

Relationships between the molecular structure and the flammability of polymers: Study of phosphonate functions using microscale combustion calorimeter

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ABSTRACT

The present work is based on the Van Krevelen's approach proposed by Lyon et al. [1] to determine the relationships between the molecular structure and the flammability of molecules using Microscale Combustion Calorimeter (MCC). Via this approach, the contributions to Heat Release Capacity (HRC) and Total Heat Release (THR) were successfully calculated for two phosphorus-containing groups: phosphonate and dioxaphosphorinane. We showed that the Van Krevelen's approach was invalid when the molecules contain both phosphorus and ester or acid groups. We hypothesized that these functions interact between them during the thermal decomposition. In this study we propose to calculate "Interaction Indexes" to estimate the level of interactions according to the chemical structure. The results enable to draw first conclusions about the best chemical architecture for lowering flammability.

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1. Introduction

Polymers are more and more used in many applications, replacing other materials as metal, glass, wood... due to their versatile properties. Nevertheless, one of their main drawbacks is their high flammability. Research about the flame retardancy of polymers is then a great concern. One of the most interesting ways for improving the flame retardancy of polymers is to synthesize inherent flame retardant structure. In other words, the flame retardant species may be incorporated into polymers via copolymerization or other type of chemical modification [2].

Nevertheless, it is difficult to know which structure gives the best performance for improving the flame retardancy and a trial-error approach is expensive. Predicting the fire behavior of a molecular structure would be useful to reduce the uncertainty of this method.

Recently, a promising approach was proposed by Lyon et al. [3] based on the use of Microscale Combustion Calorimeter (MCC). This apparatus allows measuring heat release parameters. A very small quantity of sample (1–4 mg) is pyrolyzed under nitrogen flow at a constant heating rate (typically 1 K/s) and the released gases are sent to an oven and burnt in presence of oxygen at 900 °C. These conditions allow complete combustion. The heat release is

calculated according to the Huggett's relation (1 kg of consumed oxygen corresponds to 13.1 MJ of released energy). Total Heat Release (THR) and Heat Release Capacity (HRC) are the main measured thermal properties (Fig. 1) [4]. HRC is equal to the peak heat release rate (pHRR) divided by the heating rate. The char content (%char) was determined by weighting the sample before and after the pyrolysis and the heat of combustion (h_c) was calculated according to the relation $THR = h_c \times (100 - \%char)/100$.

The authors have measured these values for more than one hundred polymers to calculate the contributions of approximately forty common chemical groups. For this they used a multiple linear regression of data according to a Van Krevelen's approach. The thermal combustion property P of a given polymer constituted by i chemical groups called $a, b, \dots, i$ present in the polymer with a fraction $\Phi_a, \Phi_b, \dots, \Phi_i$ and having a contribution to P equal to $P_a, P_b, \dots, P_i$ was calculated as follows:

$$P = \Phi_a \times P_a + \Phi_b \times P_b + \dots + \Phi_i \times P_i \text{ (additive rule of mixtures)}$$

The contributions can be calculated in moles (fractions are given in molar percentage) or alternatively in grams (fractions are given in weight percentage).

Finally, values of HRC, %char and h_c were calculated for the studied polymers from the contributions of their respective groups. These values were compared to the measured ones and a quite good correlation was obtained. These results have justified this approach.

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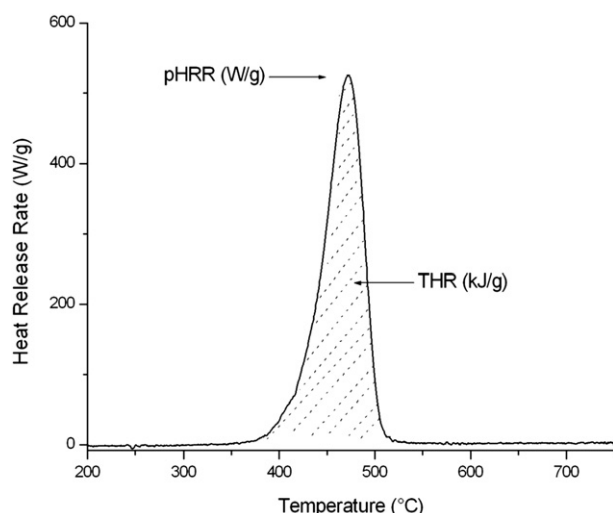


Fig. 1. Typical HRR curve using MCC apparatus (example: Polyamide 6).

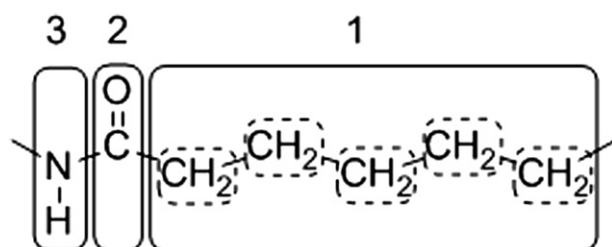


Fig. 2. Chemical structure of polyamide 6.

For example, for polyamide 6 (PA6), which consists of five $-\text{CH}_2-$ groups, one $-\text{C}(\text{O})-$ group and one $-\text{NH}-$ group (Fig. 2), the HRC is calculated as follows:

$$\text{HRC}(\text{PA6}) = \left[5 \times M_{-\text{CH}_2-} \times \text{HRC}_{-\text{CH}_2-} + M_{-\text{C}(\text{O})-} + \text{HRC}_{-\text{C}(\text{O})-} + M_{-\text{NH}-} \times \text{HRC}_{-\text{NH}-} \right] / \left[5 \times M_{-\text{CH}_2-} + M_{-\text{C}(\text{O})-} + M_{-\text{NH}-} \right]$$

$$\text{HRC}(\text{PA6}) = [5 \times 14 \times 1029 + 28 \times -450 + 15 \times 407] / [5 \times 14 + 28 + 15]$$

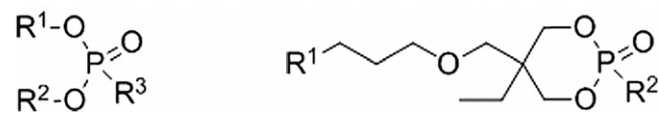


Fig. 3. Chemical structure of studied phosphonate (left) and dioxaphosphorinane (right) groups.

$$\text{HRC}(\text{PA6}) = 580 \text{ J/g K}$$

With $M_{-\text{NH}-}$, $M_{-\text{C}(\text{O})-}$, $M_{-\text{CH}_2-}$ the molar weights and $\text{HRC}_{-\text{NH}-}$, $\text{HRC}_{-\text{C}(\text{O})-}$ and $\text{HRC}_{-\text{CH}_2-}$ the contributions to HRC of $-\text{CH}_2-$, $-\text{C}(\text{O})-$ and $-\text{NH}-$ groups respectively. The calculated value for PA6 (580 J/g K) is in good agreement with the measured one. Three commercial grades have been tested and experimental HRC are 454, 511 and 620 J/g K for Ultramid (BASF), Technyl C206 (Rhodia) and Domamid 24 (Arkema) respectively.

Nevertheless, for some polymers, the calculated values do not match the measured ones, in particular for HRC. One reason is probably that this theory does not take into account the possible interactions between the different groups present in the polymer. In the database developed by Lyon et al., the contributions of some chemical groups are negative. Heat release is calculated from the oxygen depletion method (Huggett's relation) and negative heat release would mean a production of oxygen, which is an inconsistency. The authors do not take into account interactions, but our hypothesis is that negative contributions are due to interactions between different chemical groups in the polymers.

Despite these limitations, this first attempt is a very promising approach for the prediction of molecules flammability from their chemical structure.

MCC could not allow the characterization of the overall fire behavior of a polymer. Indeed, this apparatus is not sensitive to some physical effects, like barrier effect. Moreover, combustion efficiency is equal to 1 (complete combustion) and a flame inhibition by a flame retardant cannot be detected in standard tests (combustion at 900 °C with an excess of oxygen). Consequently, correlations between heat release determined by MCC and by other tests like cone calorimeter are not systematic [5–9]. Nevertheless, MCC is the ideal method to study the influence of chemical phenomena on the condensed phase pyrolysis.

In the present work, we pursued this pioneering study to calculate new chemical structures contributions, especially phosphorus-containing structures. Phosphorus is known to be one of the best elements for flame retardancy properties. Nowadays, we observe a large development of studies about phosphorus molecules in order to replace halogenated compounds due to their toxicity [10]. Phosphorus flame retardants could act in gas and in

Table 1
Contributions of the chemical groups composing the studied molecules (Lyon [1,3]).

Structure	Contribution to HRC (J/g K)	Contribution to THR (kJ/g)	Structure	Contribution to HRC (J/g K)	Contribution to THR (kJ/g)
$-\text{CH}_3$	1233	33.3	$-\text{CF}_3$	-58	-8.3
$-\text{CH}_2-$	1029	36.4	$-\text{CF}_2-$	50	2.9
$-\text{CH}-$	438	51.5	$-\text{CH}_2-\text{O}-$	193	14
$-\text{C}-$	-442	85	$-\text{C}_6\text{H}_5^a$	942	32.5
$-\text{C}(=\text{O})-\text{O}-$	-307	-1.5	$-\text{C}_6\text{H}_4^a$	172	9.2

^a From our polystyrene data.

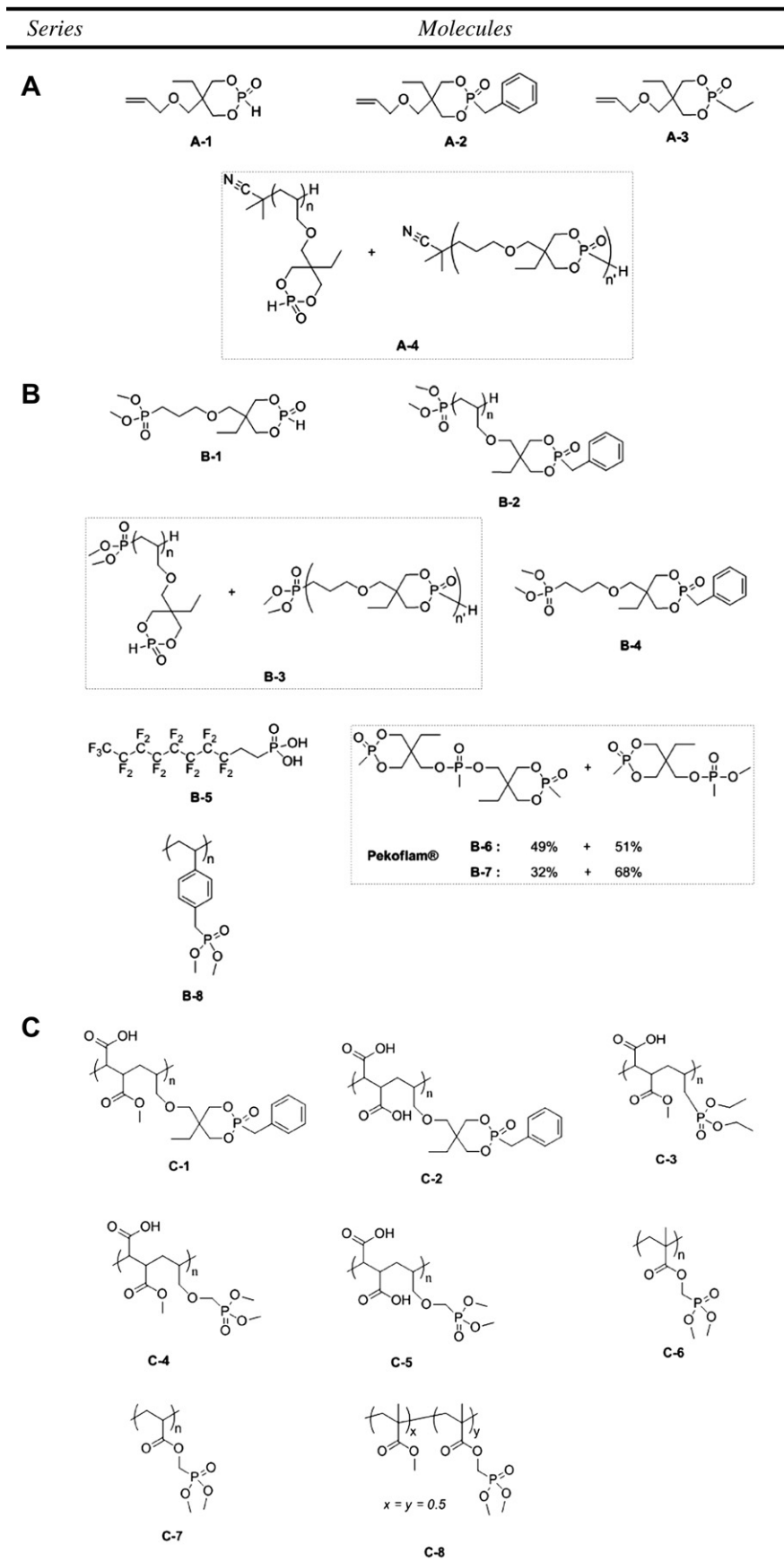


Fig. 4. Chemical structures of all studied molecules. (for C-8, x and y are the molar fractions of both comonomers according to ^1H NMR analysis).

condensed phase. According to Scharrel [10], the efficiency of the phosphorus flame retardant depends on its chemical structure but also on the interaction during pyrolysis with its chemical environment, including the polymeric material. Phosphorus was used under different oxidation degrees in commercial additives: red phosphorus, phosphates (Fyrolflex®, Fyrquel®), phosphonates (Pekoflam®), phosphinates (Exolit®)...

D. Price et al. [11] have compared the efficiency of different phosphorus structures to reduce the flammability of PMMA using two approaches: reactive approach (chemical incorporation of phosphorus groups into PMMA via copolymerization) and additive approach (physical incorporation of phosphorus groups into PMMA as an additive). The authors concluded that the reactive approach with phosphate groups led to the most efficient retardant effect. Hergenrother et al. [12] and Braun et al. [13] have studied the flame retardancy of epoxy resins containing various organophosphorus groups. The effect of the oxidation degree of the phosphorus group was pointed out. The authors showed that char promotion is the main mode-of-action for compounds with high oxidation degree. For compounds with low oxidation degree (phosphine oxide) a strong action in the gas phase was observed. Phosphonate and phosphinate (medium oxidation degree) showed an intermediate behavior. The presence of phosphorus-phenoxy groups [13] and the chemical environment of phosphorus-containing groups [12] were also highlighted. For these studies the authors tested their different formulations using cone calorimeter, limiting oxygen index and thermogravimetric analysis. For these analyses a considerable amount of synthesized materials is needed. This point partly explains that “systematic studies working out the structure–property relationships are still rare” in flame retardancy science [10]. A Van Krevelen's approach as proposed by Lyon et al. to predict the behavior of a chemical structure would be a very useful tool.

In a first time, despite its limitations, we used the database proposed by Lyon et al. [1,3] to calculate the contributions of two new phosphorus groups. In a second time, we proposed to evaluate the interactions rate by comparison between calculated and measured values of THR and HRC. This approach allowed us defining “Interaction Indexes” for THR and for HRC. We think that these indexes could be an interesting tool for the choice of the best polymer structure in the point of view of its flammability. It is a step

forward for tailoring the polymers flammability from their chemical architecture.

2. Experimental part

The two studied phosphorus groups are given in Fig. 3. The exact name of the second one is 5-R²oxy-2-R¹-2-oxido-1,3,2-dioxaphosphorinane but in the whole article, we have abbreviated this name in dioxaphosphorinane. The list of synthesized molecules, oligomers and polymers containing these groups are given in Fig. 4. Molecular weights and polydispersity indexes (PDI) are given in Table 2. Under the free-radical conditions, the homopolymerization or copolymerization of phosphonated monomers occurs in acetonitrile with azobisisobutyronitrile (AIBN) as initiator with a molar ratio concentration of 0.10–0.02 at 70–80 °C. After 24–48 h, these polymers were precipitated into diethyl ether, methanol or water to obtain a gel or a powder and molecular weights were evaluated by means of size exclusion chromatography (SEC). SEC was performed on a Varian apparatus equipped with a RI Shodex refractive index detector. Two PL-gel mix D columns were used at 70 °C with a 0.8 ml min^{−1} flow rate of dimethylformamide (DMF), calibrated using polymethylmethacrylate standards. Only for B-8, we used a Q-50 Varian SEC with two PL-gel mix C columns at 35 °C with a 1 ml min^{−1} flow rate of tetrahydrofuran (THF), calibrated using polystyrene standards. More details about these molecules can be found in previous works of Negrell-Guirao et al. [14–18].

It should be noticed that it was not possible to decompose the dioxaphosphorinane group into more simple groups because the contributions of the heterocycle were not available from the database of Lyon et al.

Two commercially available flame retardants Pekoflam® containing similar phosphonate groups were also studied. The Pekoflam® series is based on a mixture of two molecules (see Fig. 4 B-6 and B-7). The rate of each molecule was determined by ¹H NMR analysis.

First, we used the database proposed by Lyon et al. [1,3] to calculate the specific contributions to THR and HRC of phosphonate groups. The different values used for this calculation are given in Table 1. Some assumptions were considered in our study. The first

Table 2

Molecular weight and main flammability properties of the studied molecules: THR and HRC (measured in MCC), Phosphorus content and residue at 600 °C (measured in thermogravimetric analysis).

Molecule	Molar weight of repetitive unit (g/mol)	Molecular weight (g/mol)	PDI	sumHRC (J/g K)	THR (kJ/g)	Phosphorus content (wt.%)	Residue at 600 °C (wt.%)
A-1	220	—	—	426	20	14.1	6
A-2	310	—	—	460	26.8	10.0	0
A-3	248	—	—	492	22.4	12.5	4
A-4	220	850 and 106,000	1.5 and 3.3	400	19.9	14.1	4
B-1	330	—	—	566	15.1	18.8	18
B-2	606 ^a	—	1.4	564	24.2	13.4	6
B-3	770 ^a	—	1.5	609	18	16.1	15
B-4	420	—	—	612	19	14.8	16
B-5	528	—	—	145	5	5.9	2
B-6	365 ^b	—	—	426	15.9	21.4	7
B-7	348 ^b	—	—	370	16.1	23.3	1.5
B-8	226	1000	1.2	541	18.7	13.7	32
C-1	440	8300	1.8	384	15.7	7.0	19
C-2	426	8300	1.8	221	15.9	7.3	23
C-3	308	1700	2.3	115	8	10.1	25
C-4	310	1800	2.9	52	3.8	10.0	42
C-5	296	1800	2.9	36	3.8	10.5	41
C-6	208	3700	2.3	217	11.4	14.9	23
C-7	194	4900	2.2	276	9.1	16.0	30
C-8	308	6500	1.9	181	16.1	5.0	23

^a Molar weight of complete molecule (and not of repetitive unit) was considered to take into account the presence of one phosphonate group at chain end.

^b Molar weight of repetitive unit is the mean molar weight of the blend of both molecules in Pekoflam®.

one concerns the double bond $\text{CH}_2 = \text{CH}-$ of the dioxaphosphorinane monomers which becomes after polymerization $-\text{CH}_2-\text{C}(\text{R})\text{H}-$. We hypothesized that the contributions of $\text{CH}_2 = \text{CH}-$ does not change after polymerization. The second hypothesis concerns the contribution of the phenyl group $-\text{C}_6\text{H}_5$. Indeed to be more precise the value of its contribution was calculated from polystyrene. We did not use the value obtained by Lyon et al. [3] that we believe underestimated. Finally, we neglected the contribution of the proton of the carboxylic acid group. Indeed, in our study we observed that a carboxylic acid group $-\text{C}(=\text{O})\text{OH}$ and the carboxyl part of an ester group $-\text{C}(=\text{O})\text{O}-$ have the same contributions.

The flammability properties of the studied molecules were determined using a MCC developed by Fire Testing Technology Ltd. Each molecule was analyzed twice. Heating rate was fixed at 1 K/s. Standard conditions (as described in the introduction part) were used to allow complete combustion. In many cases, the decomposition of the sample involved several steps. For this study sumHRC was considered rather than HRC. SumHRC is the sum of every peaks of heat release rate after deconvolution carried out with the FTT software. We have considered the minimum number of peaks which matched well the HRR curve. The residue obtained at 600 °C was measured using thermogravimetric analysis (Perkin–Elmer) under nitrogen flow with a heating rate fixed at 10 K/min. Results are given in Table 2. The studied molecules were divided in three series (A, B or C). Phosphorus content is comprised between 5 and 23 wt.% according to the molecule structure. No correlation between sumHRC (or THR) and Phosphorus content was observed.

Series A gathers the molecules containing only dioxaphosphorinane groups. Series B corresponds to molecules containing phosphonate groups with or without dioxaphosphorinane groups but without carboxylic acid or ester groups. Series C includes copolymers containing phosphonate or dioxaphosphorinane groups with carboxylic acid or ester groups.

3. Results

We would like to point out that studied molecules are monomers, oligomers and copolymers. For this study the hypothesis was done that there is no effect of the size of the molecule toward the measured THR and sumHRC. Walters [19] had already shown that this effect was negligible, at least for THR. Indeed, a very good

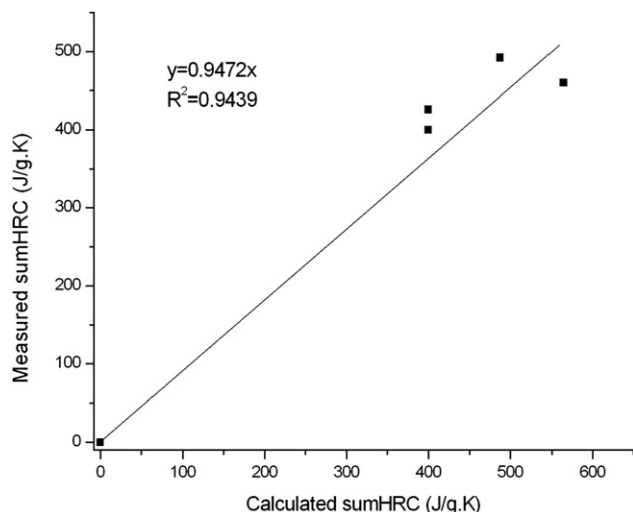


Fig. 5. Measured versus calculated sumHRC for molecules from the series A.

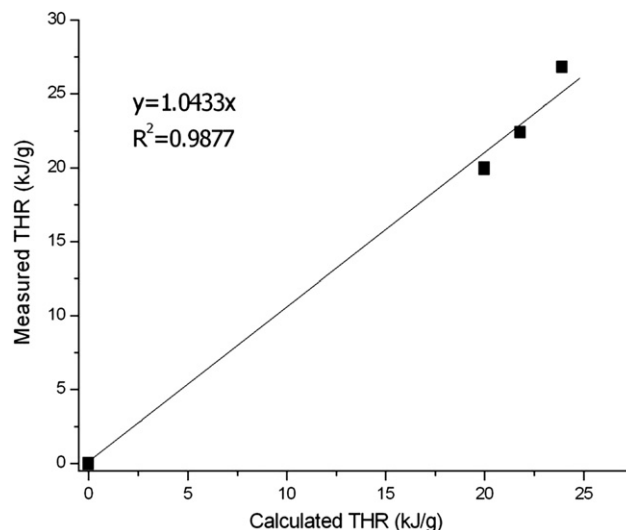


Fig. 6. Measured versus calculated THR for molecules from the series A.

correlation between calculated and measured THR was found for more than one hundred molecules. The authors used the same contributions to THR whatever the size of molecules (small molecules and macromolecules). Our results suggest the same conclusion for THR and for sumHRC. Indeed, the molecule A-4 is a polymer synthesized from the polymerization of the monomer A-1. Both molecules have the same molecular structure but very different molecular weight. Nevertheless, their sumHRC and THR are very close (Table 2).

3.1. Determination of dioxaphosphorinane and phosphonate groups contributions

To determine the contributions to sumHRC and THR of the dioxaphosphorinane group from the series A, the values of this contribution were fitted until a good correlation between the measured and the calculated sumHRC (or THR). The measured versus calculated sumHRC are reported in Fig. 5. For a dioxaphosphorinane contribution to HRC equal to 400 J/g K, the slope and the coefficient of determination R^2 are very close to 1. By the same

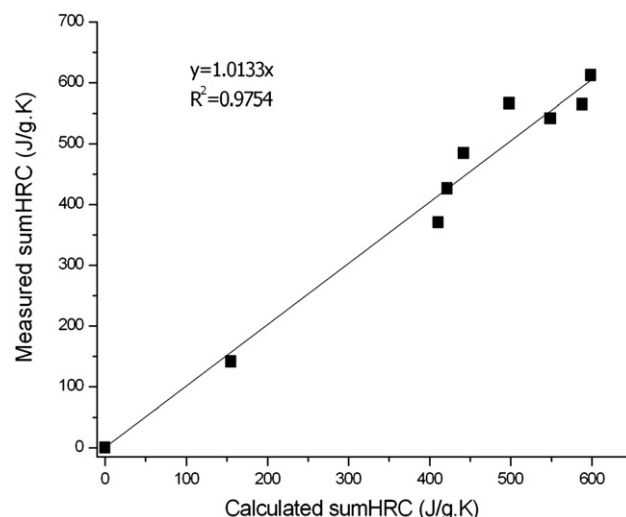


Fig. 7. Measured versus calculated sumHRC for molecules from the series B.

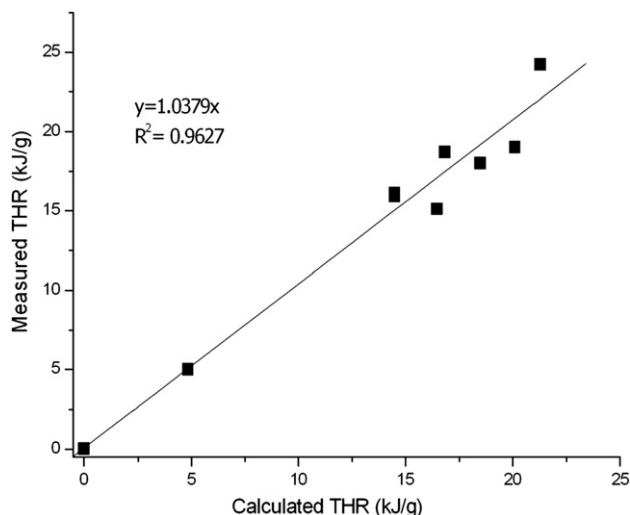


Fig. 8. Measured versus calculated THR for molecules from the series B.

method, the dioxaphosphorinane contribution to THR was calculated equal to 20 kJ/g (Fig. 6).

The same approach was used to calculate the contributions to THR and sumHRC for the phosphonate group from the series B (Figs. 7 and 8). A good correlation was obtained with contributions equal to 500 J/g K for HRC and 0.5 kJ/g for THR.

The values for R^2 are between 0.94 and 0.99, i.e. higher than those obtained by Lyon et al. [1]. We think this is due to the fact that our molecules have similar structures. Moreover, these values show that the linear rule of mixtures is an approximation. We think that probably other parameters affect the thermal behavior like the position of chemical groups in the structure or the possible interactions between these groups.

When we compare the values calculated for the dioxaphosphorinane and the phosphonate groups, the contributions to sumHRC are close while a large difference can be noticed for the THR. Our hypothesis is that the studied dioxaphosphorinane group contains many carbons while the phosphonate group contains only phosphorus and oxygen elements. Therefore the combustion of the dioxaphosphorinane group should release more energy. On the contrary, the contribution to sumHRC of dioxaphosphorinane is lower than for phosphonate group, in spite of the presence of $-\text{CH}_2-$ groups with high contribution (1029 J/g K). Therefore, we could assume that an aliphatic chain that a heterocyclic phosphonate group contributes less to HRR than a phosphonate group.

The contributions to HRC for three other phosphorus-containing groups were measured by Lyon et al. [3] (Fig. 9). Values obtained for these groups are very different. Nevertheless, the comparison cannot be done with our results obtained from another method of calculation. In the following part, we showed that the contributions of the phosphorus groups change with the presence of carboxylic acid or ester groups. The values extracted from Lyon's database for

phosphorus groups are average values calculated from different polymers. The exact structure of these polymers and the chemical environment of the phosphorus groups have not been specified. The calculation of these contributions did not take into account possible interactions.

3.2. Evidence of some interactions

Figs. 10 and 11 represent the measured versus calculated sumHRC and THR for the molecules from the series C. The calculation is based on contributions previously calculated for the phosphonate and dioxaphosphorinane groups. Values obtained for series A and B are also represented for comparison.

When contributions obtained from the series A and B are used for the calculation, the correlation between the calculated and the measured sumHRC and THR is very poor for most of the molecules from the series C. A systematic negative deviation could be observed: the measured sumHRC and THR are significantly lower than the calculated ones.

To explain the poor observed correlation for the series C, we first assumed that the theoretical contributions of carboxylic acid and ester groups obtained from the database of Lyon et al. [1,3] are too far from the experimental ones. We attempted to calculate new values for these groups according to the same approach as previously, considering our values of contributions for the dioxaphosphorinane and the phosphonate groups. However no correlation has been obtained satisfactorily.

The second hypothesis was that the contributions of the dioxaphosphorinane and the phosphonate groups are modified in presence of carboxylic acid or ester groups. We suggest that these modifications are due to interactions between these groups. So, no new values for these contributions could be calculated with a high correlation coefficient because these interactions between phosphonate or dioxaphosphorinane groups and carboxylic acid or ester groups could change for each molecule. Indeed, we think that these interactions could be influenced by different parameters: the position of each group in the structure and the ratio between the interacting groups. However, we can note for the series C that the interactions are always beneficial. For all the molecules, the measured sumHRC (or THR) is lower than the theoretical sumHRC (or THR), which means that the measured flammability is lower than the calculated one.

These interactions should correspond to a change of degradation for the phosphorus groups in presence of carboxylic acid or esters groups. The reality of this second hypothesis would not be surprising. Indeed, it is well-known that phosphonate and more generally phosphorus compounds are good flame retardants for polymers containing ester groups. For example, Pekoflam® is a commercial product used for polyester textile. According to the Table 2, the residue content at 600 °C is significantly higher for the series C than for the series A and B. The molecule B-8 is an exception with high char content due to the presence of para-substituted phenyl ring. Lyon et al. [1] have calculated intrinsic

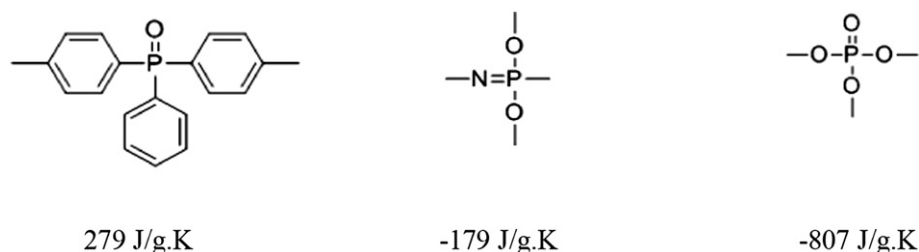


Fig. 9. Chemical structures of three phosphorus groups and their contributions to HRC calculated by Walters and Lyon [1].

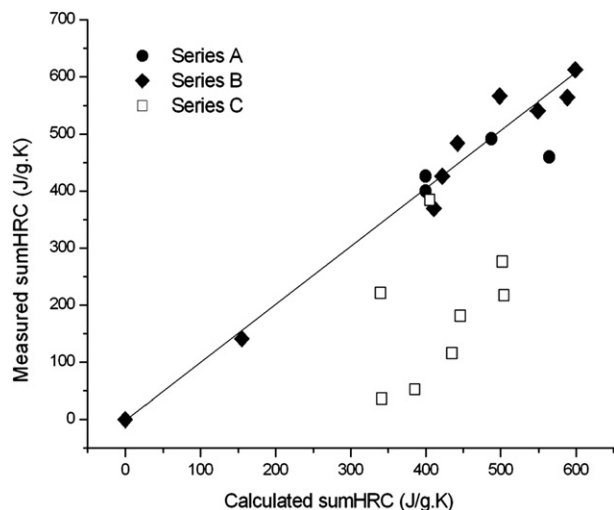


Fig. 10. Measured versus calculated sumHRC for molecules from the series C.

high char content for this chemical group. Our results suggest that interactions between phosphonate and carboxylic acid or ester groups promote the charring. A more detailed study based on the evolved gas and residue analysis would be interesting to define the degradation mechanisms for each molecule.

3.3. Quantifying the interactions

In this section we attempt a first approach to quantify the interaction level for molecules from the series C. Such quantification could be used as a tool of prediction of molecules flammability from their structures. In a first time, we calculated the “real” contributions to sumHRC and THR of the phosphorus groups for the series C. These real contributions correspond to values used to calculate theoretical sumHRC and THR to have a good correlation with measured ones. We also calculated the “theoretical” sumHRC and THR using the contributions of phosphorus groups calculated in the first part of this study. In a second time, for each molecule, the difference between the “real” contribution and the “theoretical” contribution was determined. We consider this difference as a quantitative index of the interactions. We call these indexes for

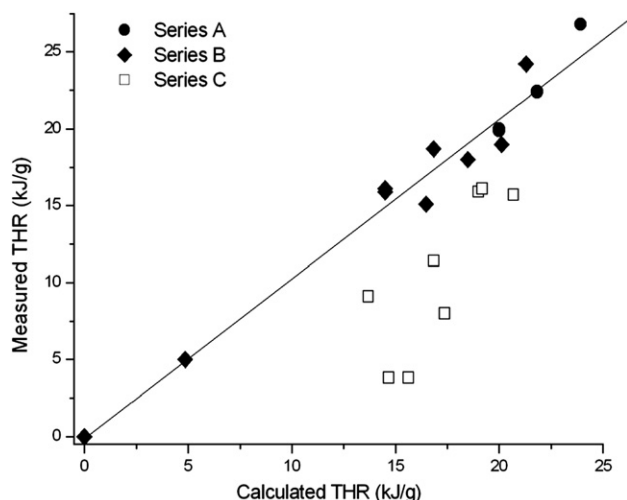


Fig. 11. Measured versus calculated THR for molecules from the series C.

sumHRC and THR “sumHRC Interaction Index” and “THR Interaction Index” respectively.

For example, the molecule C-5 contains a phosphonate group and the two carboxylic acid groups and its “theoretical” contributions to sumHRC and THR are:

$$\text{Theoretical contribution to sumHRC} = (44 \times 2 \times -307 + 79 \times 500) / (79 + 44 \times 2) = 75 \text{ J/g K.}$$

$$\text{Theoretical contribution to THR} = (44 \times 2 \times -1.5 + 79 \times 0.5) / (79 + 44 \times 2) = -0.6 \text{ kJ/g.}$$

To match with the measured values of C-5, the “real” contributions to sumHRC and THR are:

$$\text{Real contribution to sumHRC} = -467 \text{ J/g K}$$

$$\text{Real contribution to THR} = -19.9 \text{ kJ/g.}$$

From these values the interaction indexes can be calculated:

$$\text{sumHRC Interaction Index} = 75 - (-467) = 542 \text{ J/g K}$$

$$\text{THR Interaction Index} = -0.6 - (-19.9) = 19.3 \text{ kJ/g}$$

Table 3 reports the Interaction Indexes for the molecules of the series C. Each molecule is defined according to the proportion of the different groups: dioxaphosphorinane, phosphonate and carboxylic acid or ester. For example, a molecule designed by W/X/Y contains W dioxaphosphorinane groups, X phosphonate groups and Y carboxylic acid or ester groups.

Note that a positive Interaction Index corresponds to a better fire behavior. In this study only positive indexes were observed but we think that negative indexes are theoretically possible.

The Interaction Indexes obtained have been normalized according to the weight ratio of the interacting groups in the molecule. We believe that such defined Interaction Indexes allow a valuable comparison between the different chemical structures.

4. Discussion

Interactions between chemical groups are dependent on various parameters. For these groups, we think that their nature, their weight fraction in the molecule, the ratio between them and their position in the structure affect the flammability behavior. The study of the influence of each parameter requires a large number of molecules. In this section we tried to start to evaluate the influence of some of these parameters. Figs. 12 and 13 represent the sumHRC and the THR Interaction Indexes versus weight ratio of the interacting groups.

First of all, we could notice that molecules with the same W/X/Y type have similar Interaction Indexes. Only the molecule C-8 is an

Table 3
SumHRC and THR Interaction Indexes for molecules from the series C.

Molecule	Type of molecules	sumHRC Interaction Index (J/g K)	THR Interaction Index (kJ/g)	Weight ratio of interacting groups
C-1	1/0/2	31	7.1	0.7
C-2	1/0/2	165	4.3	0.72
C-3	0/1/2	591	17.3	0.54
C-4	0/1/2	620	22	0.54
C-5	0/1/2	542	19.3	0.56
C-6	0/1/1	487	9.2	0.59
C-7	0/1/1	357	7.2	0.63
C-8	0/1/2	490	5.7	0.54
C-8	0/1/1	665	7.8	0.4

exception. This first result seems to validate our hypothesis i.e. a direct relationship between the ratio and the nature of the interacting groups and the total interaction level.

4.1. Influence of the nature of the phosphorus group

The comparison between C-3, C-4, C-5, C-8 in one hand and C-1 and C-2 in another hand showed much stronger interactions with carboxylic acid or ester groups for phosphonate than for dioxaphosphorinane. The sumHRC Interaction Index is 490–620 J/g K for the phosphonate group and only 31–165 J/g K for the dioxaphosphorinane group. The THR Interaction Index showed the same results: 17.3–22 kJ/g for C-3, C-4 and C-5 versus 4.3–7.1 kJ/g for C-1 and C-2. The molecule C-8 is an exception (which will be discussed later).

We assumed previously that in absence of interactions a dioxaphosphorinane group contributes to sumHRC less than a phosphonate group (400 J/g K versus 500 J/g K). The present results also show a more beneficial effect for phosphonate group than for dioxaphosphorinane group in presence of interactions with carboxylic acid or ester groups. Dioxaphosphorinane interacts with carboxylic acid or ester groups to a lesser extent than phosphonate group. One explanation could be that the cyclic structure of dioxaphosphorinane does not allow interaction with a close carboxylic acid or ester group.

4.2. Influence of the position of the interacting groups

The polymers C-3, C-4 and C-5 have two carboxylic acid or ester groups for one phosphonate group in their structural unit. The polymer C-8 contains one ester group directly attached to the phosphonate group. But C-8 is a random copolymer (see Fig. 4) and the proximity with the ester of a methylmethacrylate unit is not known. Thus for us, the structure type for C-8 is not 0/1/2 but probably 0/1/1, as for C-6 and C-7. The consideration of C-8 as a 0/1/1 molecule prompted us to recalculate the Interaction Indexes: only one ester group interacts with one phosphonate group (Table 3 and Figs. 11 and 12). The sumHRC Interaction Indexes of C-6, C-7 and C-8 (considered as 0/1/1) are 487, 357 and 665 J/g K and the THR Interaction Indexes are 9.2, 7.2, 7.8 kJ/g respectively. The THR Interaction Index of C-8 is especially much lower than the THR Interaction Indexes of C-3, C-4 and C-5 (type of the molecule 0/1/2). The value for C-8 corresponds better to C-6 and C-7 values.

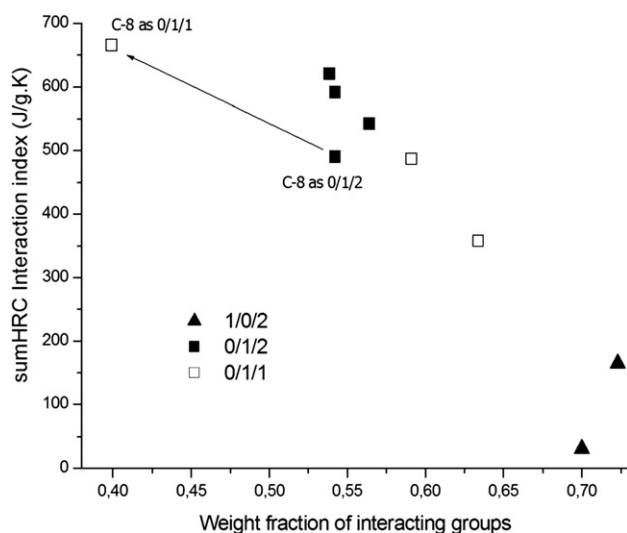


Fig. 12. SumHRC Interaction Index versus weight ratio of interacting groups.

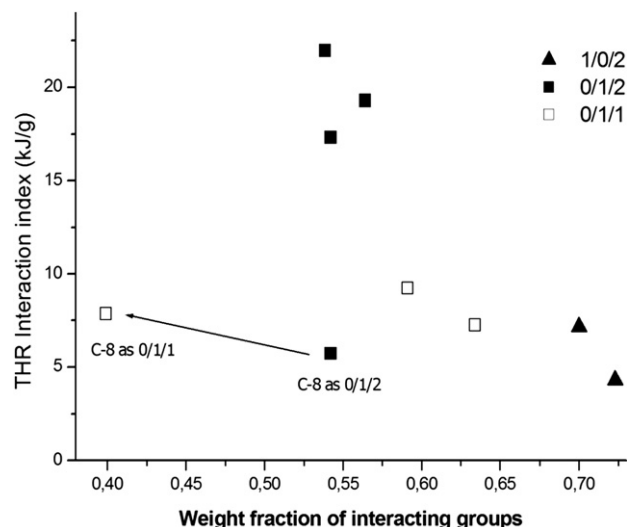


Fig. 13. THR Interaction Index versus weight ratio of interacting groups.

Nevertheless, to validate this hypothesis the structure of C-8 and its degradation mechanism need to be accurately determined.

4.3. Influence of carboxylic acid (or ester)/phosphonate ratio

The highest interactions were observed when two carboxylic acid or ester groups are associated with one phosphonate group. The comparison between C-3, C-4 and C-5 in one hand and C-6 and C-7 in another hand shows that one carboxylic acid or ester group for one phosphonate group gives poorer results. The weight fraction of interacting groups is approximately the same for all these molecules (slightly higher for C-6 and C-7). So, the comparison between these different structures is possible.

Nevertheless, the ester group is directly linked to the phosphonate group for C-6 and C-7. On the contrary, for C-3, C-4 and C-5, the phosphonate group and the carboxylic acid or ester groups are carried by two different monomer units. This difference of structure could also explain the difference between Interaction Indexes.

According to these conclusions, it is possible to propose the C3-type structure as the best structure in terms of flammability. Such structure is characterized by the presence in ratio 1 to 2 of phosphate and ester or carboxylic acid groups in close (but different) pendant chains. We believe that these first conclusions need to be verified by more experimental work. Moreover, the calculated values depend strongly on the previous results obtained by Lyon and coworkers. In this article, our first objective is to expose a new method of quantitative estimation of interactions between chemical groups. New results, especially about the interactions between nitrogen, phosphonate and carboxylic acid or ester groups are in progress.

5. Conclusion

In this work, we have calculated the contributions to flammability properties of two new groups: dioxaphosphorinane and phosphonate groups according to the Van Krevelen's approach. Our results led us to consider interactions between these groups and carboxylic acid or ester groups present in the same molecules. A new method to estimate quantitatively these interactions was proposed. The first conclusions were drawn concerning the flammability decrease by combining phosphonate and carboxylic acid or ester groups. Our first conclusions about the studied structures are:

- Carboxylic acid or ester groups interact more with a phosphonate group than with a dioxaphosphorinane group.
- Interactions between these groups promote the char formation
- A ratio [ester (or carboxylic acid)/phosphonate] equal to 2 gives better results than a ratio equal to 1, especially for lowering THR.

We hope that this method could help polymer researchers to predict the best structures to synthesize in order to obtain low flammable materials. Among the studied molecules in our study, C3-type molecules seem very good flame retardant structures. However, further study is needed to understand the precise degradation mechanism of these molecules in order to identify the reasons for which such structure is especially promising.

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