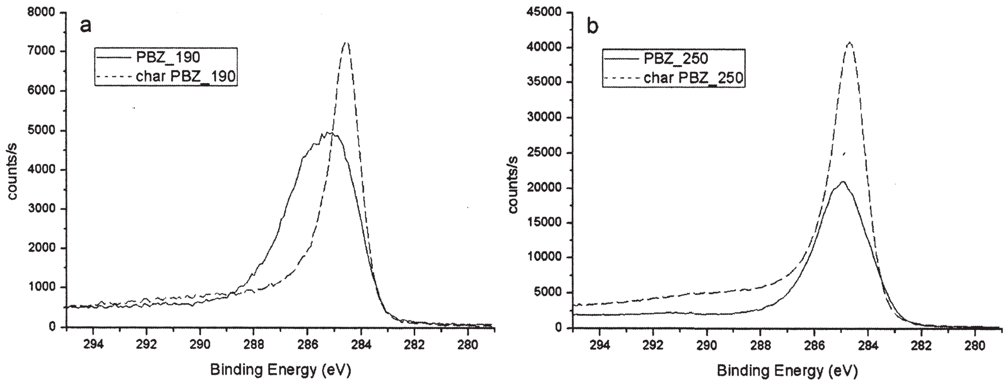

Fig. 3. C 1s high resolution spectra for a) PBZ_190 and b) PBZ_250 and the residual char obtained at 800°C

Characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VERTEX 70 spectrometer in 4000 – 600 cm^{-1} region. The samples were analyzed by attenuated transmission reflectance (ATR). For FT-IR spectra, samples were prepared by heating the polybenzoxazines with 10 °C/min in nitrogen at different sintering temperatures.

For the TGA-MS experiments, a thermogravimetric analyzer TGA Q500 (from TA instrument) was coupled to a ThermoStar TM GSD 301 T Mass Spectrometer (from Pfeiffer Vacuum) through a quartz capillary tube (heated at 200°C). In order to use isoconversional methods, the samples (2.1 ± 0.1 mg) were scanned from 30 to 800°C using three different heating rates (5, 10, 20 °C/min), under nitrogen atmosphere. For the MS identification of evolved fragments, a unique heating rate (10°C/min) for each sample was used, for the same temperature interval, under argon atmosphere. The mass spectrum was recorded from 16 to 100 m/z.

For XPS analysis a K-alpha instrument from Thermo Scientific with a monochromatic Al K_α (1486.6 eV) was used. A pass energy of a 200 eV and 20 eV was employed for survey spectra and high resolution spectra, respectively.

Results and discussions

Structural changes

The FT-IR spectra of both polybenzoxazines samples and the corresponding residual chars at different sintering temperatures are presented in figure 2. The FT-IR spectrum of the benzoxazine monomer was discussed in our previous work [4], the main absorption bands being at 1222 cm^{-1} (C-O-C), 1363 cm^{-1} (C-N) and 955 cm^{-1} (benzoxazine group attached to aromatic ring). For PBZ_190 and PBZ_250 spectra these bands are no longer present which indicates complete reaction of the monomer.

For both PBZ_190 and PBZ_250 absorption bands in the region 1550 - 1700 cm^{-1} are observed. This region is characteristic for the vibration of C=N bond, which appears from the Schiff base formed during the cleavage of Mannich bridge structures [9,10]. The presence of Schiff base structures is confirmed also by the absorption band from 1205 and 1207 cm^{-1} for PBZ_190 and PBZ_250 respectively, characteristic for the C=$\underline{\text{N-H}}$ bond. The region 1550-1700 cm^{-1} is different for the two polybenzoxazines. For PBZ_250 just a large band is observed at 1618 cm^{-1} but in the case of PBZ_190 two main bands are noticed at 1578 and 1675 cm^{-1}. This indicates that in the case of PBZ_190 not only Schiff base structures were formed but also amide structures (amide II - 1675 cm^{-1}) [14]. By the thermal polymerization of benzoxazine monomers, phenolic and phenoxy structures are obtained. Phenoxy structures are less stable compared with phenolic structures, and at higher temperatures a rearrangement of phenoxy in phenolic structures occured [15].

A decrease of the characteristic absorption bands from the polybenzoxazines is noticed by increasing the sintering temperatures. At 400 °C, a slower decrease is observed for

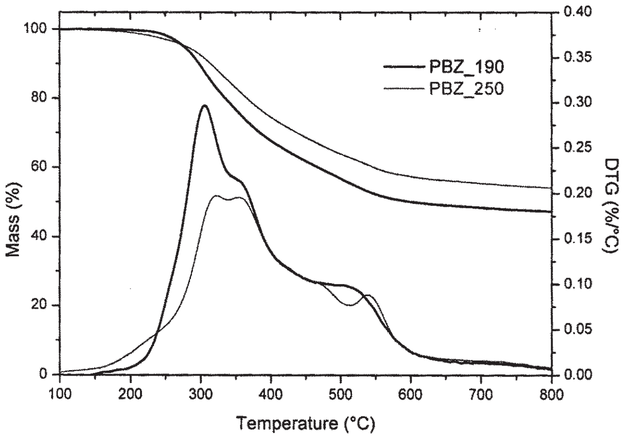

Fig. 4. TGA and DTG curves for PBZ_190 and PBZ_250 registered at 10 °C/min heating rate

Table 2
DEGRADATION TEMPERATURE AND RESIDUAL CHAR OBTAINED AT DIFFERENT HEATING RATES

	Heating rate (°C/min)	$T_{d1\%}^{*}$ (°C)	$T_{d5\%}^{*}$ (°C)	Char yield at 800 °C (%)
PBZ_190	5	225	261	48.84
	10	239	278	47.33
	20	244	288	45.57
PBZ_250	5	195	269	55.26
	10	203	282	54.15
	20	209	298	54.04

*$T_{d1\%}$; $T_{d5\%}$ - the temperatures at which the material exhibits 1% and 5% respectively mass loss

the main polybenzoxazine adsorption bands. The band characteristic for the C-H deformation vibration from the aromatic ring (742 cm^{-1} for PBZ_190 and 736 cm^{-1} for PBZ_250) was consumed. At 500 °C this band appears again, this time being slightly shifted to higher wavenumbers. This was previously explained by the cleavage of benzene ring substituents caused by the cleavage of Mannich bridges which leads to a modification of the aromatic ring substitution [8].

For PBZ_250, at sintering temperatures higher than 600 °C, two large bands can be observed, one from 1000 to 1450 cm^{-1} and second from 1450 to 1700 cm^{-1}. The first large bands arises from the coalescence of C-N, C=N and C=C vibration modes. The second one is caused by the C=N vibration mode. These two bands exhibit a higher intensity in PBZ_250 than in PBZ-190. The condensed aromatic compounds are responsible for the char formation [10].

In order to confirm the formation of aromatic condensed compounds in the residual char, XPS analysis was used to investigate the residual char obtained at 800°C (table 1). An increase of C content was obtained after the pyrolysis. The residual char includes also significant amounts of N, the decrease of O percent being higher than for N.

The high resolution spectra for the C 1s peak are shown in figure 3 for PBZ_190 and PBZ-250 respectively. For PBZ_190 the C 1s peak ends at higher binding energy values (289 eV) than PBZ_250 (288 eV). After pyrolysis the C 1s peak of the residual chars shifts to lower binding energy values (~284.2 eV) which proves the increase of C=C content. Also, the peaks exhibit a symmetric shape (peaks end at BE ~ 286 eV) which supports the decrease of groups including oxygene and nitrogen which were detected in polybenzoxazines structure before pyrolysis.

Thermal gravimetric analysis (TGA)

The TGA results show that the degradation process starts at higher temperatures for PBZ_190 than PBZ_250 (fig. 4). The presence of amide groups in PBZ_190 is advantageous from the thermal stability point of view [14]. For both materials, the residual char (from TGA curves) decreases if the degradation heating rate is increased. When the degradation temperature is raised slowly, the decomposition products have a longer time to give secondary reactions like recombination which can lead to an increase of formation of the char yield. The PBZ_250 char yield at 800 °C for all heating rates is higher than those obtained from PBZ_190 (table 1). The FT-IR spectra of both PBZ_190 and PBZ_250 residual chars at 800 °C show more intense bands for condensed aromatic compounds in the case of PBZ_250 than PBZ_190 which is in good agreement with the higher char quantity obtained for PBZ_250.

Isoconversional methods

The isoconversional methods allow calculating the activation energy as a function of the process conversion using multiple experimental data sets with different temperature programs (usually different heating rates). These methods do not need any arbitrary assumption of a model function (known also as "model-free methods").

The kinetics of a thermally stimulated reaction in solid phase is described by eq. (1):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp\left(-\frac{E}{RT}\right)f(\alpha) \qquad (1)$$

where:
α is the conversion degree,
t - time, $d\alpha/dt$ - reaction rate,
T - absolute temperature,
$f(\alpha)$ - reaction model,

k(T) - temperature-dependent rate constant (usually obeys an Arrhenius-type expression),

A - preexponential factor,

E - activation energy,

R - ideal gas constant.

For TGA experimental data, the conversion degree α was determined as a fraction of the mass loss: $\alpha = (m_0 - m_t)/(m_0 - m_\infty)$, where m_0 and m_∞ are the initial and final sample weights and m_t - the sample weight at time *t*.

In this work, the integral method proposed by Kissinger [16], Akahira and Sunose [17] (KAS method, eq. 2) was used for isoconversional kinetic study, in agreement to recent recommendation of ICTAC Kinetics Committee (KAS method providing more accurate result) [18].

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \ln\left(\frac{AR}{E_\alpha}\right) - \ln[g(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} = ct. - \frac{E_\alpha}{R}\cdot\frac{1}{T_{\alpha,i}} \qquad (2)$$

where:

i is the number of the experiment,

$\beta_i = dT_i/dt$ - heating rates,

E_α – activation energy corresponding to conversion α,

$T_{\alpha,i}$ – temperature at a given conversion α for the experiment *i*.

The activation energy is determined from the plot of left side of eq. (2) versus $1/T_{\alpha,i}$ at constant conversion degree α, for the *i* heating rates.

For both PBZ_190 and PBZ_250 samples, the $\ln(\beta/T^2)$ shows a linear dependence on 1/T with good correlation coefficients (exemplified in figure 5 for PBZ_190).

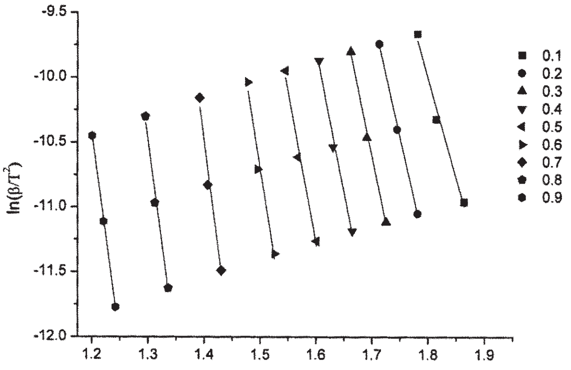

Fig. 5. Plot of $\ln(\beta/T^2)$ as a function of 1/T at different conversion degrees according to KAS method for PBZ_190

The activation energy of the degradation process for both PBZ_190 and PBZ_250 varies significantly upon conversion suggesting that the degradation process involves multi step reactions (fig. 6). The increase of activation energy at higher conversion is a typical behaviour of the thermosets degradation [19]. At early stages of degradation (α <0.3), PBZ_190 activation energy is higher than that of PBZ_250. If α>0.3, the activation energy of PBZ_250 raised faster reaching higher values than for PBZ_190 (450 KJ/mol vs 280 KJ/mol). The activation energy values are similar to those reported in the literature for aerogel and bulk polybenzoxazine structures [10].

The results are in good agreement with the TGA data for which the char yield obtained for PBZ_250 is higher than for PBZ_190, higher activation energies being required for PBZ-250 degradation than for PBZ_190.

TGA results showed that PBZ_250 starts degradation at a lower temperature than PBZ_190. According to FT-IR spectra of PBZ_190 and PBZ_250, both polybenzoxazines include structural defects like Schiff bases for PBZ_250 and a mixture of Schiff bases and amide groups for PBZ_190. The Schiff base exhibits a lower thermal stability which may account for the overall lower thermostability of PBZ_250 than PBZ_190. Moreover the amide group exhibits a higher thermal stability leading to the increase of both thermal stability and activation energy of PBZ_190.

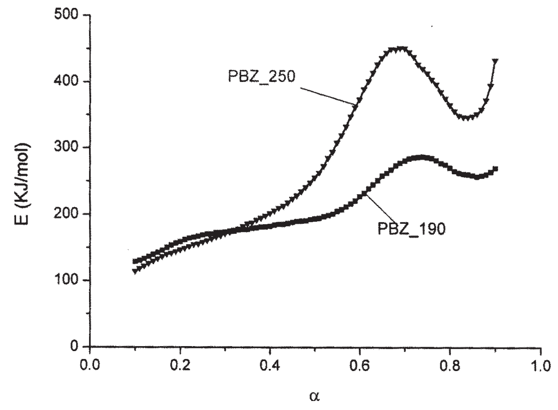

Fig. 6. Dependence of activation energy (E) against conversion for PBZ_190 and PBZ_250

Identification of the evolved gases by TGA-MS

TGA-MS is a very useful technique for the identification of the evolved fragments during the thermal degradation of a sample. The mass spectra of the products released during the heating process until 700°C are depicted in figure 7 and 8. For the two samples the same volatile fragments were released, but a difference in the profile of the evolved gases may be observed. Pyrolysis of the samples starts after 300 °C involving a mild pyrolysis until 500 °C. The assignment of the fragments generated during the decomposition is: m/z = 12 (C^+), m/z = 14 (N^+), m/z = 16 (O^+), m/z = 22 (CO_2^{++}), m/z = 26 (CN^+), m/z = 30 (CH_2O^+), m/z = 43 ($C_3H_7^+$), m/z = 44 (CO_2^+), m/z = 46 (NO_2^+), m/z = 50 ($C_4H_2^+$), m/z = 51 ($C_4H_3^+$), m/z = 52 ($C_4H_4^+$), m/z = 63 ($C_5H_3^+$), m/z = 65 ($C_5H_5^+$), m/z = 78 ($C_6H_6^+$), m/z = 91 ($C_7H_7^+$) and m/z = 92 ($C_7H_8^+$) [8].

The main signals correspond to the aromatic ring decomposition (m/z = 50, 51, 52, 63, 78) or from the benziloxy radical from the phenol structure (m/z = 53, 63, 65, 91, 92) [20]. For both spectra it can be seen than these fragments exhibit an increase of the intensity at temperature higher than 250°C, reaching a maximum between 300-400°C. This represents the main fragment degradation within the mild pyrolysis interval.

A significant difference between PBZ_190 and PBZ_250 is related to the m/z = 12 (C^+) fragment. For PBZ_190 this signal reaches a maximum value in the interval 450-550 °C, while for PBZ_250 the maximum value is at 550 °C. A similar evolution was observed for fragments with m/z = 44 or 30. The evolution of these gases is in good agreement with the shape of the DTG vs. temperature curves, for which an increase of the degradation rate is observed for PBZ_250 at temperatures higher than 500°C compared with PBZ_190 for which the rate of degradation tends to remain constant between 450 – 550°C. For fragments which arise from Mannich base degradation (m/z = 26 and 46) the signals exhibit higher intensity in the case of PBZ_190 than for PBZ_250 at temperatures higher than 300°C. Also, the lower residual char obtained for PBZ_190 compared to PBZ_250 is explained by the higher release of C, CO_2 or CH_2O which

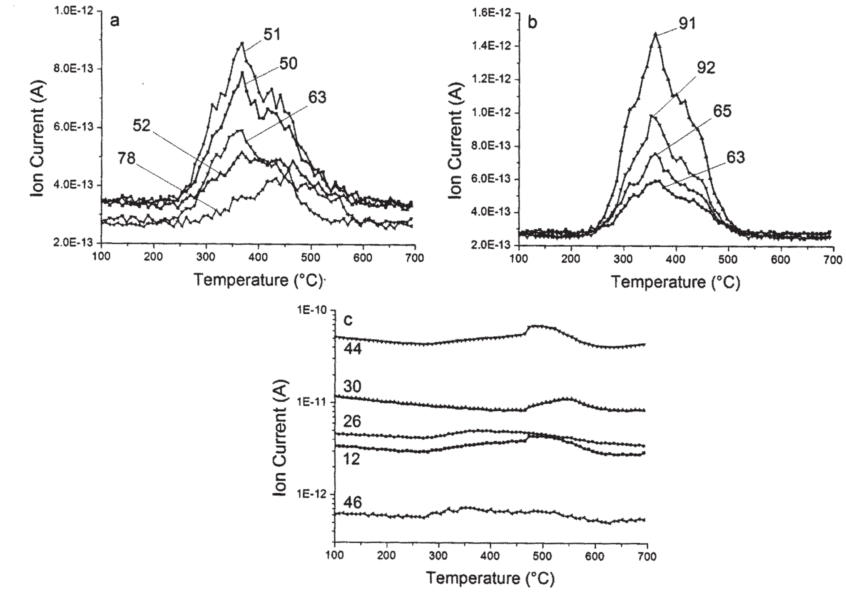

Fig. 7. Evolution of fragments evolved during the temperature-programmed pyrolysis of PBZ_190

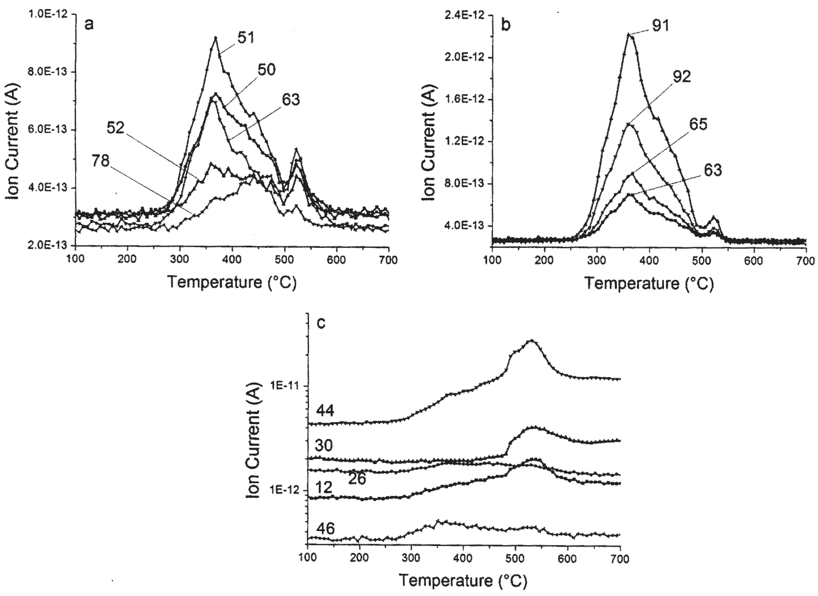

Fig. 8. Evolution of fragments evolved during the temperature-programmed pyrolysis of PBZ_250

are involved in the formation of the residual char in the case of PBZ_250.

Conclusions

In this study two curing protocols were used to synthesize polybenzoxazines starting from an aromatic diamine based benzoxazine monomer. For PBZ_190 FT-IR spectrum shows the presence of secondary structures like Schiff bases and amide groups while for PBZ_250 just Schiff bases are present. The higher thermal stability of amide group increases the thermal stability of PBZ_190 which starts decomposition at higher temperatures than PBZ_250. At higher sintering temperatures, a higher amount of condensation products is formed for PBZ_250 which explains the higher char yield obtained for PBZ_250 compared to PBZ_190. The evolution of gases evolved during thermal degradation shows that in the case of PBZ_190 higher amounts of C or CO_2 are released. At conversions higher than 0.3, PBZ_250 exhibits a higher activation energy than PBZ_190. Curing of benzoxazine monomers at higher temperatures leads to structures with higher char yield which is usually assimilated with less flammable structure since less flammable gases are released during the thermal decomposition.

Acknowledgements:: Authors recognise financial support from the Sectoral Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/89/1.5/S/54785 and POSDRU/107/1.5/S/76903.

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Manuscript received: 25.03.2013