Thermal decomposition of polyimides containing phosphine-oxide units

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Abstract

This work details analyses of the thermal decomposition behaviour of three phosphine-oxide containing aromatic processable polyimides. The polymers exhibited high thermal stability with initial decomposition temperatures in the range of 473–483°C and a char residue at 900°C in the domain of 48.6–58.4%. The values of non-isothermal decomposition kinetic parameters were determined using the Friedman isoconversional method, as recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC). The data evidenced a complex decomposition process of the main chain, being probably initiated by the cleavage of the weaker P–C bonds, followed by the decomposition of the macromolecular backbone. The volatile products formed during the thermal decomposition of polyimides were analysed by TGA-FTIR. All spectra evidenced peaks associated with water, CO₂, CO and aliphatic and aromatic decomposition products predominant from 500° to 800°C. By using Py-GC-MS studies the fragments originating from the thermal decomposition of the polyimides up to 600°C were identified. Based on these data, it was suggested that the thermal decomposition pathways of the three polyimides undergoes the same mechanism. Additionally, an oversimplified decomposition mechanism for the polyimides was proposed. The morphology of the char residue obtained after TGA experiments showed a continuous and dense structure. The EDX mapping identified the C, N, O and P atoms uniformly dispersed in the residual char surface.

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1. Introduction

Classical aromatic polyimides are well known for their excellent thermal and thermo-oxidative stability, good mechanical and dielectric properties, chemical and solvent resistance [1]. The excellent thermal resistance and physical strength are based on the conjugation of the aromatic rings and to the presence of strong intermolecular forces, which are mediated by the imide bonds [2]. Compared to other polymeric materials such as phenols, epoxies, polyesters and polyamides, polyimides possess a higher oxygen index and char yield [3]. Therefore, the choice of polyimide to develop high-performance materials for various applications is based on these considerations. In order to avoid some drawbacks of classical aromatic polyimides such as low solubility, processability, transparency and high glass transition temperatures, the need to modify the main polyimide chain becomes imperative. The challenges consist in improving the overall processability while retaining the desirable and attractive properties e.g. by reducing the rigidity of polymer backbone or the interchain interactions.

The limitation of conventional polyimides in some applications may be overcome by introducing thermally stable flexible or asymmetric linkages, large polar or non-polar pendant substituents [4-8]. Depending on their structural characteristics such polyimides may be successfully used in different industrial segments. They have an important role in high technology applications such as aerospace, automotive, chemical and electronic industry [9-13]. Recently, aromatic polyimides have found a wide range of applications in the microelectronics and photoelectronics industries as alignment films in displays, circuit boards, photoresists and dielectric films [12,14-16]. Other domains include membranes for gas separation or filtration [17-19], aerogels/sponges or foams and matrices for high temperature applications [20-22].

The strategies to improve the processability of polyimides include the introduction of specific moieties in the chemical structure of the polyimides so as to obtain targeted properties. Thus, the introduction of phosphorus, either as a constituent part in the polymer chain or as an additive, can enhance its inherent flame retardant behaviour. Phosphorus-based compounds do not have problems associated with halogen-based flame retardants which increase the amount of smoke and toxic decomposition products evolved during polymer combustion [23]. Compared with other phosphorus groups, the use of phosphine oxide has several advantages, due to the hydrolytically stable P–C bonds (compared to phosphate) and the oxidatively stable P=O bonds (compared to trivalent phosphines) [24-27]. The incorporation of short bridges such as ether (–

O–), carbonyl ($-\text{C}=\text{O}-$), hexafluoroisopropylidene ($-\text{C}(\text{CF}_3)_2-$) into polyimide backbones has led to an increase of solubility and a decrease in glass transition temperature, without a consistent compromise of useful properties [28-31].

The need of highly thermostable polyimides is demanded in modern applications. For example, in aerospace industry, the engine monitoring require that the sensor-containing polyimide films should be as close as possible to the engine, leading to their exposure at high temperatures [32,33]. Moreover, the exploration of new sources for clean energy, geothermal and electrical energy has significantly motivated the development of high temperature electronic materials [34]. High temperature sensors for structure health monitoring can ensure enhanced lifetime and reliability, less maintenance and downtime, and can thus reduce the cost of renewable energy sources [35]. Therefore, the search for new thermostable polymers exhibiting outstanding properties to fulfil the requirements of the industry is a continuous challenge.

The study of polymer thermal decomposition has been used not only for the evaluation of global kinetic parameters and of thermal resistance but also has guided improvements in their backbone chemistry [36]. There are numerous studies on the decomposition behaviour of polyimide in the literature [37-39] It is evidenced that the pyrolysis pathway [40-42] and kinetics [43-46] of aromatic polyimides requires a temperature of more than 500°C and produces a low value CO- and CO₂- rich gas as well as more than 50 wt% carbonized solid [2].

The present study aims a thorough investigation on the thermostability of a series of structurally comparable polyimides. The thermal and thermo-oxidative decomposition of the polymers was monitored by TGA. The global kinetic parameters were identified by using Friedman isoconversional method. Evolved gas analysis using coupled techniques such as TGA-FTIR and Py-GC-MS were performed in order to elucidate the decomposition mechanism of the polyimides. The residue obtained after TGA process was analyzed by SEM, EDX to establish the char structure and to identify the phosphorus species remaining in the solid.

2. Experimental

2.1. Materials

Aromatic polyimides were prepared by solution polycondensation reaction of an aromatic diamine, namely bis(3-aminophenyl) methyl phosphine oxide, with different aromatic dianhydrides containing various flexible units such as, 4,4'-oxydiphthalic anhydride,

benzophenone-3,3',4,4'-tetracarboxylic dianhydride or 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (Fig. 1). The reaction was performed in two steps using N-methyl-2-pyrrolidone (NMP) as solvent. The concentration of the reaction mixture was adjusted to 15% w/w. The water of imidization was evacuated by a slow stream of nitrogen which was used also as inert medium [47].

Fig. 1. Structure of the polyimides.

2.2. Measurements

Infrared spectra were recorded on FT-IR Bruker Vertex 70 analyzer, by using KBr pellets.

^1H -NMR and ^{31}P -NMR were recorded on Bruker Avance400 NMR spectrometer (frequencies of 400.13 and 100.61 MHz, respectively) in DMSO- d_6 at 25°C. Chemical shifts are reported in δ units (ppm) relative to the remaining resonances of the solvent at 2.49 ppm for ^1H -NMR. The ^{31}P -NMR spectra are externally referenced to a sample of neat H_3PO_4 at 0.0 ppm.

Thermogravimetric analysis (TGA) was performed on a NETZSCH TG209 F1 Iris instrument. The sample of around approx. 8 mg was heated from 25 to 900 °C at a heating rate of 10 °C min $^{-1}$. The measurements were performed two times with a total nitrogen gas flow of 50 mL min $^{-1}$. Non-isothermal kinetic measurements were performed on a STA 449F1 Jupiter device from Netzsch (Germany) by recording thermograms at three different heating rates (10, 20, 30 °C min $^{-1}$).

¹). The obtained data were processed with the “Thermokinetics 3” software supplied by Netzsch (Germany).

Evolved gases analysis of the polyimides was investigated with a TGA-FTIR technique using the Netzsch TG 209 F1 Iris[®] instrument coupled with the Bruker TENSOR-27 FTIR instrument. For these experiments, 10 mg of samples were heated from 50 to 800 °C at a rate of 10 °C min⁻¹ under nitrogen flow (50 mL min⁻¹). IR spectra were recorded in the spectral range from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹.

Py-GC-MS measurements were performed with samples of 30–100 µg of the polymer which were placed in a quartz tube (1 mm internal diameter x 25 mm length). The polymers specimens were then loaded in the pyrolysis probe (Pyroprobe-5200 HP) and placed in the special inlet at the interface. The polymer specimens were pyrolyzed at 600 °C under helium atmosphere for 30 s. The volatiles were separated by a Hewlett-Packard 5890 Series II gas chromatograph and analyzed by a Hewlett-Packard 5989 Series mass spectrometer. GC column filled with cross-linked 5% PH-ME siloxane, 0.53 mm diameter and 30 m length, was employed. The GC oven was programmed to hold at 50 °C for 1 min. The oven was then heated from 50 to 250 °C at a heating rate of 10 °C min⁻¹ and held at 250 °C for 5 min. Masses were scanned from m/z 40 -500.

The distributions of P atoms on the surface of polyimides char residue were measured by using scanning electron microscope SEM type Quanta 200 operating at 30 kV with secondary and backscattering electrons in high vacuum mode. The elemental analysis on the char residue surface was obtained by using coupled dispersive X-ray spectroscopy (EDX).

3. Results and discussions

3.1. Structural characterization of polyimides

The chemical structure of the polyimides was evidenced by FTIR, ¹H NMR and ³¹P NMR spectroscopy (Table 1 and Table 2). Thus, in the FTIR spectra of all polymers strong bands of absorption which appeared in the range of 1785–1778 cm⁻¹ and 1723–1719 cm⁻¹ were attributed to asymmetrical and symmetrical stretching vibrations of carbonyl groups in the imide rings. The vibrations of C–N stretching and the ones corresponding to imide ring bending deformation were identified in the domain of 1366–1371 cm⁻¹ and at about 743–714 cm⁻¹, respectively. Phosphine oxide unit was evidenced in the FTIR spectra of all polymers by the absorption bands at 1177–

1157 cm⁻¹ (P=O unit) and at 1177–1157 cm⁻¹ (P–Ar linkage). The absorption bands from 3065–3070 cm⁻¹ and 2916–2918 cm⁻¹ were assigned to aromatic C–H and aliphatic C–H stretching, respectively. Polyimide **PI-O** which incorporates aromatic ether linkages had additional absorption bands at 1237 cm⁻¹. The ketone unit from polyimide **PI-CO** was identified at 1668 cm⁻¹, while the hexafluoroisopropylidene unit introduced in polyimide **PI-6F** was evidenced at 1191 cm⁻¹.

Table 1. FTIR (cm⁻¹) data of polyimides.

Band assignment	PI-O	PI-CO	PI-6F
Aromatic C–H stretching	3066	3066	3070
Aliphatic C–H stretching	2916	2917	2918
Aromatic C=O asymmetric stretching	1778	1779	1785
Aromatic C=O symmetric stretching	1720	1719	1723
Ketone C=O stretching	-	1668	-
P–Ar stretching	1425	1424	1426
C–N stretching	1368	1370	1371
Ar–O–Ar stretching	1237	-	-
C–F stretching	-	-	1191
P=O stretching	1177	1164	1157
C–N deformation	743	714	720

The NMR spectra of polymers confirmed the formation of polyimides by identifying presence of a single peak in the ³¹P NMR spectra at about 27.40 ppm. Also, in the ¹H NMR spectra of all polymers the aromatic protons from the main chain were identified in the domain of 7.55–8.14 ppm. The methyl protons from phosphine oxide unit in all polyimides were evidenced at about 2.5–2.10 ppm (Table 2). As an example Fig. 2 illustrates the ¹H NMR spectrum with the assignment of all protons and ³¹P NMR spectrum of polyimide **PI-CO**.

Fig. 2. (a) ^1H NMR and (b) ^{31}P NMR spectrum of polyimide **PI-CO**.

Table 2. NMR (ppm) data of polyimides.

Peak assignemnt	PI-O	PI-CO	PI-6F
$-\text{P}(\text{O})\text{CH}_2-$	2.08	2.10	2.07
H_{arom}	7.55-7.97	7.67-8.11	7.63-8.14
$^{31}\text{P}(\text{s})$	27.42	27.41	27.40

The polymers had a good solubility in polar organic solvents (NMP, DMF, DMSO, DMAc) and in chloroform which is due to the introduction of the flexible $-\text{O}-$, $-\text{C}=\text{O}-$ and $-\text{C}(\text{CF}_3)_2-$ units. The presence of these linkages disrupts the tight packaging of the corresponding polymers, a known characteristic for classical aromatic polyimides.

3.2. Thermal properties

The general thermal behaviour of the studied structures was evaluated by means of DSC and TGA methods and was discussed thoroughly in a previous paper [47]. All polyimides decomposed in a single step. The structural differences produced by the introduction of ether (in **PI-O**), ketone (in **PI-CO**) or hexafluoroisopropylidene (in **PI-6F**) flexible linkages were

analysed with respect to their influence on thermal stability. The main thermogravimetric characteristics obtained from the TGA analysis are presented in Table 3.

Table 3. Thermal properties of polyimides.

Sample	Work atm.	T ₅ (°C)	T ₁₀ (°C)	T ₂₀ (°C)	T ₃₀ (°C)	T ₄₀ (°C)	T ₅₀ (°C)	T ₆₀ (°C)
PI-O	Air	472±1.4	484±1.4	491±2.1	526±2.8	587±12.1	699±21.9	753±14.1
	N ₂	473±0.0	486±0.0	496±2.1	556±6.3	850±14.1	-	-
PI-CO	Air	467±0.5	486±4.5	507±7.7	523±7.0	531±8.4	538±7.7	552±16.2
	N ₂	479±0.2	498±0.0	530±0.5	648±1.4	851±10.6	-	-
PI-6F	Air	480±1.3	493±1.4	504±0.0	514±0.7	535±0.7	559±2.1	575±0.0
	N ₂	483±1.7	496±0.7	512±1.2	530±1.4	584±2.8	763±6.3	-

T₅, T₁₀, T₂₀, T₃₀, T₄₀, T₅₀, T₆₀ – temperatures corresponding to 5%, 10%, 20%, 30%, 40%, 50% and 60% mass loss, respectively.

The mass loss of all polyimides increases with the increase in temperature, in both working atmospheres. The results show that the thermal stability, in air, of all polyimides is slightly lower than in inert nitrogen atmosphere, for all weight loss data. When T₅ is taken as thermal stability criterion, the thermal stability in inert atmospheres increases in the following order: **PI-O** < **PI-CO** < **PI-6F**, while the same criterion, in air, gives a small change as follows: **PI-CO** < **PI-O** < **PI-6F**.

The highest value of T₅ (483°C) in both working atmospheres was registered for polyimide **PI-6F** which contains bulky hexafluoroisopropylidene units. In case of polymers **PI-O** and **PI-CO** the TGA data are very similar and exhibit lower decomposition temperatures as compared to **PI-6F**, both in nitrogen and in air. The polymer (**PI-CO**) containing ketone unit has slightly higher thermal stability, when the experiments were performed in nitrogen. The carbonaceous residue obtained at 900°C for all polyimides are high and thus they can be considered charring polymers. **PI-6F** exhibited the lowest value from the series (48.58%) while the char yield for **PI-O** and **PI-CO** were similar 57.7% and 58.4%, respectively. The char residue of all polyimides registered stable and high values between 600 and 900°C, the differences in the amount of char residue being small, in the range of 9.28–15.44%. Charring in fire is an anaerobic process, so the residues obtained after TGA measurements might be an indication for a

condensed-phase activity for these polyimides, as showed in Table 4. The values of char yield at the end of the experiment may indicate that the carbonization played an important role in the solid-phase pyrolytic mechanism.

Table 4. Polyimides char residue values in nitrogen at different temperatures.

Sample	W ₆₀₀ (%)	W ₇₀₀ (%)	W ₈₀₀ (%)	W ₉₀₀ (%)
PI-O	68.32±0.4	65.71±0.4	62.60±0.4	57.7±0.4
PI-CO	73.82±0.1	67.38±0.2	62.86±0.2	58.38±0.8
PI-6F	57.86±0.1	51.29±0.1	49.48±0.1	48.58±0.2

W₆₀₀, W₇₀₀, W₈₀₀, W₉₀₀ – char residue at 600°C, 700°C, 800°C and 900°C, respectively.

It can be concluded that the introduction of phosphine oxide moiety along with flexible ether, carbonyl or hexafluoroisopropylidene units in the main chain did not affect the thermal stability of the present polyimides compared to similar polyimide structures published in the literature [6].

3.3. Non-isothermal decomposition kinetics

The kinetic parameters of thermal decomposition were evaluated by using non-isothermal experiments. The rate of conversion for thermal decomposition is given in Eq. (1), where t is time (min), A is the pre-exponential factor (s^{-1}), E is the activation energy of thermal decomposition ($kJ\ mol^{-1}$), R is the gas constant ($8.314\ J\ K^{-1}\ mol^{-1}$), T is temperature (K) and $f(\alpha)$ is the conversion function.

$$\frac{d\alpha}{dt} = Ae^{\frac{-E}{RT}} f(\alpha) \quad \text{Eq. (1)}$$

A new equation is obtained for the thermal decomposition rate if one inserts the heating rate (Eq. (2)), $\beta = dT/dt$.

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\frac{-E}{RT}} f(\alpha) \quad \text{Eq. (2)}$$

Non-isothermal kinetic parameters values of the studied structures were determined by applying the isoconversional method of Freedman, which exploits the shifts in thermograms with heating rate increase [48-50] as recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) [51]. For this purpose additional

thermal decomposition experiments were performed at three different heating rates for all three polyimides (Fig. 3).

Fig. 3. Thermograms of the studied polyimides recorded at three heating rates.

The Friedman method [52], is based on the differential form of the rate equation (Eq. (3)):

$$\ln \frac{d\alpha}{dt} = \ln \beta \frac{d\alpha}{dT} = \ln [Af(\alpha)] - \frac{E}{RT} \quad \text{Eq. (3)}$$

The $\ln d\alpha/dt$ versus $1/T$ plot, for $\alpha = \text{const}$ extracted from the thermograms obtained at three different heating rates was a straight line with the slope value being equal to that of the activation energy.

Fig. 4. Friedman plots of the studied polyimides.

Fig. 4 and Table 5 present the Friedman plots and the global kinetic parameters values, ranging between 0.1 and 0.9. Fig. 5 shows the variation of kinetic parameters values with conversion degree.

Table 5. Kinetic parameters values determined with Friedman method.

α	PI-O		PI-CO		PI-6F	
	E (kJ mol ⁻¹)	log A (s ⁻¹)	E (kJ mol ⁻¹)	log A (s ⁻¹)	E (kJ mol ⁻¹)	log A (s ⁻¹)
0.1	5	3.72	7	4.2	9	7
0.2	27	5.89	46	6.5	65	13
0.3	146	7.62	167	8.8	185	23
0.4	156	8.54	159	8.32	210	28.15
0.5	156	8.68	166	8.71	240	29.54
0.6	177	10.1	135	6.44	283	30.12
0.7	255	15.14	181	9.1	340	32.1
0.8	356	21.72	267	14.06	425	38.91
0.9	405	28.44	436	24	465	45.5

From Fig. 5 and Table 5 there may be observed a slight initial decrease in kinetic parameters values at the beginning of the decomposition process ($0 < \alpha < 0.13$), corresponding to scission initiation of some weak linkages, such as dehydration and/or initiation of depolymerization [53].

Fig. 5. Variation of E values with α according to the Friedman method.

It is common for high thermal stable polyimides to exhibit high E values, often exceeding 400 kJ mol^{-1} [25]. From Fig. 5 and Table 5 it may be observed that these values exhibit a general increasing trend with the thermal stability, reaching 405 kJ mol^{-1} for **PI-O**, 436 kJ mol^{-1} for **PI-CO** and 465 kJ mol^{-1} for **PI-6F** and being in good agreement with literature data [25,47]. The polyimide **PI-CO** shows slight decrease of E values in short α ranges ($0.3 < \alpha < 0.35$; $0.45 < \alpha < 0.58$; $0.67 < \alpha < 0.73$), a similar trend being reported in the literature [25], intercalated with continuous increases at larger α ranges ($0.13 < \alpha < 0.29$; $0.36 < \alpha < 0.44$; $0.59 < \alpha < 0.66$; $0.74 < \alpha < 0.9$). For the ranges $0.13 < \alpha < 0.35$ and $0.52 < \alpha < 0.9$, the E values of polyimides **PI-O** and

PI-6F increase rapidly, with a slow increase in the middle range $0.36 < \alpha < 0.51$. The increase of E values is a consequence of weak linkage consumption, polymer main chain decomposition and probably some unstable reaction products generated during the thermal decomposition process [53,54].

The variation of E with α underlines the complexity of the polyimides decomposition mechanisms [46,55]. Most probably, the decomposition in these polymers is initiated from cleavage of the weaker P-C bonds and continues with the decomposition of the macromolecular backbone, so that volatile compounds are produced at moderate α and char residue yield at higher α values. This observation is based on previous studies on the thermal behaviour of various phosphorus-containing polymers [54,56].

3.4. TGA-FTIR studies

TGA-FTIR was used to analyse the volatile products formed during the thermal decomposition of polyimides. The FTIR spectra of volatile products formed at different temperatures from 400 to 800 °C are presented in Fig. 6. The temperatures are chosen to display the products which are released during the experiment at specific mass losses as presented in Table 3. As there is negligible mass loss below 400 °C, only the FTIR spectra corresponding to gasses evolved above 400 °C is presented in Fig. 6. Depending on the structure of the polyimides one can notice similarities and slight differences in the type of gasses evolved at various temperatures. For all polyimides one can see typical pyrolysis gasses corresponding to water (weak bands, 3500-3900 cm^{-1} , 1300-1700 cm^{-1}), hydrocarbons (C-H vibrations around 3010 cm^{-1}), unsaturated compounds (around 1500 cm^{-1}), CO_2 (at 2350 cm^{-1}) and CO (at 2250 cm^{-1}) [57]. In case of PI-6F one observes evolution of additional gas corresponding to peak at 1150 cm^{-1} . This peak can be assigned to the evolution CHF_3 and is typical of fluorine containing polyimides [58]. Gasses containing phosphorus couldn't be identified from the TGA-FTIR experiments. It is likely that most phosphorus species remain in the condensed phase and the volatile species are difficult to be identified using this setup possibly due to overlap of the absorption bands corresponding to other species.

Fig. 6. TGA-FTIR spectra of evolved volatile products from polyimides at different temperatures.

3.5. Py-GC-MS studies of polyimides and their thermal decomposition mechanisms

Evolved gas analysis using TGA-FTIR as discussed earlier provide mostly useful information on the functional groups of the mixture of volatile species evolved during the decomposition process. In order to clarify the main components and mechanism of their formation Py-GC-MS technique was further employed.

The volatilization profiles, represented as ion current, of the fragments originating in the thermal decomposition of polyimides are shown in Fig. 7. The possible structural assignments of the pyrolyzates at 700°C are listed in Table 6. The major pyrolyzates are listed in the order of increasing retention times. The pyrolyzates were identified by mass spectra and confirmed through a comparison of their retention times to those reported in the literature.

Fig. 7. Total ion chromatogram of polyimides registered at 600°C.

Table 6. Identification of pyrolysis products of polyimides.

Retention time (min)	Name	Mass	Ions (m/z)	Structure	PI-O	PI-CO	PI-6F
3.03-3.08	Toluene (T)	92	91; 92; 65	<chem>Cc1ccccc1</chem>	+	+	+
3.71	Benzene (B)	78	78; 63; 45	<chem>c1ccccc1</chem>	+	+	-
4.47-9.38	Styrene (S)	104	104; 103; 78; 77	<chem>C=Cc1ccccc1</chem>	+	+	-

5.36-5.46	Phenyl isocyanate (PI)	119	119; 91; 64; 63		+	+	+
5.59	3-(Trifluoromethyl) phenol (tFMP)	162	162; 77; 76; 50		-	-	+
5.67-5.69	Aniline (A)	93	93; 66; 65; 92		+	+	-
5.75-5.79	Benzonitrile (BN)	103	103; 76; 50		+	+	+
6.56	N-methyl pyrrolidinone (NMP)	99	99; 98; 44; 42; 41		-	-	+
8.73	Trifluoromethane (tFM)	70	70; 69; 57; 54; 43; 41;	CHF ₃	-	-	+
10.06- 10.07	Pyrrole-1-phenyl (PP)	143	143; 115; 116; 77		+	+	-
10.72- 10.74	Dicyano benzene (dCB)	128	128; 101; 129		+	+	-
11.42- 11.45	Biphenyl (bP)	154	154; 153; 152		+	+	+
11.75- 13.10	Diphenyl ether (dPE)	170	170; 171; 141; 142; 169		+	-	-
13.15- 14.04	Fluorene (F)	166	166; 165; 163		+	-	-
16.68- 16.69	Carbonitrile biphenyl (CbP)	179	179; 178; 180		+	+	-

18.85- 18.89	Isoindole-1,3-dione- 2-phenyl (IDP)	223	223; 179; 76; 178		+	+	+
20.09- 20.14	Methylphenyl- isoindole-1,3-dione (MPID)	237	237; 193; 192; 89		+	+	-

By analysing the total ion chromatogram (TIC) of polyimides it can be observed that the polymers have in common a series of pyrolyzates, identified in a close domain of retention times (RT): toluene (RT=3.03–3.08), phenyl isocyanate (RT=5.36–5.46), benzonitrile (RT=5.75–5.79), biphenyl (RT=11.42–11.45) and isoindole-1,3-dione-2-phenyl (RT=18.85–18.89). The abundance of the fragments resulting from the decomposition process is strongly dependent on the chemical structure of the polyimides. Thus, polymers **PI-O** and **PI-CO** exhibit similar fragments compared to **PI-6F**. As compared to in **PI-6F** the abundance of fragment with $m/z=223$ (isoindole-1,3-dione-2-phenyl) is higher in case of the former two polymers. For all polyimides the abundance of the $m/z=103$ fragment (benzonitrile) is comparable, the highest abundance being registered for polymer **PI-CO**. The presence of $m/z=154$ fragment (biphenyl) is more notable in the case of polymer **PI-CO** when compared to the other polyimides. The highest abundance of toluene ($m/z=92$) can be identified in polymer **PI-CO**, while the fragment $m/z=119$ (phenyl isocyanate) has a weak presence in all polyimides. Toluene ($m/z=92$) may appear as a consequence of the polymer fragmentation and was also identified by other authors [3,59-62]. Phenyl isocyanate ($m/z=119$) detected in a relatively low concentration in the pyrolyzates was evidenced in the decomposition products of similar polyimide structures and may be formed by fragmentation and rearrangements of imide group [3,36,60,62,63]. In addition to evolution of physically adsorbed from the polymer, the scission of the ether groups also release water. This water could catalyze the hydrolysis of imide groups. The detection of benzonitrile may be due to the cleavage of carbonyl group in the imide rings to form oxygen radicals which could combine with CO to form CO₂ [3,42,60]. Biphenyl ($m/z=154$) may appear as a consequence of the fragmentation and reorganization of the pyrolyzates and it was observed

by other researchers [3,60]. Isoindole-1,3-dione-2-phenyl ($m/z=223$) evidenced in the pyrolyzates may appear from the fragmentation of the polyimide chain, being identified in other similar polyimide structures [3,36,60,61].

The decomposition of the polyimides leads to the formation of additional product originating from polymer chain fragments and subsequent rearrangements, as shown in Table 6. Benzene ($m/z=98$) which appears in the TIC of **PI-O** and **PI-CO** as a result of the fragmentation of the polymer chain was also identified by other studies [3,36,42]. Styrene ($m/z=104$) which was previously identified in all polyimides except **PI-6F** may appear as a result of the fragmentation and subsequent rearrangements of pyrolyzates [36,42]. Aniline ($m/z=93$), observed in **PI-O** and **PI-CO** TIC in a relatively high quantity may result from the fragmentation and reorganization of the corresponding decomposition products, was found in other polymers [36,62]. Diphenylether ($m/z=170$) and fluorene ($m/z=166$) both found in **PI-O**, carbonitrile-biphenyl ($m/z=179$) identified in **PI-O** and **PI-CO** and methylphenyl-isoindole-1,3-dione ($m/z=237$) found in **PI-O** and **PI-CO** may result from the re-cyclization of free radicals from polyimides main chain scission, as observed in other studies [36,60,62]. Pyrrole-phenyl ($m/z=143$) and dicyano-benzene ($m/z=128$) evidenced in polyimides **PI-O** and **PI-CO** may appear as a result of fragmentation and rearrangement of imide rings. 3-(Trifluoromethyl)phenol ($m/z=162$) and trifluoromethane ($m/z=70$) identified in TIC of **PI-6F** may result from the scission and rearrangement of the polyimide main chain. It was demonstrated that the C-CF₃ linkage in polyimide have the smallest bond order and thus, the largest C-C bond distance. Hence, the C-CF₃ linkage would be the initiation site of the corresponding polyimide decomposition [63]. N-methyl-pyrrolidinone ($m/z=99$) from TIC of **PI-6F** may also be due to the evaporation of residual solvent trapped in polyimide chain. Trifluoromethane was also found in similar fluoro-containing polyimide [61,63].

By examining the obtained data it was observed that the pyrolyzates can be classified into several groups: (1) low molecular weight compounds such as water, CO, CO₂ (visible in TGA-FTIR spectra); (2) fragments cleavage from polyimide chains and subsequent rearrangements, including aromatic hydrocarbons, aromatic amines, aromatic nitriles; (3) products obtained by isomerizations, rearrangements and cyclization reactions of the pyrolyzates at high temperatures, such as diphenyl ether, fluorine, imides, etc.

The composition and distribution of the pyrolysis products implies that the thermal decomposition of polyimides undergoes the same mechanism, which is initiated by random homolytic cleavage of the weaker carbon-phosphorus bonds, followed by the scission of carbon-oxygen or carbon-fluorine bonds in the main chain followed by carbon-nitrogen, carbon-oxygen and carbon-carbon bonds cleavage in the imide rings. These scissions give rise to smaller chains, free radicals and carbon monoxide. The subsequent steps consist of depropagation, chain transfer involving C–H and N–H hydrogen transfer processes, rearrangement and condensation reactions at high temperatures, as observed by other studies [36,60].

Associating with the pyrolysis products that have been discussed, the oversimplified mass fragmentation of polyimides **PI-O**, **PI-CO** and **PI-6F** are shown in Scheme 1, Scheme 2 and Scheme 3, respectively.

Scheme 1. Oversimplified mass fragmentation of **PI-O**.

Scheme 2. Oversimplified mass fragmentation of **PI-CO**.

Scheme 3. Oversimplified mass fragmentation of **PI-6F**.

3.6. Morphological analysis of the char residue

The residue obtained after TGA experiments was analysed to identify the morphology of the polyimide samples at the end of the pyrolysis. All polymers exhibited a continuous and dense

structure without cracks or pores on the surface of the residues. As an example Fig. 8 presents the morphology of the char residue obtained from **PI-CO** after TGA experiment.

Fig. 8. Morphology of the char residue for the polyimides after TGA experiment.

The information obtained by this analysis indicates that the formation of dense char layer enhances the char stability, which is in accordance with results obtained from TGA data. Furthermore, these suppositions are confirmed by the high values of polyimide char residues showed in Table 4 and Fig. 3. This behaviour can be attributed to the advanced pyrolysis of the protective phosphorus-rich carbonaceous layer.

Fig. 9 shows the atoms distribution of the residual char surface of **PI-CO**, as shown by electron X-ray diffraction (EDX). It is observed that the phosphorus atoms are uniformly dispersed in the residual char surface.

Fig. 9. EDX mapping of the char residue for polyimide **PI-CO** (SE mode, 20 kV, C:carbon; O: oxygen; N: nitrogen; P: phosphorus).

The presence of P atoms in the char layer and the high quantity of carbonaceous layer at the end of the experiment (as shown in Table 4) may be an indication of a condensed phase activity of the phosphorus which could enhance the inherent flame retardant behaviour of the new polyimides.

4. Conclusion

The thermal analysis of three polyimides containing phosphine-oxide units evidenced a high thermal stability. The initial decomposition temperatures had values in the range of 473-483°C and char residues in the domain of 48.58-58.38%. The non-isothermal decomposition kinetic parameters values were determined using the Friedman isoconversional method. The large activation energy values obtained for these polyimides, in the range of 405-465 kJ mol⁻¹, are common for highly thermally stable polymers. The data evidenced a complex decomposition

process of the main chain, being probably initiated by the cleavage of the weaker P–C bonds, followed by the decomposition of the macromolecular backbone.

The volatile products formed during the thermal decomposition of polyimides was analysed by TGA-FTIR. In all spectra it can be observed that the peaks associated with water, CO₂, CO and hydrocarbons are predominant from 500 to 800 °C.

Py-GC-MS studies showed that the thermal decomposition of the three polyimides undergoes the same mechanism, which is initiated by random homolytic cleavage of the weaker carbon-phosphorus bonds, followed by the scission of carbon-oxygen or carbon-fluorine bonds in the main chain and after that carbon-nitrogen, carbon-oxygen and carbon-carbon bonds cleavage in the imide rings. These cleavages give rise to chain free radicals and carbon monoxide. The following steps consist of depropagation, chain transfer involving C–H and N–H hydrogen transfer processes, rearrangement and condensation reactions at high temperatures. Based on these data oversimplified decomposition mechanisms for these polyimides were proposed.

The morphology of the char residue obtained after TGA experiments showed a continuous and dense structure without cracks or pores which enhances the char stability. The EDX mapping identified C, N, O and P atoms uniformly dispersed onto the residual char surface.

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