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Study on Thermal and Flame Retardant Properties of Phosphorus-containing Polyimides

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Abstract: *The present study aimed to design macromolecular architectures having imide core in the main chain and bearing two 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide heterocycles in the side chain of each structural units as a synergetic two components key factor to induce attractive flame retardant properties in the resulted materials. The synthesis pathway consisted in the classical polycondensation reaction strategy using a phosphorus-containing diamine synthesized in the laboratory and three commercial dianhydrides co-monomers. The chemical structure confirmation of the phosphorus-containing polyimides has been performed by means of FTIR and NMR spectroscopy. The thermal stability of the products was introspected through TGA analysis. The char yields measured at 900°C ranged between 35% and 54%. Using these parameters limiting oxygen index values were theoretically calculated. Also, the microscale combustion calorimetry measurements have been conducted, in order to investigate the combustion mechanism of the synthesized phosphorus-containing polyimides.*

Keywords: *phosphorus-containing polyimides, thermal stability, flame retardant properties*

1. Introduction

The increasing need for safe high-performance polymer-based materials entails meeting of certain requirements, of which their flame resistance combined with their impact on the environment are critical. Phosphorus-containing polymers have been the subject of numerous studies due to the superior characteristics in terms of flame resistance [1-4]. On the other hand, the use of monomers containing bulky 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) units has led to the production of polymers with improved solubility and low birefringence [5, 6].

Phosphorus-containing polyimides were developed as alternative materials, providing a compromise between excellent thermal stability of polyimides and processability of phosphorus-containing polymers [7-9]. Therefore, a various range of phosphorus-containing polyimides have been investigated as high performance materials for various applications [10-13].

The monomer DOPO has been extensively studied in epoxy formulations due to its superior flame resistance properties that it induces to the material in which it is incorporated [14-18]. However, the introduction of this monomer into the epoxy networks leads to a decrease of glass transition temperature, having negative effects on mechanical properties.

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In recent years, DOPO has attracted interest especially due to the multiple possibilities of structural diversification through functionalization. Thus, the active hydrogen of the DOPO heterocycle can react with various derivatives having groups deficient in electrons, leading to a wide range of phospha-phenanthrenic compounds [19-21].

It was demonstrated that the presence of the DOPO units has a beneficial effect on increasing the flame resistance, adhesion properties, optical transparency and environmental friendly capability, in conjunction with decreased crystallinity and water vapor adsorption capacity [6, 22].

In the present work, we report the synthesis and characterization of phosphorus-containing polyimides prepared from a bifunctional phosphorus-based diamine, as a flame retardant monomer, and three commercial dianhydrides, namely: 4,4′-oxydiphthalic anhydride, 2,2-bis[4-(3,4-dicarboxy-phenoxy)phenyl]propane dianhydride, and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride. The targeted bifunctional phosphorus-containing monomer was prepared through direct addition reaction of DOPO to CO group of 4,4’-diaminobenzophenone. The structure of the phosphorus-containing polyimides was confirmed by FTIR, ^{1}H NMR and ^{31}P NMR spectroscopy, while their thermal stability and flame-retardant properties were evaluated by thermal gravimetrical analysis (TGA) and microscale combustion calorimetry (MCC) test, respectively.

2. Materials and methods

2.1. Materials

4,4′-Oxydiphthalic anhydride (97%, M_w=310,21 g/mol), 2,2-bis[4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride (98%, M_w=410,51 g/mol), 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (99%, M_w=444,24 g/mol), 4,4’-diaminobenzophenone (97%, M_w=212,25 g/mol), N-methyl pyrrolidone (NMP) (HPLC, 99.9% purity) from Sigma-Aldrich Chemie GmbH were used as received. 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (97%, M_w=216.18 g/mol) received from TCI (Japan) was dehydrated under vacuum for 5 h at 120°C prior to use. The other solvents used in the synthesis or purification / precipitation of the polymers were of analytical grade and used as received.

2.2. Synthesis of DOPO-diamine

The synthesis of DOPO-diamine (**1**) was performed according to published procedures starting from 4,4’-diaminobenzophenone and 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide [23] Yield: 75%. ^{1}H NMR (DMSO-d_6, ppm): δ = 4.9 (s, 4H, NH_2), 5.9 (d, 4H, CH_{ar}-NH_2), 8.5-6.9 (m, 20H, aromatic protons); ^{31}P NMR (DMSO-d_6, ppm): δ = 31.10 and 29.41.

2.3. Preparation of phosphorus-containing polyimides

Phosphorus-containing polyimides (**4**) were synthesized by two-stage polycodensation reaction of the DOPO-diamine **1** with three commercial dyanhydrides, namely 4,4′-oxydiphthalic anhydride (**2a**), 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**2b**), and 4,4′-(hexafluoroiso-propylidene) diphthalic anhydride (**2c**). The typical procedure for the synthesis of polymer **4a** was as in the following example: 0.626 g (1 mmol) DOPO-diamine **1** and 6.9 mL NMP were introduced in a three-necked round flask, equipped with magnetic stirrer and nitrogen inlet and outlet. After complete dissolution of the diamine, the mixture was cooled in an ice bath and salt, and then 0.310 g (1 mmol) of dianhydride **2a** were introduced under vigorous stirring. The reaction mixture was kept below 0°C for 15 min, after which the reaction was carried out at room temperature for a time of 8 h. The resulted viscous solution was heated to 180°C under a slight nitrogen stream for 24h to ensure cyclo-dehydratation. After cooling to room temperature, the solution was diluted by the addition of NMP and precipitated in distilled water. The resulting polymeric powder was collected by vacuum filtration and then washed repeatedly with distilled water. Purification of the polymer was made by Soxhlet extraction in ethanol to remove unreacted monomers and highly volatile residual solvent. Subsequently, the sample was dried in an oven at 100^{o}C under vacuum for 12 h.

4a: Yield: 92%. FT-IR (KBr, cm^{-1}): 3067 (aromatic C–H, stretching vibration), 1785 and 1725 (C=O, asymmetric and symmetric stretching vibration), 1476 (P–Ph, stretching vibration), 1367 cm^{-1} (imide C–N, stretching vibration), 925 and 1115 (P–O–C, asymmetric and symmetric stretching vibrations), 1225 (P=O).

4b: Yield: 90%. FT-IR (KBr, cm^{-1}): 3065 (aromatic C–H, stretching vibration), 2920 and 2834, (aliphatic C–H, asymmetric and symmetric stretching vibrations), 1787 and 1720 (C=O, asymmetric and symmetric stretching vibration), 1475 (P–Ph, stretching vibration), 1366 cm^{-1} (imide C–N, stretching vibration), 927 and 1115 (P–O–C, asymmetric and symmetric stretching vibrations), 1225 (P=O).

4c: Yield: 89%. 3065 (aromatic C–H, stretching vibration), 1788 and 1726 (C=O, asymmetric and symmetric stretching vibration), 1477 (P–Ph, stretching vibration), 1366 cm^{-1} (imide C–N, stretching vibration), 1211 (C–F, stretching vibrations), 925 and 1115 (P–O–C, asymmetric and symmetric stretching vibrations), 1225 (P=O).

2.4. Methods

FTIR spectra of monomers and polymers were performed with a Bruker Vertex 70 FTIR spectrometer, in transmission mode, using KBr tablets on frequency range 4000 – 400 cm^{-1}.

^{1}H NMR and ^{31}P NMR spectra of monomers and polymers were performed at room temperature using a spectrometer BrukerAvance DRX 400, at various operating frequencies (400 MHz for ^{1}H NMR and 62 MHz for ^{31}P NMR, respectively), in DMSO-d$_6$.

Thermal stability of the polymers was investigated by using Mettler Toledo TGA-SDTA851^{e} equipment, in nitrogen atmosphere, under dynamic conditions with a flow rate of 20 mL/min and a heating rate of 10°C/min, in the temperature range of 25-900°C and with a sample mass between 2.12 and 2.67 mg.

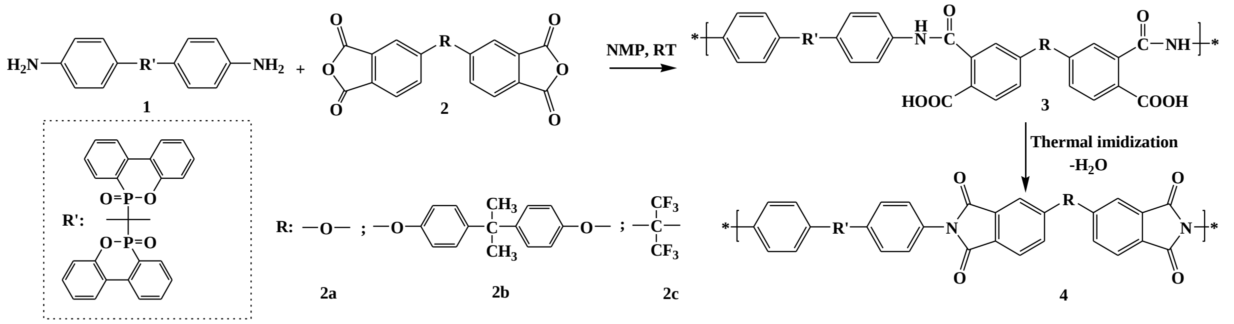
The flammability behavior of the samples was tested using FTT Micro Calorimeter. MCC tests were used to evaluate the flammability of samples in controlled temperature conditions; the temperature in the combustor was 900°C, and the pyrolyzer was heated up to 750°, at a heating rate of 1°C/s. The tests performed complied with “Method A” (ASTM D7309-13).

Scanning electron microscopy (SEM) was performed on a TESLA BS 301 microscope, at 20 kV, with a magnification of 380-3600. The images were recorded on film surfaces deposited on gold supports and coated by sputtering with thin gold films using an EK 3135 EMITECH device.

3. Results and discussions

The studies carried out in this paper aimed the designing and preparing of polyimides-type macromolecular architectures bearing bulky side phosphaphenanthrenic substituents, with flame retardant properties.

The polyimides **4** were synthesized by two-stage polycondensation reaction, of DOPO-diamine **1**, with various commercial dianhydrides, namely, 4,4′-oxydiphthalic anhydride (**2a**), 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**2b**), and 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (**2c**), using NMP as solvent (Scheme 1).



Scheme 1. Synthesis of phosphorus-containing polyimides **4**

The structure of the synthesized polymers was investigated by FTIR and ^{31}P NMR spectroscopy. The FTIR spectrum of **4b** (Figure 1) revealed absorption bands characteristic of the imide unit at 1787 cm^{-1} (asymmetric stretching vibrations of the C=O imide bond), 1720 cm^{-1} (symmetrical stretching vibrations of the C=O imide bond), 1366 cm^{-1} (tensile vibrations of the C–N imide bond) and 740 cm^{-1} (vibrations of deformation of the imide ring). Also, characteristic absorption bands were observed for phosphaphenanthrene unit at 1475 cm^{-1} (stretching vibrations of the P–Ph), 1225 cm^{-1} (P=O), 1115cm^{-1} (asymmetric stretching vibrations of the P–O–C) and 927 cm^{-1} (symmetrical stretching vibrations of the P–O–C).

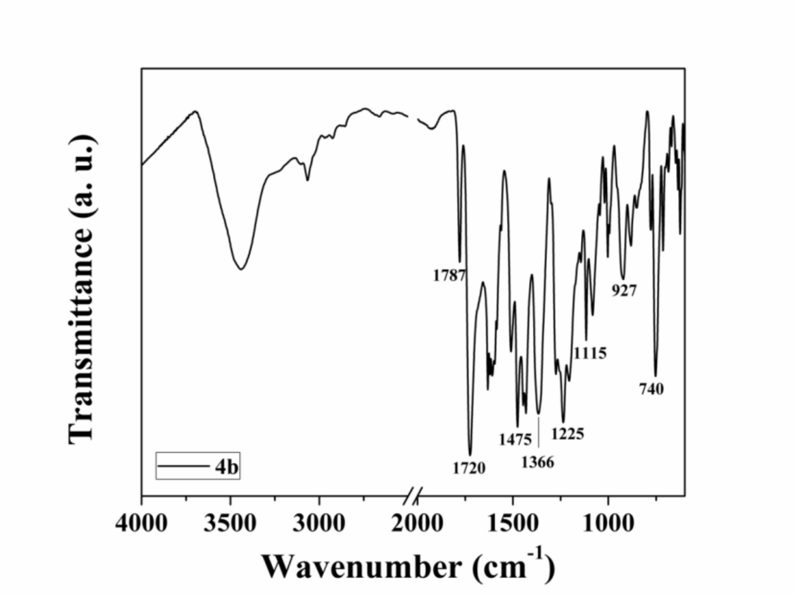


Figure 1. FTIR spectrum of phosphorus-containing polyimide **4b**

The representative ^{31}P NMR spectra of the polymers **4** were presented in Figure 2. The polymers exhibited a doublet in all three cases around 29 and 28 ppm, respectively, due to the presence of two DOPO units in the structure. These results confirmed the formation of the targeted phosphorus-containing polyimides [24, 25].

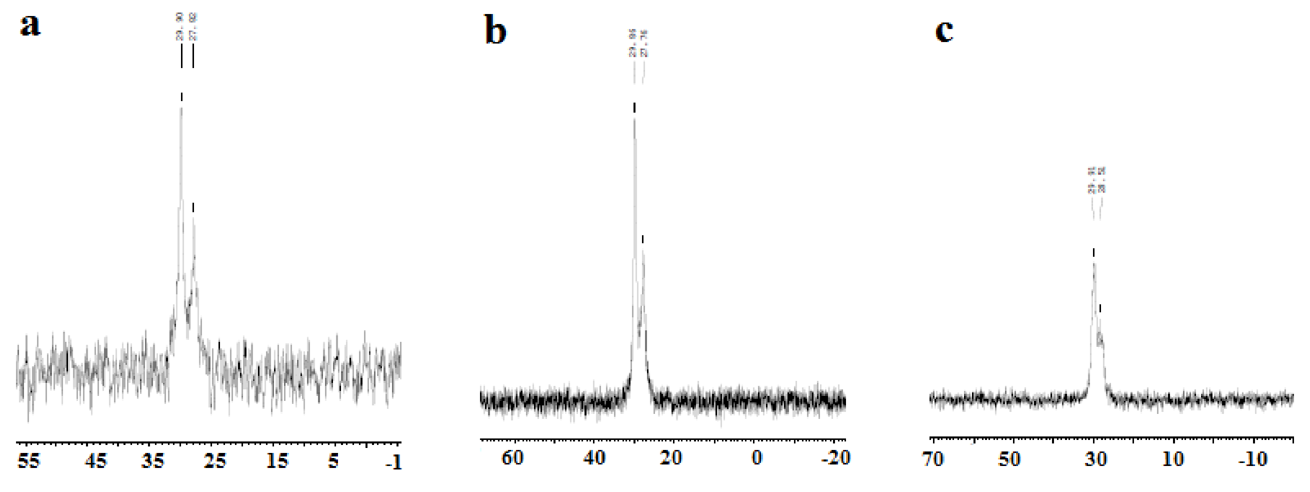


Figure 2. ^{31}P NMR spectra of phosphorus-containing polyimides **4a** (a), **4b** (b) and **4c** (c)

3.1. Thermal properties

The thermal properties of the polymers were evaluated by TGA analysis. The thermogravimetric (TG) and differential thermogravimetric (DTG) data are shown in Table 1 and Figure 3.

Table 1. Thermal properties of phosphorus-containing polyimide **4**

Samples	$T_{max}{}^{2}$ $T_{onset}{}^{1} \rightarrow T_{endset}{}^{3}$ (°C)			$\eta_{600°C}{}^{4}$ (%)	$\eta_{900°C}{}^{5}$ (%)
	Stage 1	**Stage 2**	**Stage 3**		
4a	185 158→213	386,468 359, 449→→489	611 567→670	70	54
4b	162 133→205	465 372→489	596 567→837	65	42
4c	175 150→223	458 408→479	554 522→718	60	35

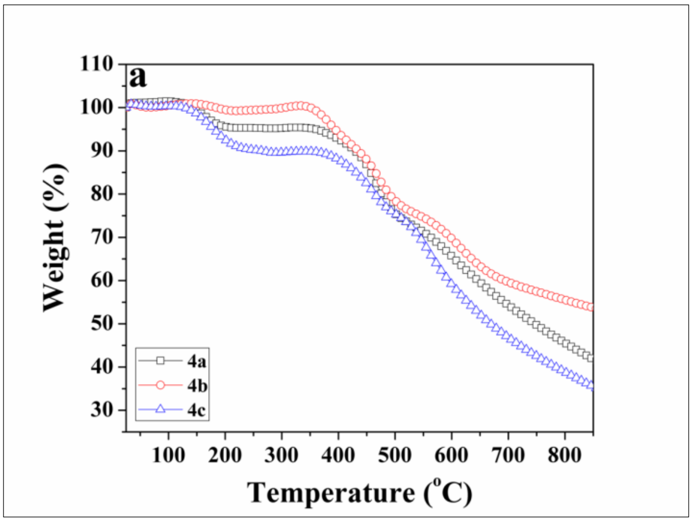
[1]initial decomposition temperature; [2]the temperature at which the decomposition rate is maxim; [3]final decomposition temperature; [4]carbonaceous residue yield measured at 600°C; [5]carbonaceous residue yield measured at 900°C

The introduction of $–C(CH_3)_3$- units into the structure of a polyimide decreases the thermal stability. Three distinct stages of decomposition were observed on the DTG thermograms (Figure 3b). The first decomposition peak centered around of 133°C, corresponds to a weight loss of 1.6-10.48% and it is probably due to the destruction P–O–C bonds more sensitive to degradation [5, 16, 26]. The second stage of decomposition involves temperatures ranging from approximately 386°C to 465°C, during which the rate of weight loss was very fast, with the loss of mass mainly due to the decomposition of the polymer chains. The third stage was described by an asymmetric Gaussian curve with a wider temperature distribution. At this stage the polymer carbonization and the decomposition of the residues took place, a hypothesis supported by the higher weight loss (> 34%). The lowest value of the char yields was obtained for **4c** containing hexafluoroisopropylidene units. Phosphorus-containing polyimides **4** showed complex decomposition processes involving several mechanisms: random splitting of the chain with the formation of smaller fragments, breaking of terminal links, elimination of lateral units, crosslinking, vaporization, diffusion, initiation-recombination cycles, gas phase reactions, etc. [27].

All polymers presented high char yields, between 60 and 70%, when this parameter was considered at 600°C and between 35 and 54%, when this parameter was considered at 900°C, respectively. Using the van Krevelen and Hoftyzer equation we performed calculation of the limiting oxygen index (LOI) [28].

$$LOI = 0.4xCR+17.5 \tag{1}$$

where CR is the char yield measured at 900°C.



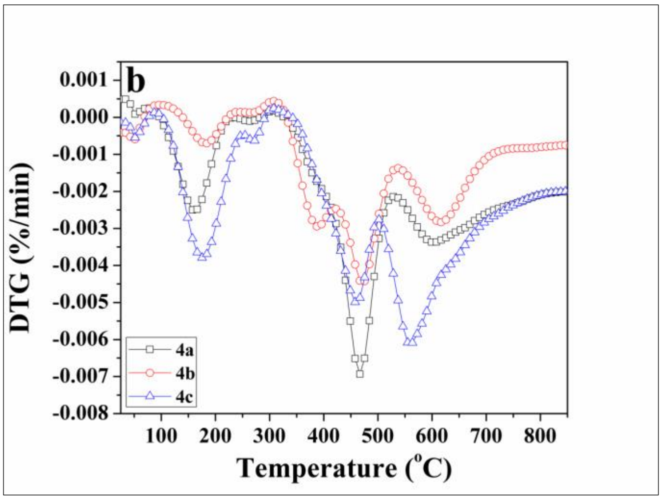


Figure 3. TG (a) and DTG (b) curves for the phosphorus-containing polyimides **4**

The calculated LOI values of phosphorus-containing polymers derived from their char yields were 39.1%, 34.4% and 31.5%, respectively. On the basis of LOI values, such compounds can be classified as self-extinguishing polymers.

3.2. Combustion behaviors

In general, the flammability of materials is characterized by the amount of heat released when the material is exposed to combustion (fire) [29]. The results of MCC analysis for the above samples are summarized in Table 2.

Table 2. Data obtained from MCC analysis of phosphorus-containing polyimides **4**

Polymer	**Char Yield (wt%)**	**Decomposition Rate (%)**	**HRC[1] (J/(g*K))**	**THR[2] (kJ/g)**	**pHRR[3] (W/g)**	**TPHRR[4] (°C)**	**Time (s)**
4a	49.31	50.69	109.37	9.09	186.02	509.07	204.00
4b	44.29	55.71	165.28	11.30	305.15	501.25	181.50
4c	39.56	60.44	127.78	8.14	191.57	503.08	207.50

[1]heat release capacity; [2]total heat release; [3]peak to heat release rate; [4]temperature of peak to heat release rate

In this analysis, at micro level, of the performance on fire behavior using MCC, the most important parameter is HRC. Low HRC values indicate low flammability in the MCC test and low real-scale fire hazard [30]. Another important parameter is char yield, the percentage mass of residue left over from combustion. As the percentage of carbonaceous residue is an indication of the amount of unburned fuel in a material treated with flammable substances, it is expected that the material with a higher percentage of carbonized residue will produce a lower amount of heat during combustion. Therefore, a correspondence relationship is expected between the two parameters. A low HRC and a high char yield, in principle, indicate an increased resistance during combustion. Analyzing the test results, we noticed that in terms of HRC, THR, temperature and time of occurrence of pHRR, the best results are recorded for **4a** and **4c**.

The char yield for the samples **4** was in the range between 39.56% and 49.31%, the highest value was observed for **4b**. The char yield obtained for the polymers **4** in MCC experiments which was equal with 49.31% (**4a**), 44.29% (**4b**) and 39.56% (**4c**), respectively, was compared to the values obtained in the TGA data 54% (**4a**), 42% (**4b**) and 35% (**4c**). The observed differences could be explained by the variation of heating-cooling rate, or the amounts of the sample used for these measurements.

Figure 4 presents the heat release rate curves for the phosphorus-containing polyimides **4**. All polymers exhibited two peaks in the heat release rate curve. The first peak can be attributed to the formation of a thin layer of coal that remains intact for a short period of time. Subsequently, the carbonized surface was destroyed by the vigorous emission of volatile products from the sample underlying. The second peak heat release rate appears around 200 s for **4a**, and **4c,** polymers which contained ether and –C(CF_3)$_3$ linkages in the unit structure and 181.5 s for **4b** which contained ether and –C(CH_3)$_3$ linkages**,** more sensitive to degradation. From Table 2 it can be observed that the pHRR values of **4a** (186.02 W/g) and **4c** (191.5 W/g) are lower when compared to **4b** (305.15 W/g). A decreased value of the parameter pHRR in the case of **4a** and **4c** is probably due to the formation of a stable and compact layer, which has slowed down the heat transfer from the inner layers of the sample during the ignition process. Similar results were reported in another studies, the highest value of **4b** can be correlated with the molar contribution of components to heat release capacity [31]. Also, in the case of THR the similar trend, as in the case of pHRR, could be observed. The temperature of maximum heat release rate was in the range 501.24-509.07^{o}C, being similar to the polyimides reported in the literature [32, 33]. In conclusion, it can be said that the phosphorus-containing polyimides exhibit varying levels of flame retardancy, depending on their chemical structure.

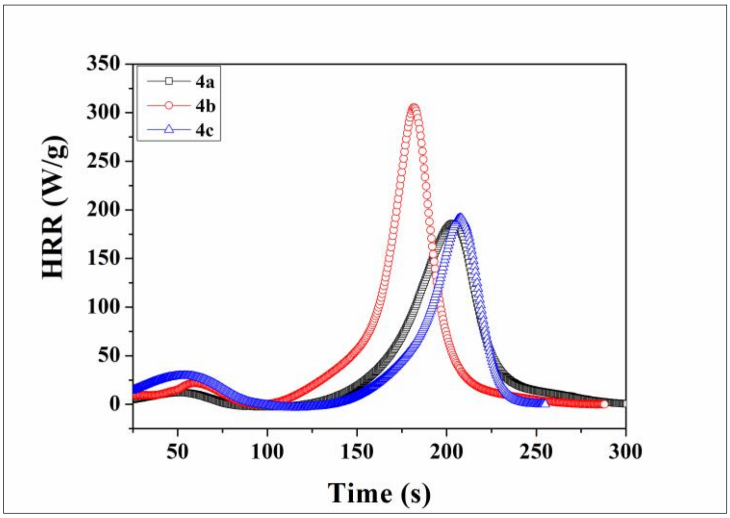


Figure 4. The HRR curves for the phosphorus-containing polyimide **4**

The morphology of the char yield of the samples **4** was studied by SEM analysis (Figure 5). The residue obtained after treating the polymer powder at 900^{o}C was characterized by a relatively smooth and continuous surface, which does not allow the diffusion of molecules to the outside or heat to the inner layers, thus preventing advanced thermal decomposition.

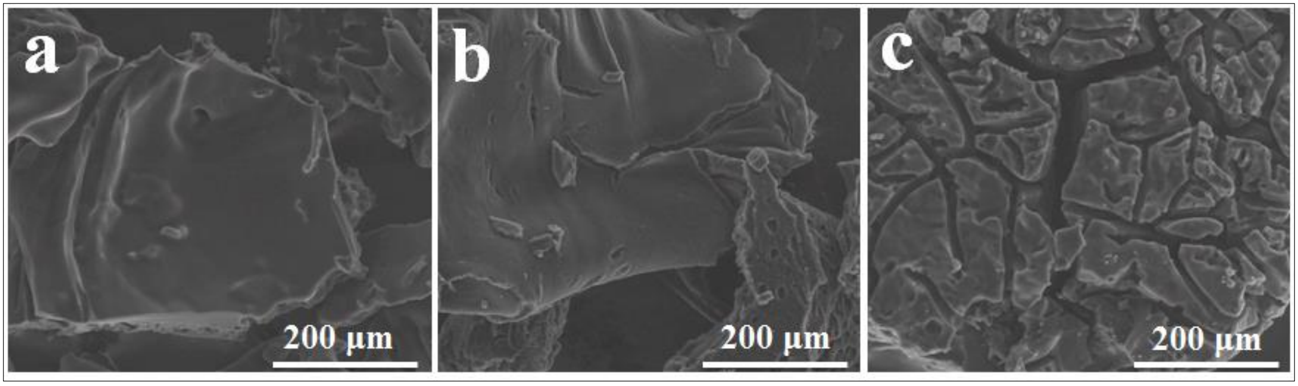


Figure 5 . SEM images of the char yield for the phosphorus-containing polyimides **4**

4. Conclusions

Phosphorus-containing polyimides were synthesized by two-steps polycondensation reaction using a DOPO-diamine and three commercial dianhydrides. Chemical structure of the phosphorus-containing polyimides was confirmed by FTIR, ^{1}H NMR and ^{31}P NMR spectroscopy. The thermal stability analysis revealed that the structure of phosphorus-containing polyimides play an important role in the degradation of these compounds. Phosphorus-contaninig polymers **4a** and **4c** have been found to be more thermally stable than **4b**. Similar results were obtained by performing MCC tests. In the case of polymer **4a**, the pHRR value was 61% lower than that obtained for polymer **4b**.

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