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Theoretical and empirical approaches to understanding the effect of phosphonate groups on the thermal degradation for two chemically modified PMMA

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A B S T R A C T

The influence of phosphonated groups on thermal degradation and flammability has been investigated in the case of two chemically modified PMMA. Thermogravimetric analysis as well as pyrolysis combustion flow calorimetry have been used to define the efficiency of phosphorus in both condensed and vapor phases. A theoretical study was also performed to determine the contribution of phosphonated groups to the effective heat of combustion, residue content and heat release capacity. Empirical and theoretical approaches agreed to highlight that PMMA modified with monophosphonated comonomer is more efficient in both condensed and vapor phases in terms of flammability and char formation. These results were attributed to the ability of phosphonate groups to interact with ester groups and also to the weakness of the P–C–N bonds. Moreover, this study proposes a method for designing the chemical environment of phosphonate group in polymers to achieve better flame retardancy.

Keywords:

PMMA

Phosphonated copolymers

Thermal stability

Flammability

1. Introduction

The physical and chemical incorporation of phosphorus flame retardant (PFR) into PMMA in order to improve its flammability have been investigated by several authors [1–3]. These works have highlighted the efficiency of chemical incorporation (i.e. via copolymerization) compared to physical incorporation of PFR in terms of PMMA flammability. Generally, the chemical incorporation (reactive approach, FR covalently attached to polymer chains) of FR has several advantages over the physical approach (additive). First, using the reactive approach avoids the problem of migration or blooming of FRs due to immobility of inherent FRs which stay within the polymer matrix. Secondly, a lower loading percentage of FR is needed

compared to physical approach to obtain the same level of flame retardancy. Furthermore, a homogeneous dispersion of FR is possible at the molecular level using reactive approach [3]. Based on these results, we studied in a previous work the flammability of a PMMA chemically modified by an aminobisphosphonated comonomer [4]. This chemically modified PMMA presented a better thermal stability than that of pure PMMA and led to an important char formation (18%). The results revealed the positive effect of phosphorus both in condensed and vapor phase that is beneficial for improving the thermal stability and flammability properties.

The present study consists of two parts: first in an empirical part, a comparison of a MMA-aminobisphosphonated copolymer (copo.(MMA-MANP2C3)) and a MMA-monophosphonated copolymer (copo.(MMA-MAPC1)), in terms of thermal stability and flammability properties, is reported. This part is mainly focused on determining the

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Nomenclature

X_{char}	char yield (g/g initial polymer)	f_{Pcond}	fraction of phosphorus in the condensed phase (g/g initial phosphorus)
X_{Pini}	initial phosphorus content (g/g initial polymer)	f_{Pvap}	fraction of phosphorus in the condensed phase (g/g initial phosphorus)
X_{Pcond}	phosphorus content in the condensed phase (g/g initial polymer)		
X_{Pvap}	phosphorus content in the vapor phase (g/g initial polymer)		

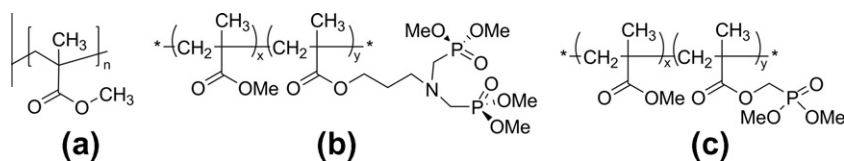
effect of phosphorus groups either in condensed or in vapor phase. The second part focuses on a theoretical study, based on the work of Lyon et al. [5], to determine the relationship between molecular structure and flammability of these copolymers and the efficiency of chemical groups on flame retardancy.

2. Materials and methods

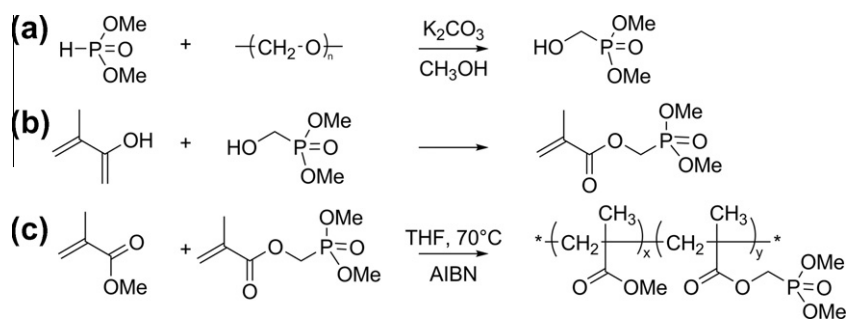
Monophosphonated copolymer (Scheme 1c – named copo.(MMA-MAPC1)) was prepared in three step reactions. First, dimethyl- α -hydroxymethylphosphonate was obtained from the reaction between dimethyl hydrogenophosphonate and paraformaldehyde in the presence of methanol and anhydrous K_2CO_3 (Scheme 2a). In the second step, methacrylation of dimethyl- α -hydroxymethylphosphonate was carried out using methacrylic acid in presence of dicyclohexylcarbodiimide (DCCI) *N,N*-dimethyl-4-aminopyridine (DMAP) (Scheme 2b). The last step consists in radical copolymerization of methylmethacrylate (MMA) and dimethyl(methacryloxy)methyl phosphonate in chloroform at 70 °C in presence of 2,2'-azobisisobutyronitrile (AIBN) (Scheme 2c). PMMA and two copolymers (Scheme 1) were synthesised via radical polymerization method. The synthesis of PMMA and copo.(MMA-MANP2C3) was described in a previous work [4]. The chemical structure of the products was assessed from ^1H , ^{31}P and ^{13}C NMR. In the case of the copolymers, the molar ratio between comonomers was fixed at 1:1. The phosphorus percentages are 12.7 wt.% and 10 wt.% for copo.(MMA-MANP2C3) and copo.(MMA-MAPC1), respectively (calculated from NMR). The obtained phosphorus percentages using EDX analysis (at ambient temperature 13.7 wt.% and 10 wt.% for copo.(MMA-MAPC1) and copo.(MMA-MANP2C3), respectively) are closely similar to those measured from NMR analysis. The synthesis and characterization of samples were reported in details elsewhere [6,7].

Thermal gravimetric analysis (TGA) was carried out on a Perkin Elmer Pyris-1 instrument. The temperature range was from 50 °C to 900 °C at a ramp rate of 10 °C min $^{-1}$ under nitrogen and air atmosphere. Specimen weighed about 8 mg. This TGA instrument was coupled to a Fourier transform infrared spectrometer (FT-IR) (Bruker-IFS66) to analyze the evolved gases. (The heating rate and temperature range are identical to a simple TGA analysis). FT-IR measurements were carried out in the range of 4000–400 cm $^{-1}$, with 8 scans and spectral resolution of 1 cm $^{-1}$. The residues were directly observed using a Scanning Electron Microscopy (FEI Quanta 200 SEM). All images were obtained under high vacuum at a voltage of 15.0 kV with a spot size of 2.8 mm and a working distance of 8.2 mm. Analysis of the phosphorus percentage in char residue was performed by Energy Dispersive X-Ray spectroscopy (EDX) analysis using Oxford INCA Energy 300 system and a detector of 133 eV resolution (at Mn). The residues were collected from isothermal degradation in TGA analysis (under nitrogen) at different temperatures and then ground between two microscope glass slides for being homogeneous and compressed for forming a compact and smooth layer before analysis. Flammability results were obtained from Pyrolysis Combustion Flow Calorimeter (PCFC) instrument (FTT Company) (Specimen size \sim 2–4 mg, heating rate = 1 K s $^{-1}$). The Total Heat Release (THR) and Heat Release Capacity (HRC) values were obtained from this test (HRC is the sum of all peaks of heat release rate after deconvolution carried out with the FTT software).

These characterization methods were used to define thermal stability (TGA), flammability (PCFC) and efficiency of phosphorus in both condensed and vapor phases (EDX, TGA/FT-IR). Some analysis methods were specially used to analyze the condensed phase such as EDX (determining the percentage of phosphorus in residue) or vapor phase such as coupled TGA/FT-IR (determining the nature of evolved gases during the thermal degradation). Furthermore, it seems obvious that the comparison and matching



Scheme 1. Chemical formula of (a) pure PMMA, (b) aminobisphosphonated copolymer (copo.(MMA-MANP2C3)) and (c) monophosphonated copolymer (copo.(MMA-MAPC1)) ($x = y$ stoichiometry determined by NMR ^1H).



Scheme 2. Three-step synthesis of monophosphonated copolymer, copo.(MMA-MAPC1)[6].

of some results in one phase can provide useful information for the other phase (e.g. determining the percentage of phosphorus in condensed phase can provide the percentage of phosphorus in vapor phase).

3. Results and discussion

3.1. Part A: empirical approach

3.1.1. Phosphorus effect in condensed phase (Residue analysis – SEM/EDX)

Fig. 1 shows the TGA curves and corresponding derivate curves (DTG) of PMMA compared to monophosphonated copolymer (copo.(MMA-MAPC1)) and aminobisphosphonated copolymer (copo.(MMA-MANP2C3)) under inert atmosphere. According to other authors [8–11] the different steps of degradation of PMMA correspond to the different types of polymer chains obtained from radical polymerization. The first step of degradation (around 290 °C) takes place by scissions at unsaturated ends (resulting from termination by disproportionation) involving a homolytic β scission to the vinyl group. The second step (around 390 °C) is a random scission within the polymer chain.

In contrast to PMMA and copo.(MMA-MANP2C3), copo.(MMA-MAPC1) shows a different degradation pathway. The first and second stages of degradation of copo.(MMA-MANP2C3) seem identical to PMMA. In the case of copo.(MMA-MAPC1) these stages are shifted to 330 °C and

420 °C. The onset temperature (285 °C, determined at 5 wt.% of weight loss) of copo.(MMA-MAPC1) is higher than that of copo.(MMA-MANP2C3) (238 °C). However, the degradation rate of copo.(MMA-MAPC1) is faster than copo.(MMA-MANP2C3) (between 300 °C and 600 °C). The char yield X_{char} of copo.(MMA-MAPC1) (22 wt.%) is slightly higher than that of copo.(MMA-MANP2C3) (18 wt.%) and a stabilization of mass percentage is observed after 700 °C for copo.(MMA-MAPC1) (Table 1).

The fraction of phosphorus in residues ($X_{\text{Pcond}}/X_{\text{char}}$) was determined using EDX analysis and presented in Fig. 2. Residues enrich in phosphorus as temperature increases. In the case of copo.(MMA-MANP2C3) residue, phosphorus content reaches a maximum around 430 °C.

From these latter results, the estimated thermogravimetric curve of (atomic) phosphorus can be calculated using the previously described method in Ref. [4]. This curve permits to follow the partition of phosphorus between condensed f_{Pcond} and vapor phase f_{Pvap} as a function of temperature. f_{Pcond} is calculated using this formula:

$$f_{\text{Pcond}} = \frac{X_{\text{char}} \frac{X_{\text{Pcond}}}{X_{\text{char}}}}{X_{\text{Pini}}}$$

$$f_{\text{Pvap}} = 1 - f_{\text{Pcond}}$$

where $X_{\text{Pcond}}/X_{\text{char}}$ corresponds to the phosphorus fraction in residues quantitatively measured by EDX, X_{Pini} corresponds to the initial phosphorus content measured by

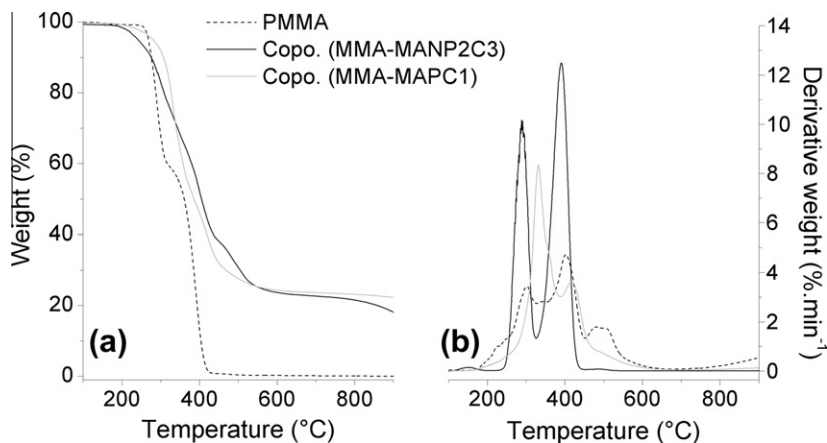


Fig. 1. TGA (a) and DTG (b) curves for pure PMMA, copo.(MMA-MANP2C3) and copo.(MMA-MAPC1) at a heating rate of 10 °C min⁻¹ under nitrogen.

Table 1

TGA parameters of pure PMMA, copo.(MMA-MANP2C3) and copo.(MMA-MAPC1) under nitrogen atmosphere.

Composition	Phosphorus (wt.%) [*]	T _{5%} (°C)	T _{10%} (°C)	T _{50%} (°C)	X _{char} (wt.%) ^{**}
PMMA		270	274	362	0
Copo.(MMA-MANP2C3)	12.7	238	274	407	18
Copo.(MMA-MAPC1)	10	285	311	387	22

^{*} Measured by NMR.

^{**} Char yield at 900 °C.

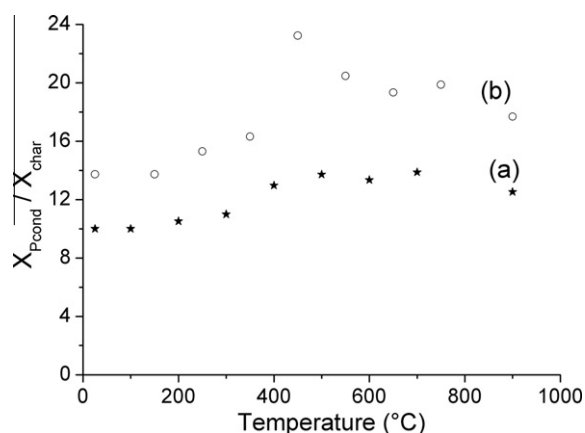


Fig. 2. Phosphorus fraction in residue during TGA test for copo.(MMA-MAPC1) (a) and comparison of this result with that of copo.(MMA-MANP2C3) (b).

EDX (13.7 wt.% and 10 wt.% for copo.(MMA-MANP2C3) and copo.(MMA-MAPC1), respectively).

Fig. 3 shows calculated thermogravimetric curves (a) and their corresponding derivatives (b) for atomic phosphorus, thermogravimetric curves of copolymers have been superposed for comparison.

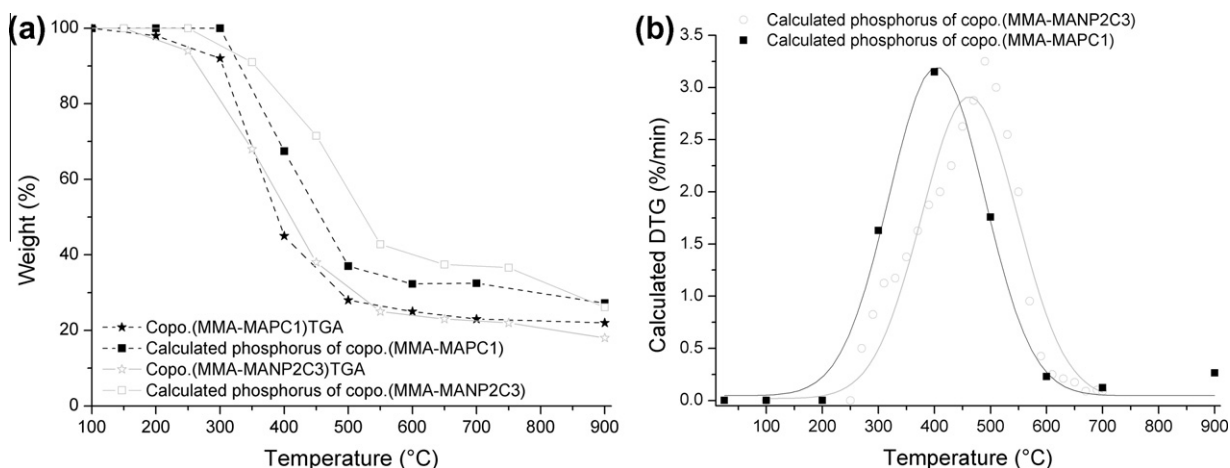


Fig. 3. Comparison of TGA curves and calculated phosphorus percentage curves (a), comparison of derivative curves of phosphorus percentage as a function of temperature for both copolymers (b).

Fig. 3a indicates that the fraction of phosphorus remaining in the residue (f_{pcond}) is higher for copo.(MMA-MANP2C3) than for copo.(MMA-MAPC1), 36% against 31% at 750 °C. Paradoxically, the ability of copo.(MMA-MANP2C3) to promote charring appears lower than that of copo.(MMA-MAPC1), as measured from TGA test and highlighted in Table 1. Therefore, a good indicator of the efficiency to promote charring can be obtained, thanks to normalization, by dividing the percentage of char by the percentage of phosphorus in the condensed phase.

Charring Efficiency of Phosphorous(CEP)

$$= \frac{X_{char}(copo) - X_{char}(PMMA)}{f_{pcond} \times X_{Pini}}$$

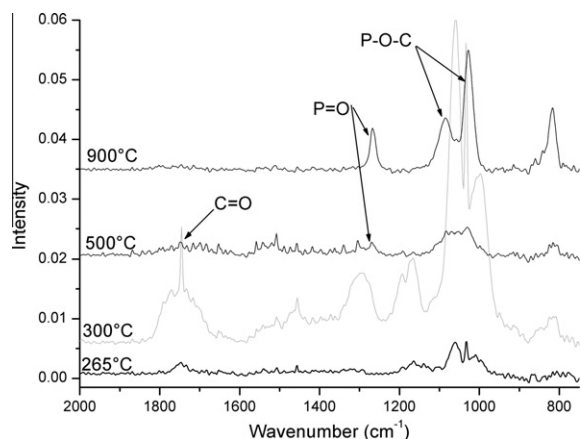
Calculating this ratio leads to 4.46%char/%P and 7.74%char/%P for copo.(MMA-MANP2C3) and copo.(MMA-MAPC1), respectively (Table 2). These results clearly show that phosphonate groups of copo.(MMA-MAPC1) have a higher ability to promote char formation than those of copo.(MMA-MANP2C3).

A possible hypothesis to explain these data could be that the phosphonate groups may interact more easily with ester groups of PMMA, in the case of copo.(MMA-MAPC1). These interactions lead to a thermal stabilization of the copo.(MMA-MAPC1) as proved by the shift of the first peak of degradation (Fig. 1, at 330 °C) and by a higher char residue (Table 1). Conversely, in the case of copo.(MMA-MANP2C3), phosphonate groups may interact preferentially between themselves because of the “claw-like” conformation and there will be less interaction between phosphonate groups and ester groups of PMMA. Thus, the degradation steps are similar to those of PMMA (1st and 2nd steps), except at high temperature (460 °C) where a third step of degradation occurs. Fig. 5b reveals that phosphorus is released in the vapor phase mainly in this range of temperature, contrary to copo.(MMA-MAPC1) where phosphorus is released around 380 °C. Interactions between phosphonate groups in copo.(MMA-MANP2C3) may explain the shift of phosphorus release to higher temperature.

Table 2

Values of charring efficiency of phosphorus (CEP) for the two copolymers.

	Copo.(MMA-MANP2C3)	Copo.(MMA-MAPC1)
CEP	4.46	7.74

**Fig. 4.** Vapor phase FT-IR spectra at various temperatures during the thermal degradation of copo.(MMA-MAPC1).

3.1.2. Phosphorus effect in vapor phase

Similarly to condensed phase, the efficiency of phosphorus in the vapor phase could be assessed. TGA coupled to FT-IR spectroscopy is a very useful tool for probing the thermal degradation of polymers [12]. In this study, it was essentially used to determine the presence of phosphorus in evolved gases and also the temperature of phosphorus release, during the degradation. These results helped us to understand the role of phosphorus during the thermal degradation.

In the above mentioned previous work, the evolved gases of copo.(MMA-MANP2C3) has been studied [4]. Fig. 4 shows the infrared spectrum (taken at 265 °C, 300 °C, 500 °C and 900 °C) of evolved gases from the

degradation of copo.(MMA-MAPC1) in nitrogen. The FT-IR absorption bands between 1030 cm⁻¹ and 1060 cm⁻¹ (at 300 °C) can be attributed to P-O-C vibration. Other identified bands are C=O (1740 cm⁻¹) and P=O (1267 cm⁻¹).

Fig. 5a presents the evolution of P-O-C, P=O and C=O band intensities as a function of the temperature of the released products during the TGA analysis. The maximum values of P-O-C and C=O release are reached around 360 °C. The release of P=O begins around 450 °C and gradually increased until the end of analysis (900 °C). The release of P=O in this range of temperature is probably due to partial degradation of char residue.

The comparison of P-O-C band intensities as a function of temperature (Fig. 5b) showed that phosphorus species are released progressively between 250 and 450 °C in the case of copo.(MMA-MAPC1) whereas they mainly evolved at low temperature (around 250 °C) and at high temperature (around 500 °C) in the case of copo.(MMA-MANP2C3).

The PCFC test is a suitable tool for assessing the flammability of small quantity (1–4 mg) of polymers. The Heat Release Rate (HRR) curves obtained from this test are shown in Fig. 6. Table 4 outlines that the THR and HRC parameters of phosphonated copolymers are largely lower than those of pure PMMA. Comparing copolymers enables to affirm that THR values are very similar. In order to highlight a possible effect of char residue on THR, the Effective Heat of Combustion (EHC) was determined. This parameter can be obtained from:

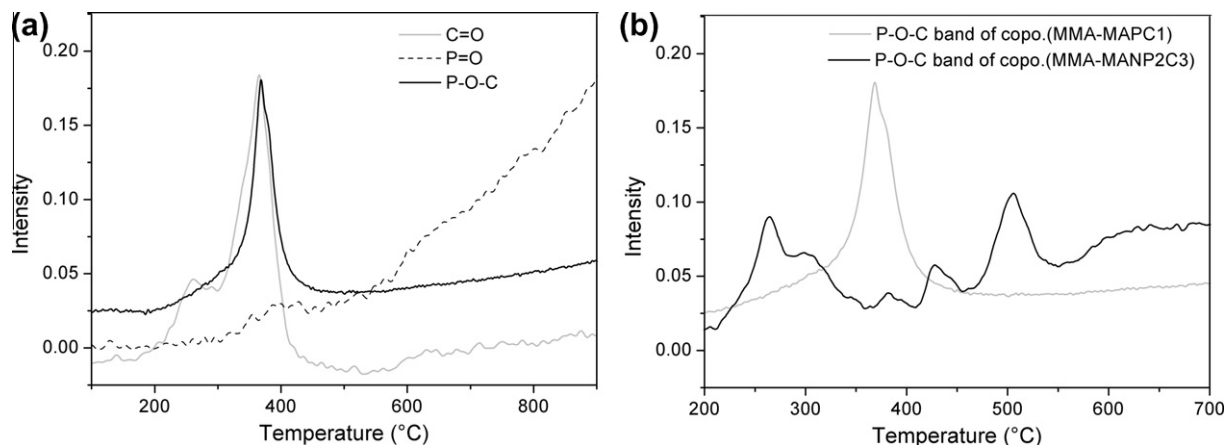
$$EHC = \frac{THR}{(1 - X_{char})}$$

The results indicate that EHC values are also very close for both copolymers.

The efficiency of phosphorus in the vapor phase (EPV) can be defined as the ratio of the decrease of EHC (Table 4) divided by the percentage of phosphorus in the gas phase:

Efficiency of Phosphorus in the Vapor phase (EPV)

$$= \frac{EHC_{PMMA} - EHC_{copo}}{f_{Pvap} \times X_{Pini} \times 100}$$

**Fig. 5.** (a) Gram-Schmidt curves as a function of temperature of copo.(MMA-MAPC1) at: 1026 cm⁻¹ (P-O-C), 1267 cm⁻¹ (P=O) and 1740 cm⁻¹ (C=O), (b) comparison between the P-O-C bands of copo.(MMA-MAPC1) and copo.(MMA-MANP2C3).

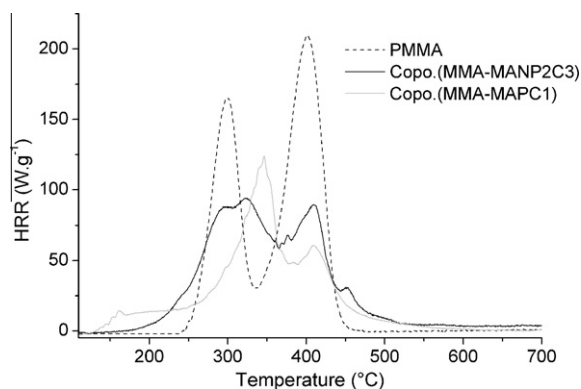


Fig. 6. HRR curves of pure PMMA, copo.(MMA-MANP2C3) and copo.(MMA-MAPC1).

Table 3

Values of efficiency of phosphorus in the vapor phase (EPV) for both copolymers.

	Copo.(MMA-MANP2C3)	Copo.(MMA-MAPC1)
EPV	0.669	0.698

The results give the values of 0.669 and 0.698 $\text{kJg}^{-1}(\%P)^{-1}$ for copo.(MMA-MANP2C3) and copo.(MMA-MAPC1), respectively (Table 3). Thus, on the whole, phosphonate groups of both copolymers seem to have similar efficiency in the vapor phase.

Finally the major difference between copolymers was found in HRC value which is significantly decreased in the case of copo.(MMA-MAPC1) (–15% compared to copo.(MMA-MANP2C3)). The superposition of DTG and HRR curves of copolymers with DTG curve of atomic phosphorus is displayed in Fig. 7a (copo.(MMA-MAPC1)) and Fig. 7b (copo.(MMA-MANP2C3)). In the case of copo.(MMA-MAPC1), the similarity between DTG and HRR curves shows that the energetic value (HRR) of released gases is proportional to the quantity of released gases. It seems that the evolution of phosphorus species does not affect the HRR curve or the energetic value of vapor phase. Moreover, the derivative curve of phosphorus indicates that phosphorus is released all over the degradation process. HRR and DTG curves of copo.(MMA-MANP2C3) exhibits three peaks and peak of phosphorus in derivative curve is located around 500 °C (3rd peak). In this case, the phosphorus release occurs mainly at high temperature contrary to what was observed with copo.(MMA-MAPC1). Furthermore, in this temperature range, the HRR is not proportional to DTG. Thus, the difference in HRC values observed between copolymers (Table 4) may be attributed to the way phosphorus species are released. HRC decrease is more pronounced when phosphorus is released simultaneously with MMA and all over the degradation (case of MAPC1).

Indeed, it has been suggested that the simultaneous presence of nitrogen and phosphorus can lead to a synergistic action on flame retardancy of some polymers. The phosphorus–nitrogen combination has been extensively studied and reviewed in the literature [13,14]. Generally,

Table 4

Pyrolysis combustion flow calorimeter data.

	HRC ($\text{Jg}^{-1}\text{K}^{-1}$)	THR (kJg^{-1})	EHC (kJg^{-1})	X_{char} (wt.%) at 750 °C*
PMMA	460	26	26	0
Copo.(MMA-MANP2C3)	214	15.7	20.1	22
Copo.(MMA-MAPC1)	181	16.1	21.2	24

* Obtained from TGA under N₂.

the positive effect of such combination is observed when nitrogen and phosphorus atoms are chemically bonded. Nevertheless, we expected a similar positive effect from copo.(MMA-MANP2C3) as phosphorus and nitrogen are only separated from a methylene spacer. However, the above observed results prove the weakness of such chemical bond, thus inducing a lower efficiency for copo.(MMA-MANP2C3) both in the condensed and in the vapor phase as compared to copo.(MMA-MAPC1), despite a lower phosphorus content.

In this first part, the flame retardant efficiency of phosphonate groups, in two different chemical environments, was calculated using an experimental approach. In the next part, the efficiency of phosphonate group will be calculated using a theoretical approach. This approach does not consider the interaction between chemical groups. It means that the contribution of phosphonate group to flammability properties should be similar for both copolymers. Therefore, if the contribution of phosphonate group, in both copolymers, is not similar, we could conclude that the chemical environment has an impact on flammability properties. In the future, this approach may be useful for chemists to determine the chemical structure of polymer in order to have the best efficiency of phosphonate groups.

3.2. Part B: theoretical approach

3.2.1. Molecular structure and flammability relationship

The flammability of a polymer is obviously related to its molecular structure. R. Lyon et al. [5,15] have proposed to calculate the HRC (or sumHRC), EHC and residue percentage of some polymers according to Van Krevelen's approach [16]. Authors have determined the contributions to these properties for several chemical groups from eighty four polymers using PCFC test. The flammability properties of each polymer have been calculated using a theoretical method that consists in summing the molar contributions to HRC, EHC or residue percentage for the specific chemical groups of this polymer. The interactions between chemical groups were neglected. They found a quite good correlation between the calculated and measured values, even if great discrepancies were observed in some cases.

According to this method, we attempted to calculate the contributions to HRC, EHC and residue percentage of the phosphonate group studied in our work. The contributions of the phosphonate group were separately calculated for both copolymers (as represented in Scheme 3, the selected phosphonate groups (P_2O_6 and PO_3)). According to the approach of Lyon et al. [5], the contributions of the

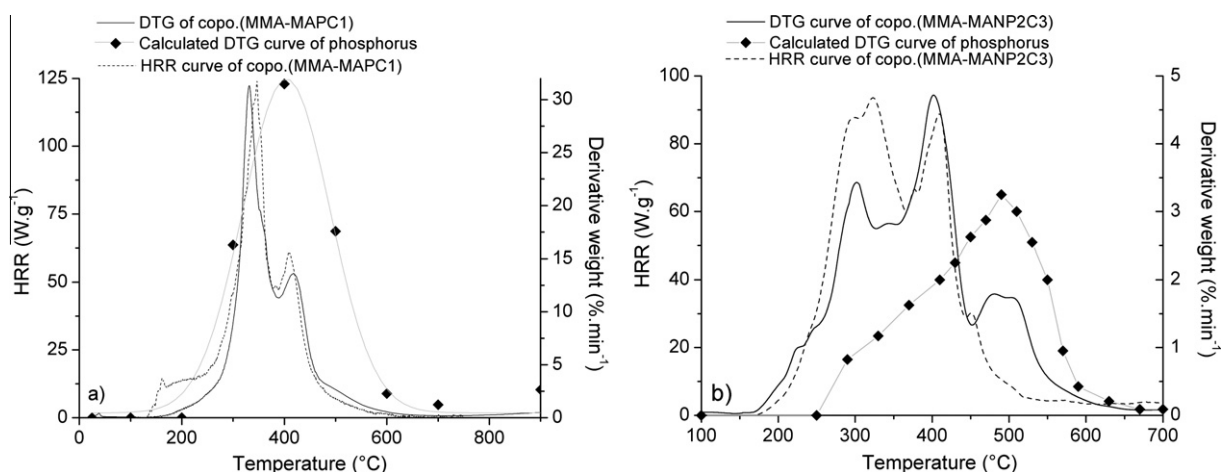
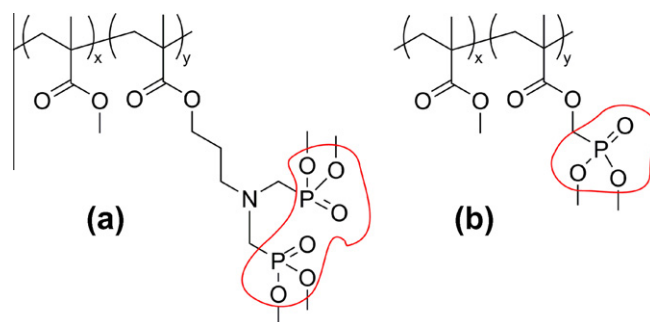


Fig. 7. Superposition of DTG and HRR curves with calculated DTG curve of atomic residue for copo.(MMA-MAPC1) (a) and for copo.(MMA-MANP2C3) (b).



Scheme 3. Studied copolymers containing the phosphonate group, (a) copo.(MMA-MANP2C3) (b) copo.(MMA-MAPC1).

Table 5

Summary of results of PCFC tests and residue percentage at 750 °C in TGA analysis (N2) and EHC (calculated from THR and residue percentage).

Molecule	Molecular weight of repetitive unit (g.mol ⁻¹)	sumHRC (J.g ⁻¹ K ⁻¹)	THR (kJ.g ⁻¹)	Residue at 750 °C (%)	EHC (kJ.g ⁻¹)
A	100	400	24.4	0	24.4
A-1	387	193	14.3	29	20.1
A-2	244*	214	15.7	22	20.1
A-3	180*	220	16.9	19	20.9
A-4	108*	391	22.4	2.2	22.9
B-1	308	217	11.4	30	16.3
B-2	194*	181	16.1	23	20.9

* Equivalent molecular weight calculated according to the fractions of both comonomers.

phosphonate group should be similar for both copolymers. If it is not the case, we could conclude that the contributions to flammability properties of the phosphonate group depend on its chemical environment.

The database proposed by Lyon et al. [15] was used for the contributions of the other groups present in these copolymers (Table S1).

Pure homopolymers and five copolymers with different molar ratios of comonomers were synthesised and investigated (Copolymerization procedure is identical to the one described earlier in Section 2). All studied molecule structures are given in Table S2.

All samples were tested using PCFC apparatus and all data were summarized in Table 5.

The contributions to HRC, EHC and residue content were chosen for the phosphorus-containing groups to fit well the experimental data (Figs. 8–10) – (Details of calculation in Supporting data-S3).

A quite good correlation is obtained between experimental and calculated values, in particular for residue content and EHC properties. Discrepancy is higher for sumHRC. Moreover, for MMA-MAPC1 copolymers, it is obvious that the theoretical curves fit quite well the experimental tendency: for example, sumHRC decreases quickly when comonomer content increases from 0 to 28 wt% and then becomes almost stable (Fig. 10). Calculated contributions to the flammability properties are given for the phosphonate group in both copolymers in Table 6.

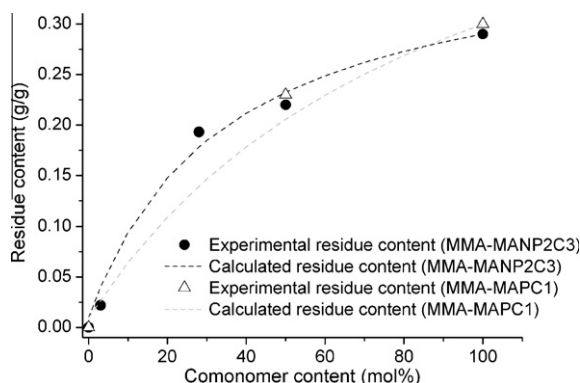


Fig. 8. Residue content versus comonomer content.

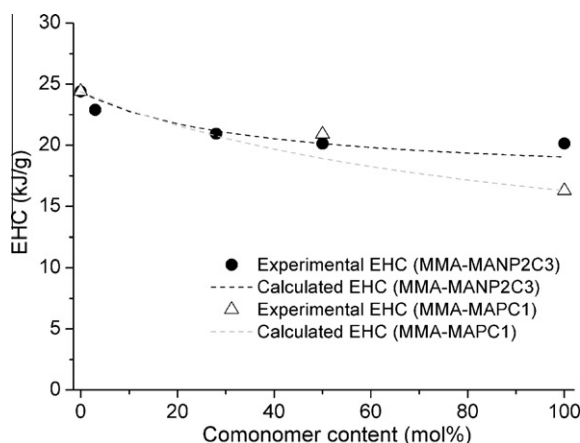


Fig. 9. EHC versus comonomer content.

Negative values are obtained for contributions to sumHRC and EHC. It means that the phosphonate group has an efficient flame retardant effect while negative values are indicative to interactions between this group and some other groups present in the polymer. EHC values for the phosphonate group in MMA-MANP2C3 is positive but lower than the contributions for other chemical groups in the molecular structure (except the ester group, see Table S2). Thus, the phosphonate group contributes to decrease this parameter value (according to the additive law of mixtures). Lastly, the residue content is significant for the phosphonate group, while other groups in the molecular structure contribute only slightly to residue content.

It should be noticed that the contributions to EHC and residue content is slightly better in the case of the copolymer (MMA-MAPC1). According to our theoretical results, we could conclude that the chemical environment of the phosphonate group has only a small influence on its contributions to EHC and residue content. On the contrary, a great difference in the contributions to sumHRC is calculated. The phosphonate group in the copolymer (MMA-MANP2C3) contributes to the decrease of sumHRC in a larger extent than the phosphonate group in the copolymer (MMA-MAPC1). This result indicates that the chemical environment influences strongly the contribution

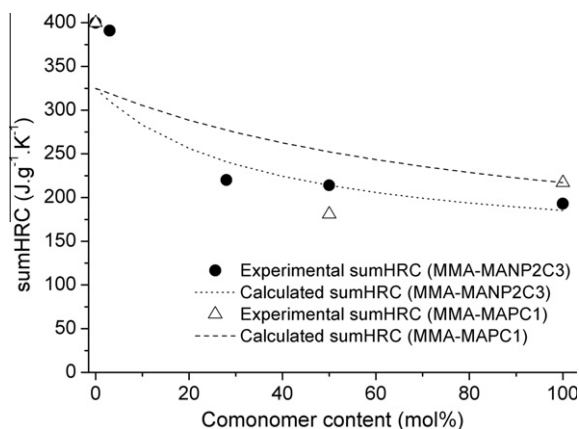


Fig. 10. sumHRC versus comonomer content.

Table 6

Contributions to sumHRC, EHC, residue content for the phosphonate group (in MMA-MAPC1 and MMA-MANP2C3).

Contributions of the phosphonate group to:	MMA-MAPC1	MMA-MANP2C3
sumHRC ($\text{Jg}^{-1}\text{K}^{-1}$)	-258	-549
EHC (kJg^{-1})	-0.75	4.7
Residue content (gg^{-1})	0.78	0.7

to sumHRC of the phosphonate group, contrary to the hypothesis of “non-interacting groups” in the simplified approach proposed by Lyon et al. [5]. Moreover, HRC is directly related to the peak of heat release rate, which is the most important single parameter to assess a fire hazard. Thus choosing the best chemical environment is the first important parameter to optimize the flame retardancy effect of the phosphonate group.

4. Conclusions

Two phosphorus modified PMMA were investigated. Both empirical and theoretical studies revealed the better flame retardancy effect of phosphonate group, in both condensed and vapor phase, in copo.(MMA-MAPC1) compared to that of copo.(MMA-MANP2C3). It seems that the simultaneous presence of phosphorus and nitrogen does not necessarily lead to a synergistic effect and the weakness of P-C-N bond, compared to P-N bond, may explain the absence of synergistic effect. The better efficiency of phosphorus in copo.(MMA-MAPC1) compared to that of copo.(MMA-MANP2C3) can be due to accessibility of phosphonate group to react with ester group of MMA part. It seems that the claw like conformation of copo.(MMA-MANP2C3) may decrease these interactions because phosphonate groups interact preferentially between themselves. The theoretical approach showed that the sumHRC is more influenced by the chemical environment of phosphorus than other parameters (EHC and residue). The interesting properties of copo.(MMA-MAPC1) in term of flammability, as well as the maintaining of transparency, associated to the ease of its synthesis may allow to be commercialized on large scale.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.eurpolymj.2011.12.015](https://doi.org/10.1016/j.eurpolymj.2011.12.015).

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