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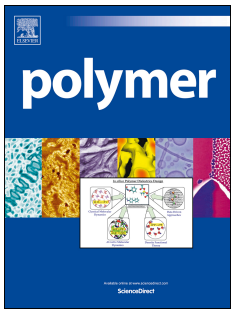

Predicting the flammability of polymers from their chemical structure: An improved model based on group contributions

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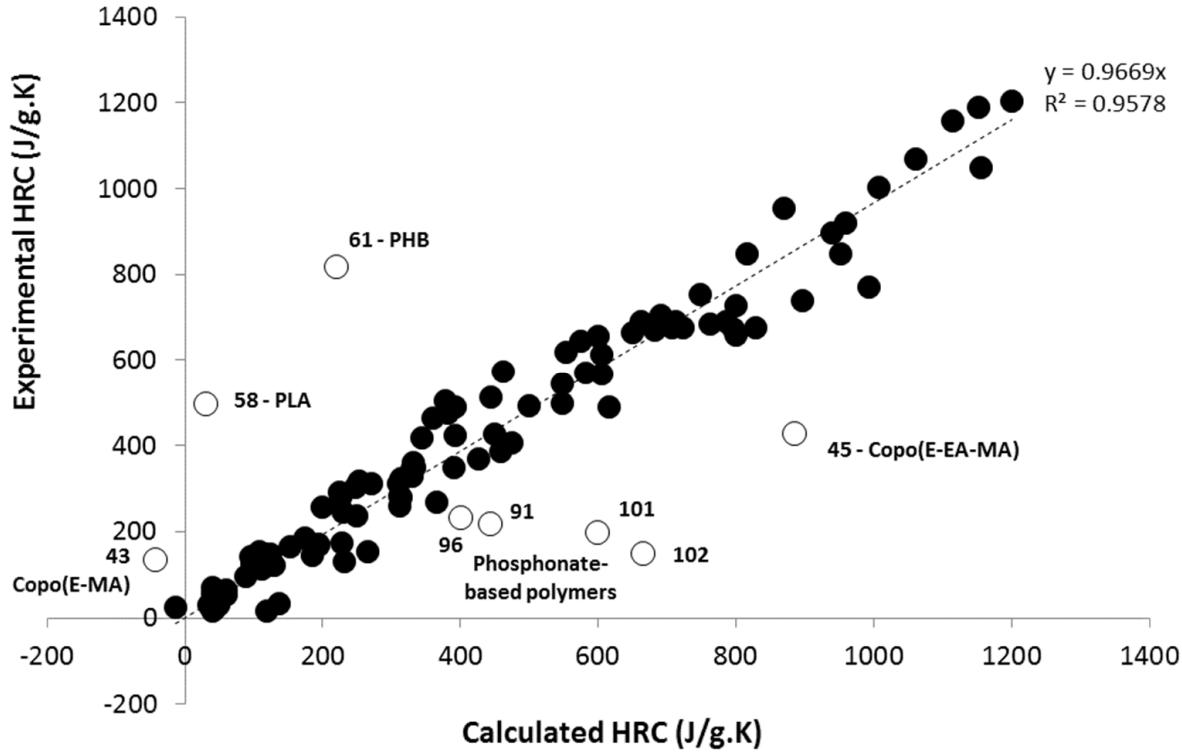

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Predicting the flammability of polymers from their chemical structure: An improved model based on group contributions

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[2] Institut Charles Gerhardt, Montpellier, UMR CNRS 5253, Equipe Ingénierie et Architectures Macromoléculaires, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'école normale, 34296 Montpellier Cedex 5, France

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Keywords: Polymer flammability, PCFC, Van Krevelen approach

Abstract

A new method is proposed to calculate the flammability of polymers from their chemical structure using a Van Krevelen approach. The model is inspired from a pioneering work of Lyon which assigns one flammability contribution to each chemical group. The flammability property of the whole polymer is the sum of the contributions of chemical groups constituting the polymer. Two intrinsic properties (namely heat release capacity and total heat release) measured using pyrolysis-combustion flow calorimeter are correctly predicted for almost one hundred polymers containing contributions of only 31 chemical groups. The contributions of these groups are compared and the consistency of these values is discussed. Finally some exceptions, such as, phosphorus-containing polymers, are noted.

Introduction

Improving the flame retardancy of polymeric materials can be achieved by incorporating flame retardant additives into the matrix. Another way is to synthesize inherently flame retardant polymers. This approach is assessed to be expensive because the flame retardancy of the polymer can be measured only after it has been synthesized. Of course some specific chemical functions are well known to impart flame retardancy, such as phosphorus-based moieties but generally a long trial and error approach is needed to reach a suitable flame retarded macromolecular structure.

It would be highly desirable to have a method allowing an accurate assessment of the flammability of a polymer structure before it is synthesized. The need for such method will increase because many biosourced compounds are being considered as new building blocks for innovative polymers [1-4].

One simple method proposed initially by Van Krevelen to predict many properties of materials is the additivity of groups [5]. Briefly, a polymer is divided in simple groups having specific contributions to the properties being studied. The overall property of the polymer is the sum of these contributions multiplied by the molar or weight fraction of the corresponding groups. Such an approach has been proposed for the calculation of some flammability properties of polymers as measured in PCFC [6].

The analysis is carried out under standard conditions, i.e. an anaerobic pyrolysis followed by a complete combustion of pyrolytic gases [6-7]. These properties are heat release capacity (HRC), char content and effective heat of combustion (EHC).

It is now well-known that PCFC is not suitable for assessment of the overall reaction-to-fire of a polymer. Some effects are not taken into account such as flame inhibition or a barrier effect [8]. Nevertheless, this method allows a first assessment of the fire performances and some approaches attempting to correlate statistically these performances to the rating in various other tests such as UL94 or some flame propagation tests [9-10] have been reported.

Using the Van Krevelen method, a first database of the contributions of 38 groups has been proposed [6]. These contributions were calculated from an evaluation of flammability behavior of a set of 84 polymers. Pursuing this approach we attempted to calculate the contributions of two new groups: phosphonate and dioxaphosphorinane [11]. We showed that the Van Krevelen approach fails when these groups are present together with other groups such as carboxyls. In such molecules, phosphonate and carboxyl groups interact leading to experimental HRC values lower than calculated. Another attempt to predict the contributions of phosphonate group has been proposed [12].

However, it appears that the Lyon approach has not been widely used. One reason may be that the method used to calculate the contributions does not account for interactions which take place in some cases. Indeed for some polymers the additivity of group contributions is not suitable due to interactions between different groups of the structure. Such cases may result in inappropriate contributions. Moreover, the initial list of 38 groups contains those that were available rather than those expected to provide consistent results in contribution.

We propose an improved model based on the additivity of the contributions. The contributions of 31 groups have been determined from the flammability of a set of more than one hundred polymers. Moreover, the methodology used to build the model is presented and the consistency of results obtained illustrated. A few groups that do not yield consistent results are identified.

Methodology

Measurements of THR and HRC

Equations 1 and 2 explain how the total heat release (THR) and heat release capacity (HRC) of a polymer can be calculated from its structure.

$$THR = \sum_i w_i \times THR_i \quad \text{(equation 1)}$$

$$HRC = \sum_i w_i \times HRC_i \quad \text{(equation 2)}$$

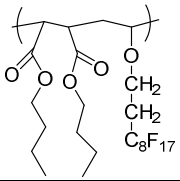
where THR_i and HRC_i reflect the contributions of the group i to THR and HRC respectively, and w_i the weight fraction of the group i in the polymer.

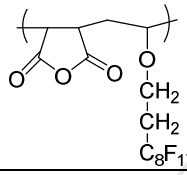
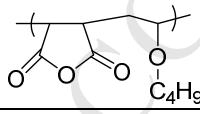
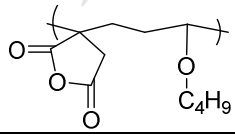
The flammability of polymers (Table 1) was analyzed using PCFC (from FTT) under standard conditions, i.e. anaerobic pyrolysis from 25 to 750°C at 1 °C/s in nitrogen and complete combustion in an excess of oxygen at 900 °C [13].

The THR corresponds to the area under the heat release peak. The HRC generally corresponds to the peak of heat release rate (pHRR) divided by the heating rate. However, in some cases, several peaks can be observed. In such a case, sumHRC may be considered. SumHRC is the sum of the HRR peaks after deconvolution carried out using the FTT software. In some cases, the deconvolution is easy because the different peaks do not overlap. In other cases, several peaks overlap. When several peaks overlap, sumHRC was determined as previously described by summing the minimum number of Gaussian, Lorentzian, asymmetric Gaussian or Lorentzian, or asymmetric Gaussian–Lorentzian hybrid peaks needed to fit the HRR curve with an accuracy of at least 95% [6]. Obviously the choice of the number of peaks influences the sumHRC.

The flammability of 107 polymers was assessed. They can be divided in three groups: commercial polymers tested in our lab, lab-made polymers also tested in our lab, and finally commercial or lab-made polymers analyzed by others [7, 14-16]. Obviously in the latter case, we are not sure that the deconvolution method used to measure sumHRC is the same as ours.

Table 1 – Polymers studied with their experimental and calculated THR and HRC

N°	Polymer	Remark	Experimental value		Calculated value[1]	
			THR (kJ/g)	HRC (J/g.K)	THR (kJ/g)	HRC (J/g.K)
1	Polyisoprene (IR)	Commercial	40.2	753	39.0	749
2	Low density and High density polyethylene (PE)	Commercial	41.3	1205	41.0	1200
3	Ethylene-octene copolymer (38.6wt% octene)	Commercial	41.8	1190	41.0	1152
4	Ethylene-octene copolymer (26.4w% octene)	Commercial	40.5	1048	41.0	1155
5	Polypropylene (PP)	Commercial	39.6	954	40.9	869
6	Polyisobutylene	Commercial	44.4	1002	40.8	1007
7	Polybutadiene	Commercial	38.7	643.5	38.6	574
8	Polymethylstyrene	Commercial	35.8	740	37.4	897
9	Polymethoxystyrene	Commercial	28.6	705	30.9	691
10	Polystyrene (PS)	Commercial	35.6	849	35.9	815
11	Styrene-butadiene rubber (25wt% styrene)	Commercial	37.1	489	37.9	616
12	Poly(methylmethacrylate)	Commercial	22.42	419	21.1	344
13	Polyacrylic acid	Commercial	12.5	165	13.2	153
14	Polymethacrylic acid	Commercial	18.4	464	17.7	359
15	Polyethylmethacrylate	Commercial	26.6	425	23.5	449
16	Polyethylacrylate	Commercial	22.6	323	21.2	313
17	Ethylene-butylacrylate copolymer (30wt% butylacrylate)	Commercial	36.4	770.5	36.3	992
18	Ethylene-methylacrylate (24wt% methylacrylate)	Commercial	36.3	848	35.5	952
19	Poly(dibutyl maleate - *alt*-1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-(vinyloxy)decane) 	Our lab	13.2	291	12.3	224
20	Polyvinylacetate	Commercial	19.2	313	17.9	271

21	Ethylene-vinylacetate copolymer (9.3wt% vinylacetate)	Commercial	40.2	1157	38.9	1114
22	Ethylene-vinylacetate copolymer (15wt% vinylacetate)	Commercial	39	1069	37.5	1061
23	Ethylene-vinylacetate copolymer (26wt% vinylacetate)	Commercial	36.8	920	35.0	958
24	Ethylene-vinylacetate copolymer (28wt% vinylacetate)	Commercial	36	897	34.5	940
25	Polyamide 6	Commercial	27.6	544	26.3	548
26	Polyamide 6-10	Commercial	29.3	671	29.4	682
27	Polyamide 6-12	Commercial	30.3	677	30.3	724
28	Polyamide 10-10	Commercial	31.2	686	31.1	763
29	Polyamide 10-12	Commercial	32	672	31.9	796
30	Polyamide 6-6	Commercial	27.4	498	26.3	548
31	Polyamide 11	Commercial	32.7	727	32.1	801
32	Polyamide 12	Commercial	32.3	676	32.7	829
33	Polyamide 4-6	Commercial	25.3	572	24.5	462
34	Polyamide: [(4,4'-(butane-1,4-diylbis(oxy))dianiline)- *alt* -(nonanedioic acid)]	[15]	18.4	348	22.4	391
35	Styrene-maleic anhydride copolymer (9wt% maleic anhydride)	Commercial	34.4	675	33.0	706
36	Styrene-maleic anhydride copolymer (26wt% maleic anhydride)	Commercial	28.4	493	27.4	499
37	Styrene-maleic anhydride copolymer (40wt% maleic anhydride)	Commercial	22.1	330	22.8	329
38	Poly(furan-2,5-dione - *alt* - 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-(vinyloxy)decane) 	Our lab	4.3	65	6.4	44
39	Poly(furan-2,5-dione - *alt* - 1-(vinyloxy)butane) 	Our lab	14	171	17.5	194
40	Poly(3-methylenedihydrofuran-2,5-dione - *alt* - 1-(vinyloxy)butane) 	Our lab	14.1	186	19.0	260
41	Poly(3-methylenedihydrofuran-2,5-dione - *alt* - 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-(vinyloxy)decane)	Our lab	6.3	56	5.3	15

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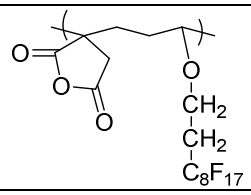
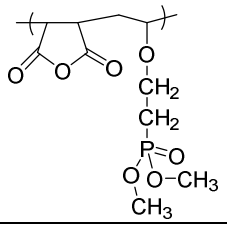
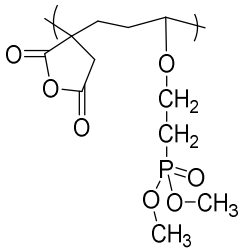
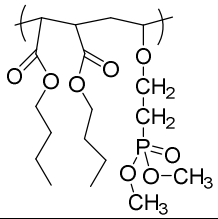
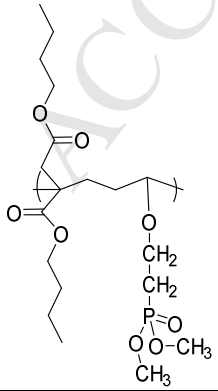
						
42	Polystyrene maleic anhydride	Commercial	23.3	279	20.0	226
43	Polyethylene maleic anhydride	Commercial	12.1	138	11.4	-44
44	Poly(maleic anhydride-1-octadecene)	Commercial	31.7	690	30.3	712
45	Poly(ethylene-co-ethyl acrylate-co-maleic anhydride)	Commercial	36.3	430	33.9	884
46	Polytetrafluoroethylene (PTFE)	Commercial	2.9	53	4.0	60
47	Fluorinated ethylene-propylene (FEP)	Commercial	3.1	65	4.1	60
48	Poly(vinylidene fluoride-co-hexafluoropropylene) (4.7wt% hexafluoropropylene)	Commercial	8.3	144	8.1	185
49	Polyvinylidene fluoride (PVDF)	Commercial	9.7	311	12.1	309
50	Perfuloromethyloxirane (PFMO)	Commercial	1.5	30	2.0	49
51	Perfuloroalcoxy (PFA)	Commercial	3.2	54	2.8	53
52	Poly(vinyl chloride)	Commercial	13.1	167	13.1	194
53	Chloroprene	Commercial	18.1	261	21.1	313
54	Poly(2,5-pyridine)	Commercial	0.7	15	3.0	40
55	Poly(3,5-pyridine)	Commercial	4.7	70	3.0	40
56	Poly(2-vinylpyridine)	Commercial	34.7	612	31.3	605
57	Poly(4-vinylpyridine)	Commercial	30.8	566	31.3	605
58	Polylactic acid (PLA)	Commercial	15.1	497	13.4	29
59	Polycaprolactone (PCL)	Commercial	25.8	571	23.6	582
60	Polybutylene succinate (PBS)	Commercial	21.2	476	18.0	381
61	Polyhydroxybutyrate (PHB)	Commercial	20.2	819	17.9	220
62	Poly(butyrate-adipate-terephtalate) (PBAT)	Commercial	20.8	368	20.3	427
63	Polyethylene terephtalate (PET)	Commercial	15.9	350	16.3	333
64	Polytrimethylene terephtalate (PTT)	[14]	18.7	490	18.0	392
65	Polybutylene terephtalate (PBT)	Commercial	20.5	513	19.5	444
66	Polycarbonate (PC)	Commercial	18.3	423	21.0	392
67	Kevlar	[7]	14.8	302	11.9	248
68	Technora	[7]	13.3	131	12.6	231
69	Poly(ether ether ketone) (PEEK)	[7]	12.4	155	11.7	108
70	Poly(ether ketone (PEK)	[7]	10.8	124	9.6	98
71	Poly(ether ketone ketone) (PEKK)	[7]	8.7	96	7.7	88
72	Poly(1,4-phenylene ether sulfone)	[7]	11.2	115	8.2	112
73	Poly(sulfone de bisphenolA)	[7]	19.4	345	17.5	330
74	Poly(phenylsulfone)	[7]	11.3	153	15.1	266
75	Bisphenol E polycyanurate	[7]	14.7	316	15.1	253
76	Bisphenol A cyanurate	[7]	17.6	283	16.3	312
77	Bisphenol C cyanurate	[7]	4.2	24	2.2	-13
78	Bisphenol C epoxy	[7]	10	505	14.2	379
79	Bisphenol C polycarbonate	[7]	3	29	3.8	35
80	Bisphenol C polyarylate	[7]	7.6	21	3.9	44
81	Poly(dichloroethyl diphenyl ether)	[7]	5.2	16	6.4	118
82	BisphenolA epoxy catalytic cure phenoxy A	[7]	26	657	27.0	599

83	hexafluorobisphenolA polycyanurate	[7]	2.3	32	9.0	138
84	Poly(vinyl alcohol) (PVOH)	Commercial	19.3	281	19.9	314
85	Ethylene-vinyl alcohol copolymer (38wt% ethylene)	Commercial	27.4	664	27.9	650
86	Polyoxymethylene (POM)	Commercial	13	236	10.0	250
87	Polyethylene oxide (PEO)	Commercial	21.6	618	19.9	552
88	Poly(furan-2,5-dione - *alt* - dimethyl (2-(vinyloxy)ethyl)phosphonate) 	Our lab	10.4	147	11.4	125
89	Poly(3-methylenedihydrofuran-2,5-dione - *alt* - dimethyl (2-(vinyloxy)ethyl)phosphonate) 	Our lab	12.9	149	12.5	115
90	Poly(dibutyl maleate - *alt* - dimethyl (2-(vinyloxy)ethyl)phosphonate) 	Our lab	21.2	387	21.6	458
91	Poly(dibutyl 2-methylenesuccinate - *alt* - dimethyl (2-(vinyloxy)ethyl)phosphonate) 	Our lab	19.9	221	19.8	443
92	Poly(dimethyl(methacryloxy) methyl phosphonate)	Our lab	11.6	246	12.3	229

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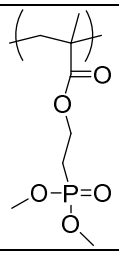
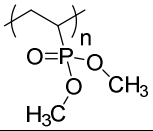
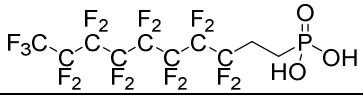
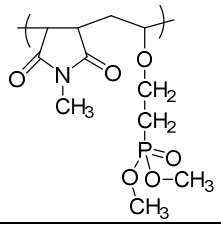
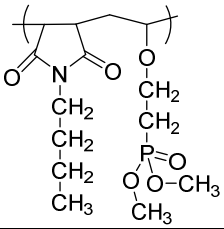
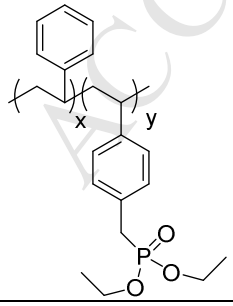
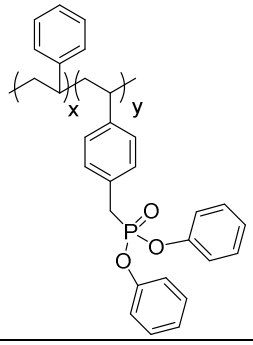
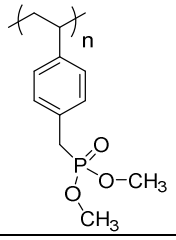
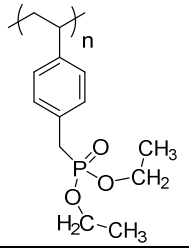
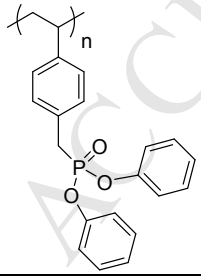
						
93	Poly(vinylmethylphosphonate) 	Our lab	11.9	269	14.7	365
94	Heptadecafluorodecyl-phosphonic acid 	Our lab	5	141	4.3	96
95	Poly(1-methyl-1H-pyrrole-2,5-dione - *alt* - dimethyl (2-(vinyloxy)ethyl)phosphonate) 	Our lab	9.3	173	13.2	227
96	Poly(1-butyl-1H-pyrrole-2,5-dione - *alt* -dimethyl (2-(vinyloxy)ethyl)phosphonate) 	Our lab	17.1	234	18.4	400
97	Styrene-diethyl-(4-vinylbenzyl)phosphonate copolymer (5wt% diethyl-(4-vinylbenzyl)phosphonate) 	Our lab	33.7	781	35.4	808
98	Styrene-diethyl-(4-vinylbenzyl)phosphonate copolymer (10wt% diethyl-(4-vinylbenzyl)phosphonate)	Our lab	33.1	839	34.9	800
99	Styrene-diethyl-(4-vinylbenzyl)phosphonate copolymer (20wt% diethyl-(4-	Our lab	33.95	691	33.8	785

	vinylbenzyl)phosphonate)					
100	Styrene-diphenyl-(4-vinylbenzyl)phosphonate copolymer (10wt% diphenyl-(4-vinylbenzyl)phosphonate) 	Our lab	33.2	660	35.0	800
101	Poly(dimethyl-(4-vinylbenzyl)phosphonate) (HPM1)[2] 	[16]	25.8	200	23.2	598
102	Poly(diethyl-(4-vinylbenzyl)phosphonate) (HPM2)[2] 	[16]	27.9	150	25.2	664
103	Poly(diphenyl-(4-vinylbenzyl)phosphonate) (HPM3)[2] 	[16]	28.3	690	26.5	662
104	Poly(1-methyl-1H-pyrrole-2,5-dione - *alt* - 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-(vinyloxy)decane)	Our lab	8.7	123	8.5	130

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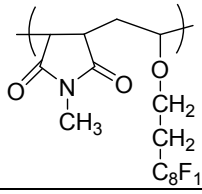
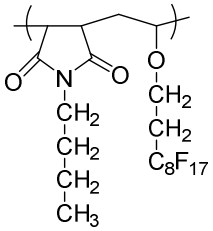
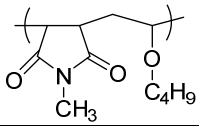
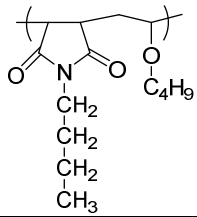
						
105	Poly(1-butyl-1H-pyrrole-2,5-dione - *alt* - 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-(vinyloxy)decane) 	Our lab	11.8	257	10.6	200
106	Poly(1-methyl-1H-pyrrole-2,5-dione - *alt* - 1-(vinyloxy)butane) 	Our lab	21.2	359	19.6	331
107	Poly(1-butyl-1H-pyrrole-2,5-dione - *alt* - 1-(vinyloxy)butane) 	Our lab	26.2	405	23.1	475

[1] Using database 1

[2] sumHRC graphically estimated from the curves in [16]

Deconstruction of a polymer containing several groups

There are numerous possibilities for the deconstruction of a polymer structure containing several significant groups. For example, the Lyon approach includes the groups -O- and -CH_2- but also -CH_2-O- and the contributions of the latter are not a linear combination of the contributions of the former [6]. It appears important to determine some guides to avoid redundancy as much as possible.

First, the carbon atom has different contributions according to the number of covalent bonds with C, H, O (or OH), N, F or Cl atoms. A double covalent bond is considered equivalent to a single covalent bond. So the group is considered equivalent to the group. Second, a series of groups is created by combination of an aromatic structure (including pyridine and naphthalene) with another group such as –O-, -CO-… Third, the contribution of an aromatic group depends on its position in the polymer (in the main chain or as pendant group). These three rules permit the generation of most of the groups to be considered. In addition, some special groups such as maleimide, maleic anhydride and phosphonate have also been created.

Nevertheless, these rules are not enough to avoid indecisions concerning the choice of groups constituting some polymers. For this study, poly(4-methoxystyrene) was dissected into four groups: CH_2, CH, phenyl and $–OCH_3$. Another choice may have been CH_2, CH, phenyl-O- and CH_3. Aromatic polyamide (numbered 34) was fragmented into CH_2, phenyl-O and NHCO groups rather than CH_2, phenyl-NHCO and CH_2-O (Figure 1). Another example is polycarbonate. Polycarbonate was deconstructed quite artificially into C, CH_3, phenyl-O and phenyl-OCO. We have preferred such deconstruction rather than the creation of a new group, phenyl-OCOO.

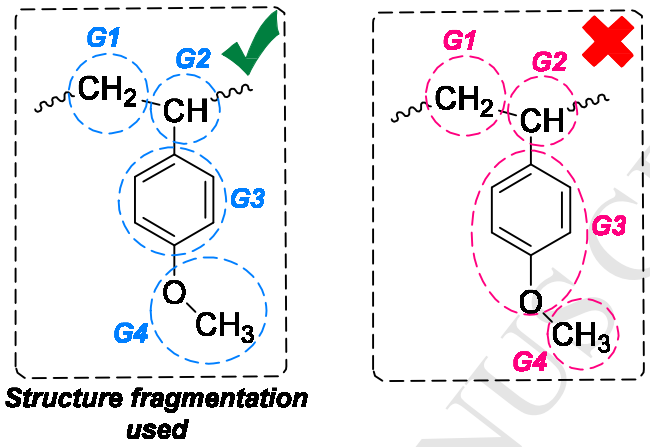


Figure 1 – Example of two possible structure fragmentations for poly(4-methoxystyrene)

These examples show that arbitrary choices have been made in building the database. Much as earlier databases, this one is not complete and will evolve with the incorporation of data from the analysis of new polymers. Additional rules may be needed in the future. Nevertheless, the rules listed above provide a rationale for the construction of a reliable database.

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Model building "step-by-step"

We showed in a previous study that the contributions of some groups depend on their environment. For example, we have observed that a phosphonate group has a rather high contribution to HRC in a series of simple molecules. However when the phosphonate group is present as well as acrylate or acrylic groups, the experimental HRC is systematically lower than the calculated one. We have assumed that this is due to interactions between these groups during the thermal degradation [11]. Indeed, it is well known that phosphorus is able to promote charring of polymers containing oxygen atoms.

Therefore if we consider all the polymers at the same time, the risk is the calculation of an average but meaningless contribution. We have preferred to build our model "step-by-step". An example of this method follows.

The first step consisted of the calculation of the contributions of some usual groups present in many polymers: C, CH, CH_2, CH_3, phenyl (pendant), CH_2-O and CH_3-O from a first series of 13 polymers containing only these groups (Figure 2). Once the contributions of these groups were obtained, we calculated contributions of various fluorinated groups. Four groups were considered but three of them have the same contributions (Figure 3). Contributions of the maleic anhydride group were calculated from a series of 10 polymers containing only groups for which the contributions had already been calculated. Poly(ethylene maleic anhydride) was not used for reasons discussed in a next section (Figure 4). White points in Figures 3 and 4 correspond to various polymers containing fluorinated or maleic anhydride groups but also other groups for which the contributions to HRC were

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calculated later. These polymers were not used for the calculation of contributions of fluorinated or maleic anhydride groups but they can be used to generate control data.

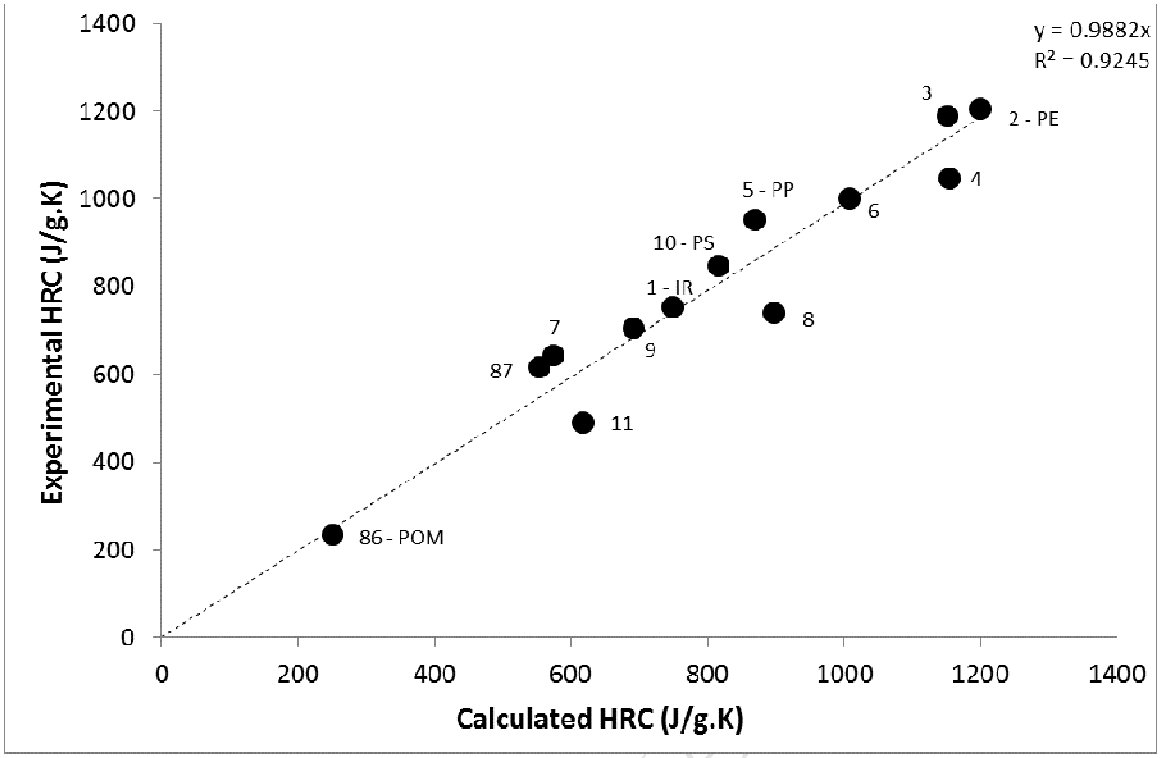

Figure 2 – Experimental versus calculated HRC for a first series of polymers (labels correspond to polymers numbered in table 1)

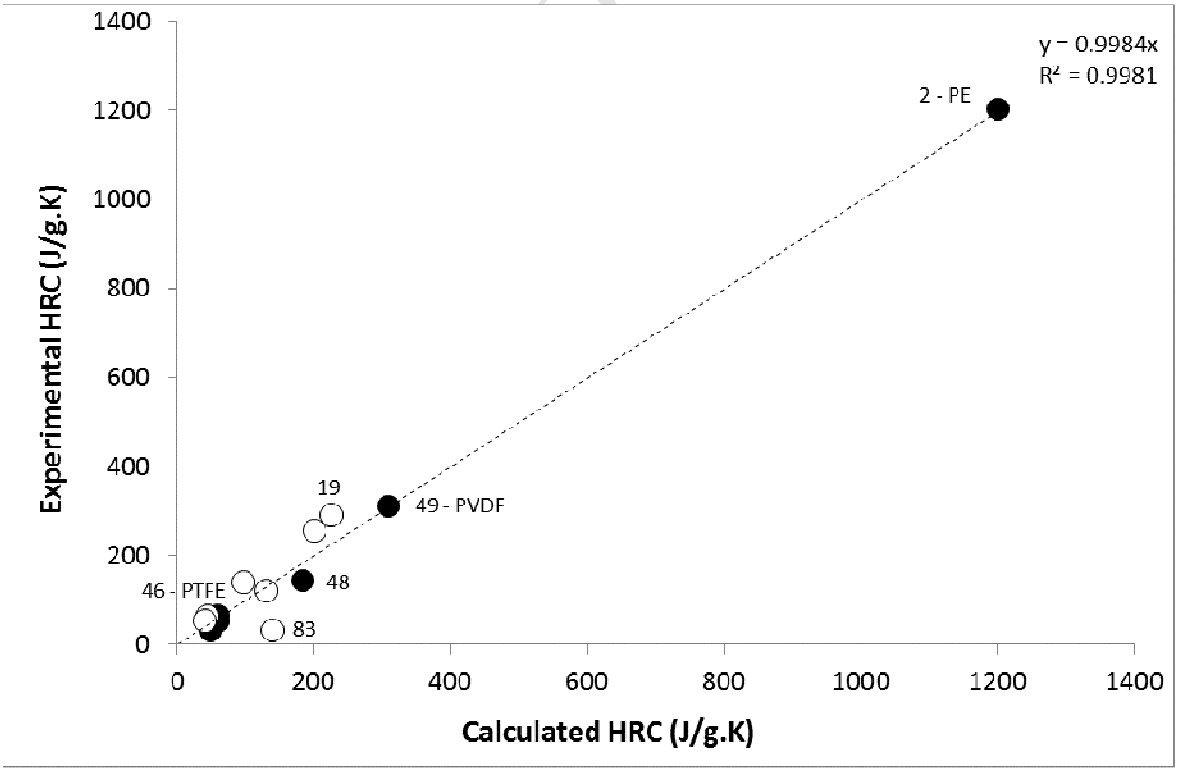

Figure 3 – Experimental versus calculated HRC for fluorinated polymers (labels correspond to polymers numbered in table 1)

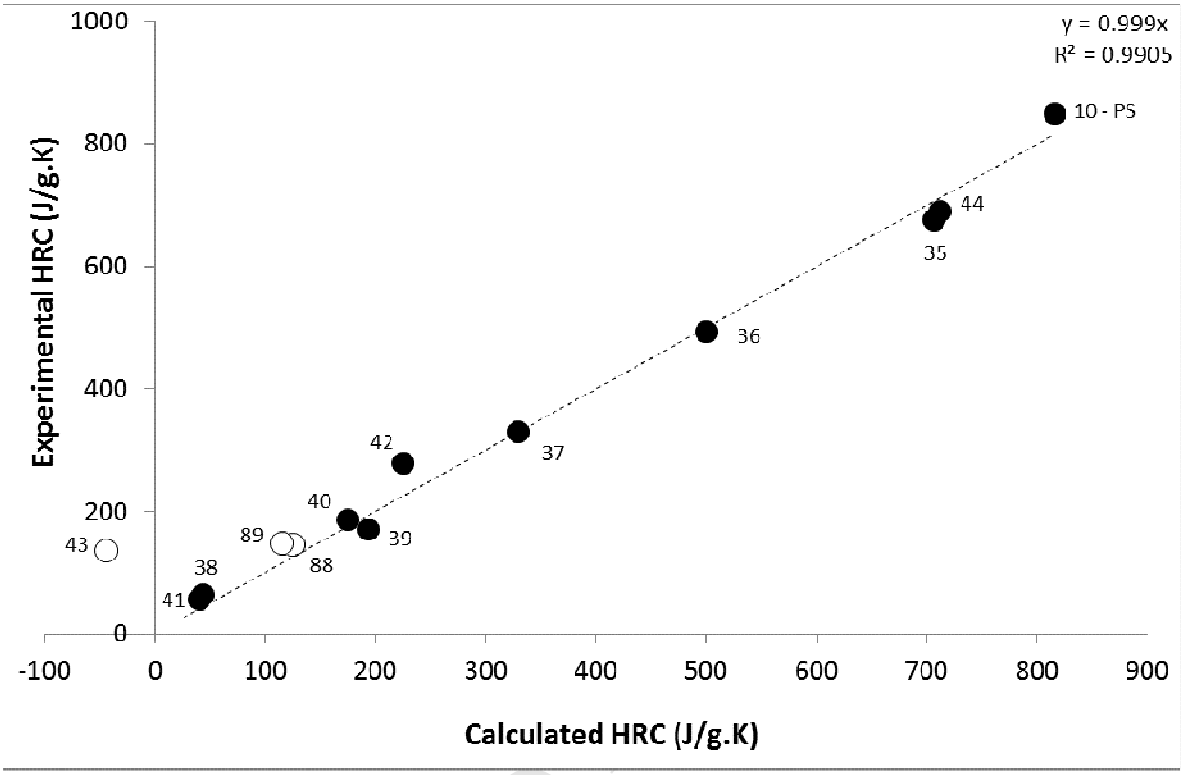

Figure 4 – Experimental versus calculated HRC for polymers containing a maleic anhydride group (labels correspond to polymers numbered in table 1)

If the contributions of some groups (as fluorinated or maleic anhydride groups) were calculated with a good accuracy, it is not the case of some other groups such as maleimide. Only four polymers were used to assess the contributions of the maleimide group (Figure 5). Two polymers also contain a phosphonate group and were not used for this calculation because the contributions of phosphonate group had not yet been evaluated (white points). Further analyses including data from additional polymers are needed to improve the accuracy of these calculated contributions.

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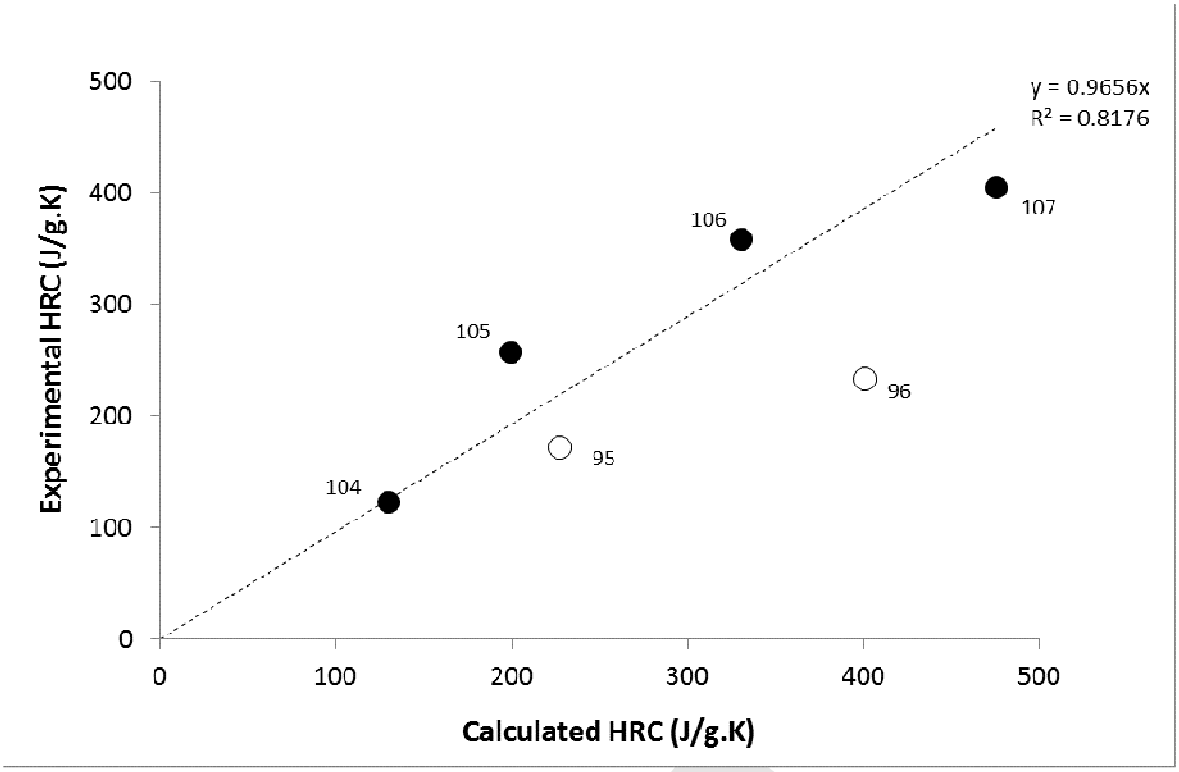
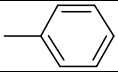


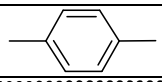
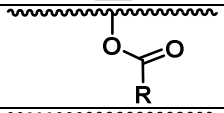
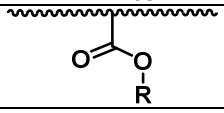
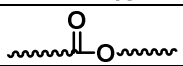
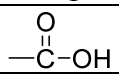
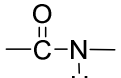
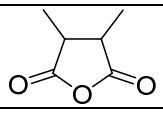
Figure 5 – Experimental versus calculated HRC for polymers containing a maleimide group (labels correspond to polymers numbered in table 1)

In Lyon's work, 38 group increments were used to predict the flammability of 84 lab-made or commercial polymers [6]. In this study, 107 polymers and 31 groups were considered. We have also proposed an alternative database for the contributions to THR. In this second database, some groups are combined (for example, C, CH, CH_2 and CH_3) but without reducing substantially the accuracy of the calculations. Only 15 groups were considered to predict correctly the THR of all polymers studied.

All groups including their contributions to THR an HRC are listed in Table 2.

Table 2 – Chemical groups and their contributions

Groups	Molar mass (g/mol)	Contribution to			Effective heat of complete combustion (kJ/g)[3]
		THR (kJ/g)[1]	THR (kJ/g)[2]	HRC (J/g.K)	
—C—	12	30	41	-200	34.9
—C–H	13	36		-100	40.3
H —C— H	14	41		1200	44.9
H —C–H H	15	45		1400	48.9
	77	35	35	900	39.5

	76	35		900	38.6
	44	-4	-4	-300	0.0
	44	-4		-500	0.0
	44	-4		-400	0.0
	45	-4		-100	2.3
	43	3	3	-500	7.3
	98	3	3	-400	12.8
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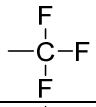
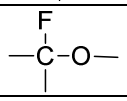
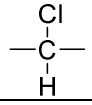
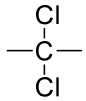
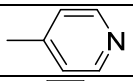
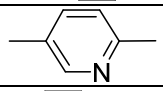
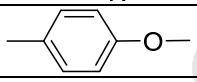
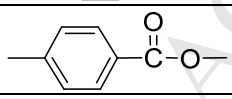
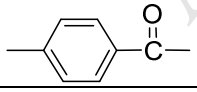
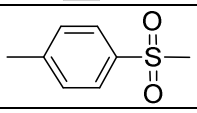
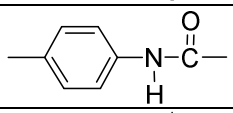
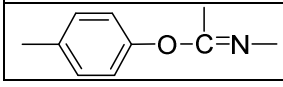
	69	2		60	6.1
	31	9		60	13.5
	47	0		20	4.5
	48	5		-100	8.7
	82	-30	-30	-600	5.1
	79	28	28	600	31.8
	78	3	3	40	29.6
	92	16	17	130	29.6
	120	18		400	22.7
	104	4	4	70	30.2
	140	3		100	21.0
	119	12	12	250	27.3
	118	12		200	26.6

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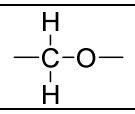
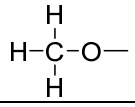
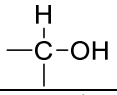
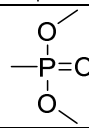
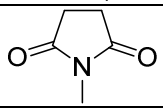
	30	10	12	250	14.0
	31	13		250	16.9
	30	10		-100	14.0
	79	-5	-5	-100	-1.3
	96	3	3	-300	15.3

[1] First database
[2] Second database
[3] From Huggett's relation [17]

Results and discussion

All polymers including experimental and calculated THR and HRC are listed in Table 1. Figures 6 and 7 show the correlation between experimental and calculated THR and HRC respectively for all the polymers tested.

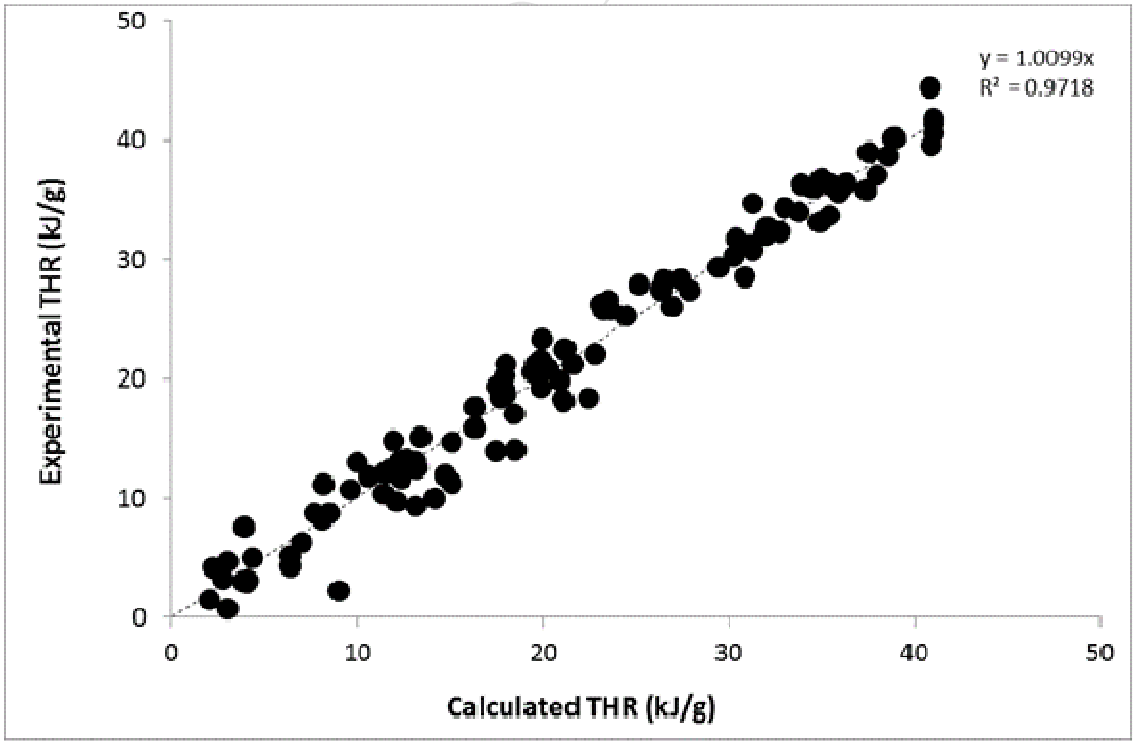


Figure 6 – Experimental versus calculated THR for 107 polymers studied in this work (using first database)

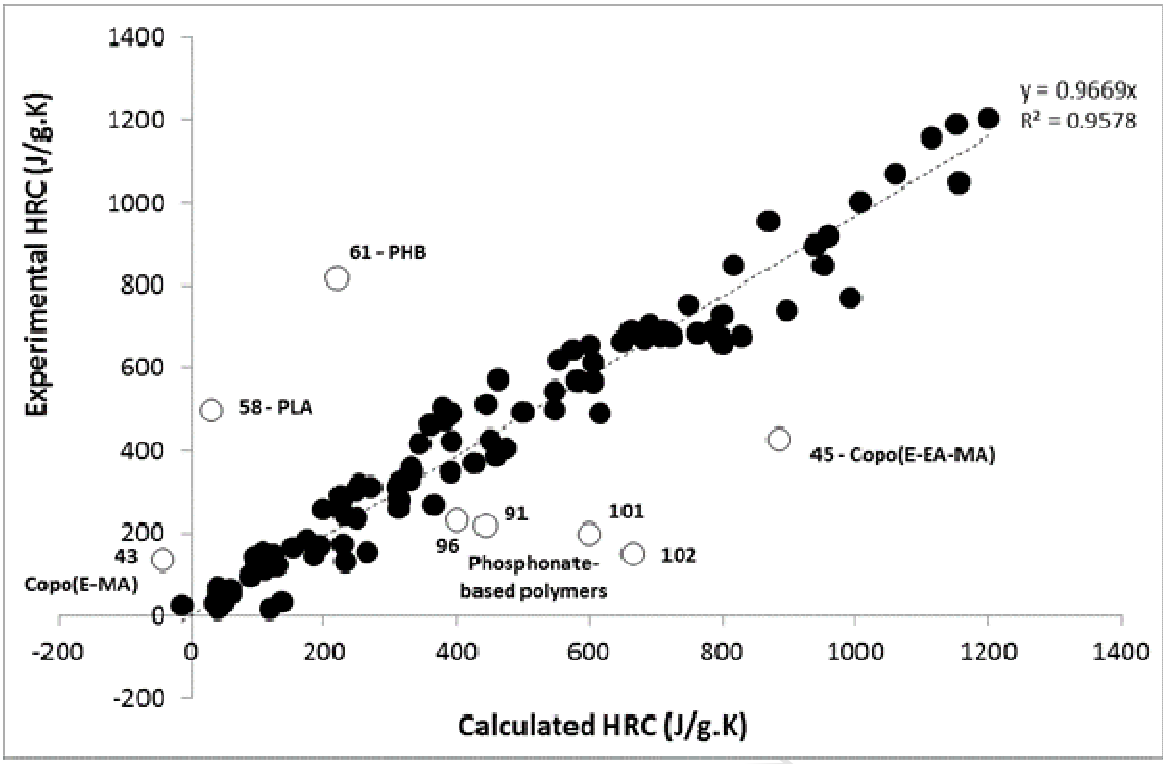


Figure 7 – Experimental versus calculated HRC for 107 polymers studied in this work (dashed line was plotted considering only black points – white points correspond to exceptions discussed later)

An error value noted E for the predicted THR is calculated as follows:

$$E\ (in\ \%) = \frac{100 \times |THR_{exp} - THR_{calc}|}{THR_{exp}} \qquad \text{(equation 3)}$$

THR_{exp} and THR_{calc} are the experimental and calculated THR respectively. The error value for the predicted HRC is calculated similarly. The mean error for THR is lower than 16%. The mean error for HRC (excluding 8 exceptions which will be discussed later) is 28%. Considering only polymers exhibiting an experimental HRC higher than 200 J/g.K, the mean error decreases to 11%.

Contribution to THR: a comparison with the Huggett relation

THR depends on the char fraction μ and the EHC (energy released by complete pyrolysis and combustion of the polymer) according to the equation 4.

$$EHC = THR + \mu \times EHC_{char} \quad \text{(equation 4)}$$

With EHC_{char} the energy released by the complete pyrolysis and combustion of the char

EHC values for the various groups studied in this work can be calculated using the Huggett relation [17]. This relation considers that 1 kg of oxygen consumed during the combustion corresponds to an energy release of 13.1 MJ, whatever the molecular structure of the polymer.

The contributions to THR for various groups versus the corresponding EHC are plotted in Figure 8. A

very good correlation can be found between both values for the majority of the groups. This means that these groups are fully decomposed into gases during degradation and do not leave char.

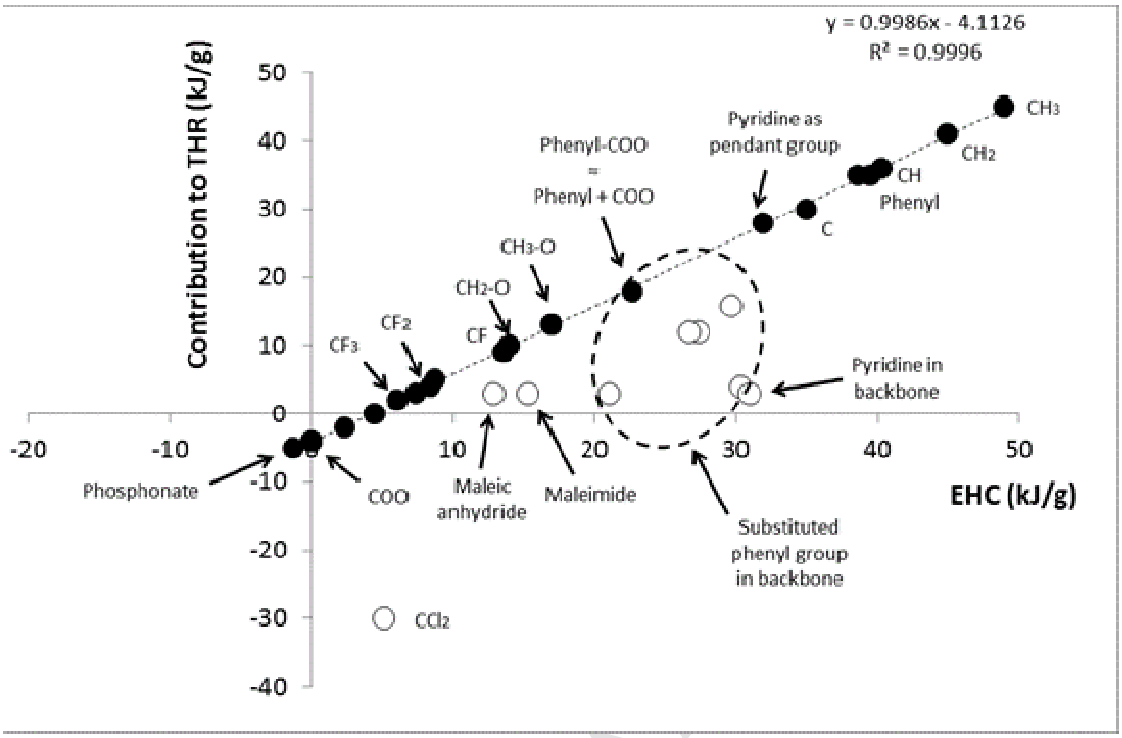


Figure 8 – Contribution to THR versus EHC calculated from the Huggett relation

On the contrary, few groups exhibit contributions to THR much lower than the calculated EHC. These groups can promote char formation during degradation, or can induce charring by other groups present in the polymer. This is particularly the case for the phenyl-CO- group, which is present in charring polymers as PEEK, PEK, PEKK and bisphenol C polyarylate. These four polymers exhibit char contents of 46.5, 52.9, 60.7, 42.7 wt% [6].

Walters et al. have shown that the char composition is close to C_5H_2 in most cases [18]. The energy released by the complete pyrolysis and combustion of such char is then 37.2 kJ/g. When the contribution to THR is significantly different from EHC calculated using Huggett's relation, it would be possible to calculate the contribution to char according to equation 5.

$$\mu = \frac{EHC - THR}{EHC_{char}} \text{ (equation 5)}$$

As an example, the contributions to char of two groups - Phenyl-O and Phenyl-CO - have been calculated using equation 5: 0.37 and 0.71 respectively. Then the char fractions of PEEK, PEK and PEKK have been calculated using these contributions: 48.9, 54.6 and 60.1 wt%. The agreement between these calculated and the experimental char fractions is very good.

A last case corresponds to the CCl_2 group whose contribution to THR is very low. This group contains two halogen (chlorine) atoms which are well known as effective flame inhibitors. It has previously been shown that some molecules containing bromine (for example poly(4-bromostyrene (PS-Br)) are not fully oxidized in PCFC under standard conditions [19]. Therefore the low contribution to THR of this group may also be due to incomplete combustion, i.e. the

observed value is lower than the value calculated according to the Huggett relation.

What is the meaning of negative or low contribution to HRC?

A negative contribution to HRC means that the group considered is able to decrease the degradation rate of other groups present in the macromolecular structure. It is quite probable that low contributions to THR and to HRC are quite well correlated. But a high contribution to THR does not mean systematically a high contribution to HRC. Both contributions for all considered groups are plotted in Figure 9.

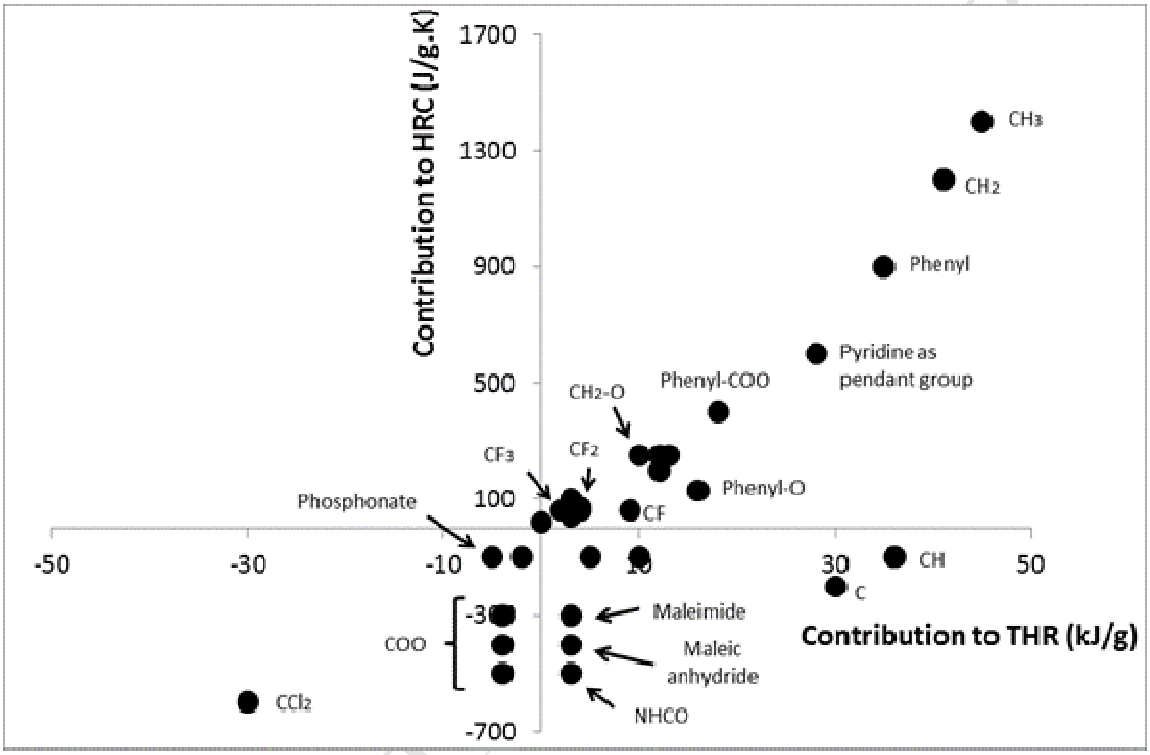


Figure 9 – Contribution to HRC versus contribution to THR for 31 groups

It can be observed that most generally contributions to THR and HRC are correlated. But there are few interesting exceptions. Especially C and CH exhibit both high contributions to THR but negative contributions to HRC. This is dramatically different from the behavior of CH_2 and CH_3 which exhibit similar contributions to THR but also very high contributions to HRC. Increasing the unsaturations or the pendant groups (i.e. increasing the degree of oxidation of carbon atoms) along the main chain of a macromolecule generally decreases the HRC. Nevertheless, most of pendant groups (such as phenyl) can also increase the HRC.

Some other groups exhibit negative contributions to HRC: COO (acetate, acrylate, ester, carboxylic acid), maleimide, maleic anhydride, amide, chlorinated groups and finally phosphonate. All these groups contain carbon or phosphorus atoms for which the degree of oxidation is high.

Among the aromatic groups, the correlation between the contributions to THR and HRC is generally good (Figure 10). This means that a group releasing little energy (due to charring) also exhibits a low rate of degradation (a low HRC). Only the phenyl-O group exhibits a low contribution to HRC with respect to its contribution to THR.

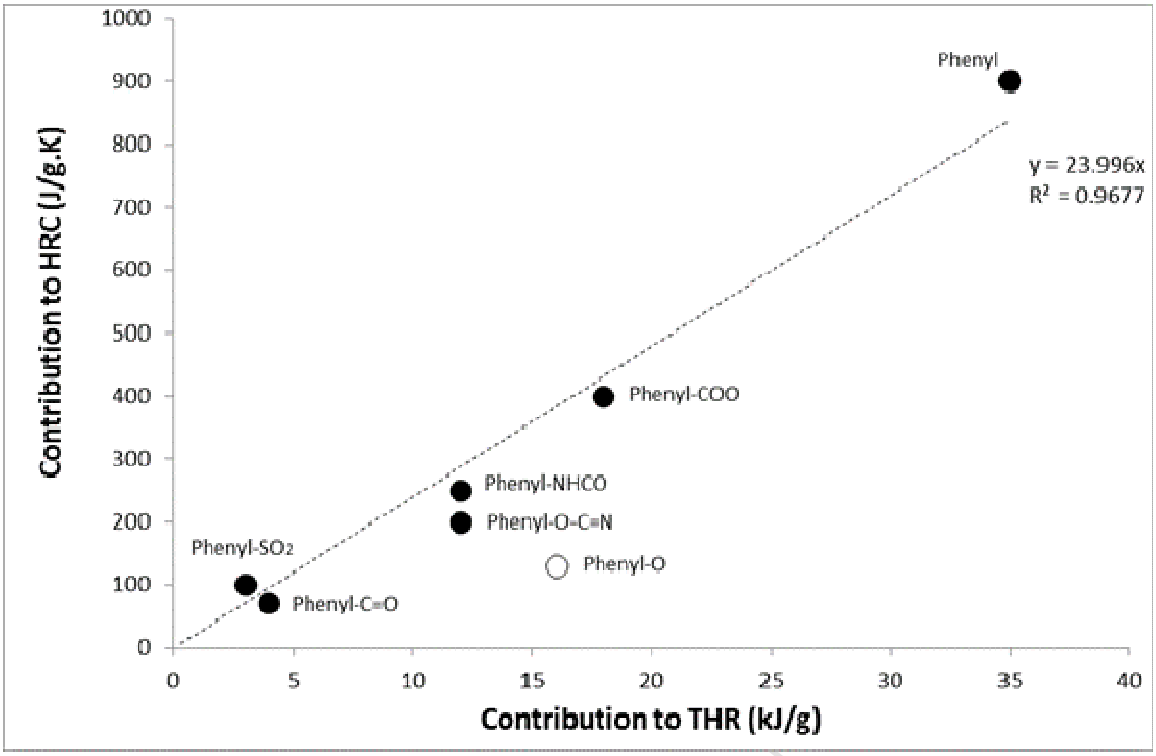


Figure 10 – Contribution to HRC versus contribution to THR for phenyl groups in backbone

Finally all groups can be divided into three sets. The first one includes the groups exhibiting well correlated contributions to THR and to HRC (for example CH_2, phenyl, CF_2). The second set includes the groups exhibiting non-correlated contributions to THR and to HRC (for example, CH, NHCO…). The third set is constituted by only one group: phosphonate, for which the contribution to HRC is quite arbitrary and is not constant for all phosphonate-based polymers. This specific case will be discussed later.

Consistency of the model

Even if the model needs to be adjusted further, it must provide consistent results, i.e. the contributions calculated must be meaningful. It appears that the contribution to HRC of C, CH, CH_2, CH_3 increases with the number of hydrogen atoms bonded to the carbon, i.e. when the degree of oxidation of the carbon atom decreases. This result, consistent with earlier projections, would appear to be quite reasonable. Indeed, to a first approximation, the rate of heat release (or the rate of mass loss) depends on the nature and the number of bonds to be broken and the number of C=O bonds to be formed in order to obtain a fully oxidized species.

Similarly, the contribution to HRC must be lower (or at least equal) when a group is present in the main chain rather than as pendant group. This is particularly the case for the pyridine group. As a pendant group, it exhibits high contributions to THR (28 kJ/g) and to HRC (600 J/g.K). On the contrary, poly(2,5-pyridine) and poly(3,5-pyridine) lead to very high char fraction (more than 0.75 for poly(2,5-pyridine)). Therefore the contributions to THR and HRC of a pyridine group in the main chain are 3 kJ/g and 40 J/g.K respectively. It is also noteworthy that no strong difference was observed between poly(2,5-pyridine) and poly(3,5-pyridine) or between poly(2-vinylpyridine) and poly(4-vinylpyridine).

It is interesting to note that the electronic structure of polymers may be dramatically different despite of the presence of the same groups. Indeed, when pyridine is present in the main chain, electrons are relocated on the whole chain (conjugated structure). Such a structure explains why such polymers are electron conductive. This is not the case when pyridine is present as pendant group.

In contrast to the pyridine group, the phenyl group does not exhibit different contributions as pendant or main chain constituent. The contributions to THR and to HRC are high: 35 kJ/g and 900 J/g.K respectively. The phenyl group is present as a pendant group in polystyrene and derivatives (poly(4-methylstyrene)…). These polymers exhibit high THR and HRC. In contrast to pyridine-containing polymers, polymers containing phenyl in the main chain do not exhibit a delocalization of electron density along on the whole chain.

In this model, the phenyl group in the main chain is also associated with other groups such as CO, COO, SO_2… in specific arrangements. One interesting case concerns the group phenyl-COO. The contributions of this group are very close to the sum of contributions of phenyl and COO groups: 18 kJ/g and 400 J/g.K versus 20.7 kJ/g and 387 J/g.K. Therefore including this group phenyl-COO may be optional. Nevertheless, such a case is not general (see the case of phenyl-NHCO group in the following).

The contributions of various phenyl groups (7 groups) were calculated for a series of 22 polymers (mainly obtained from the Lyon database [7]). Considering that most of these polymers exhibit low THR and HRC and high char content, the correlation between experimental and calculated contributions is quite satisfying (Figure 11).

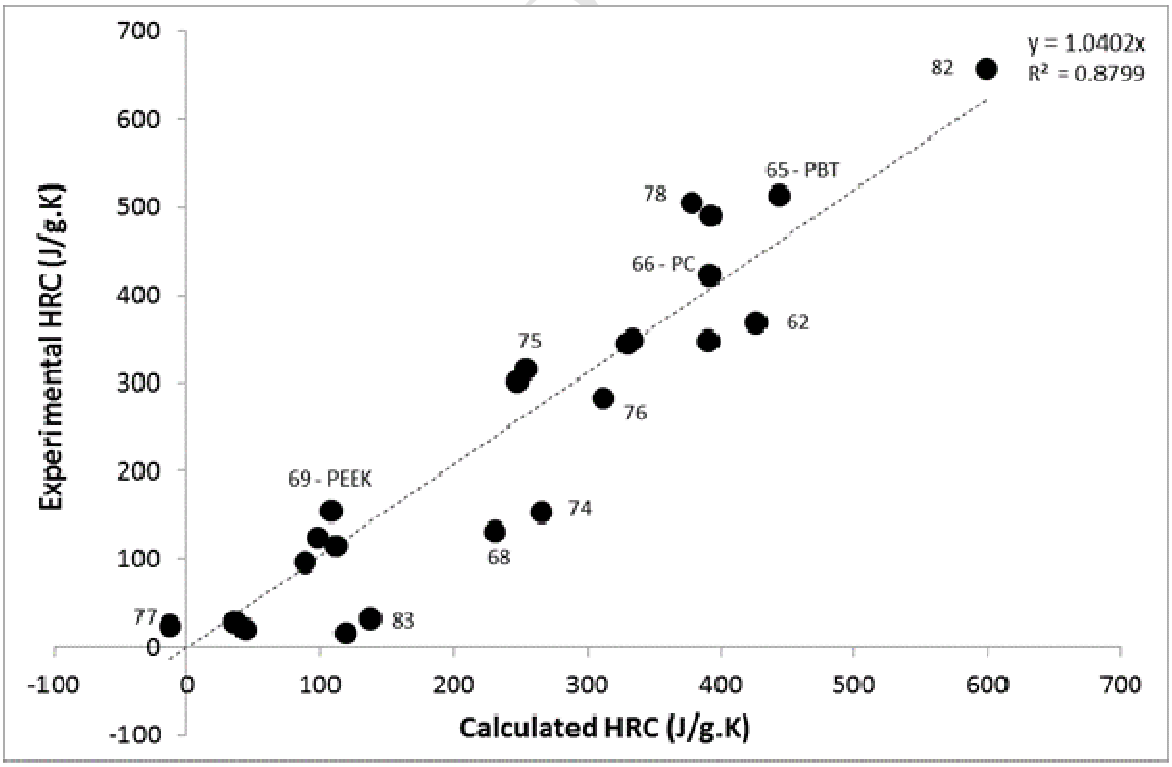


Figure 11 – Experimental versus calculated HRC for polymers containing various phenyl groups in the main chain (labels correspond to polymers numbered in table 1)

The contributions of these groups are listed in the Figure 12. All these groups exhibit significantly lower contributions than does the phenyl group when included in the main chain. It appears that the lowest contributions may be assigned to phenyl-SO_2 (present in polysulfone polymers) and phenyl-C=O (present in PEEK and derivatives). Phenyl-O exhibits moderate contribution to THR but low contribution to HRC. Moderate contributions are assigned to phenyl-COO, phenyl-NHCO and phenyl-O-C=N. As already noted the contributions of phenyl-COO are similar to the sum of the contributions of phenyl and COO. It is not the case for phenyl-NHCO. The contributions of this group are significantly lower than the sum of the contributions of phenyl and NHCO: respectively 12 kJ/g and 250 J/g.K versus 23.4 kJ/g and 394 J/g.K. This means that phenyl bonded to NHCO in the main chain improves the flame retardancy of a polymer. These groups interact synergistically.

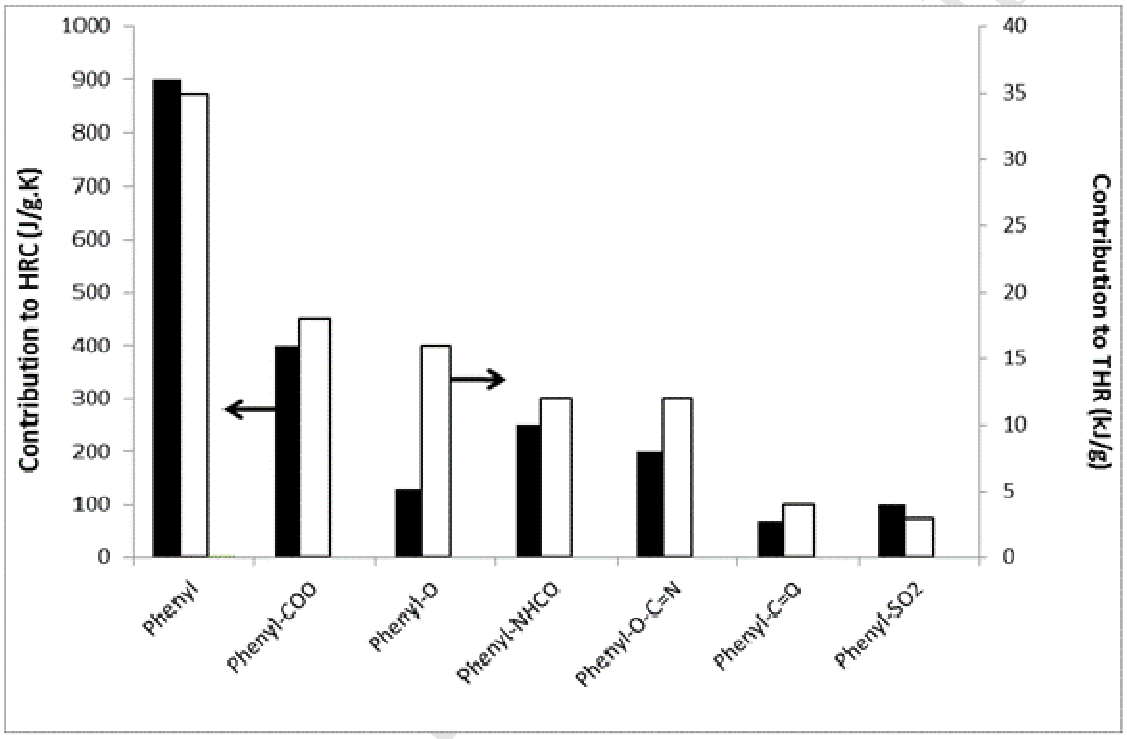


Figure 12 –Contributions to THR and HRC for various substituted phenyl groups in the polymer main chain

Exceptions to the model

As already mentioned this model (and all models based on additive contributions) is simplistic and approximate. It may be possible to add contributions corresponding to the interactions between groups but it would result in many contributions, potentially more contributions than polymers.

Therefore there are a few exceptions, i.e. some polymers for which the experimental THR or HRC do not correspond to the calculated ones. The model will be really interesting only if it is able to explain these exceptions or at least to provide new insights about them.

As observed above, there may be only one exception concerning THR: hexafluorobisphenolA polycyanurate exhibits an experimental THR lower than the calculated one. The THR of all other polymers can be calculated with quite good accuracy. On the contrary, there are few but significant exceptions concerning HRC.

Obviously some uninteresting exceptions are due to the additivity character of the model: for example, poly(ethylene-maleic anhydride) exhibits a negative HRC. It is the only polymer containing maleic anhydride for which the calculated HRC does not fit well the experimental one. It is also the simplest structure among these polymers. In this copolymer, the contribution of two methylene groups (CH_2) is too low to compensate the negative contribution of the weighty maleic anhydride. Therefore the contributions calculated in this work may be suitable only when the weight fraction of the group considered is not too high.

Another exception concerns two aliphatic polyesters: PLA and PHB. Both exhibit an experimental HRC much higher than the calculated ones. The difference between experimental and calculated values is at least 500 J/g.K in both cases. It must be noticed that both PLA and PHB have a similar structure, with a methyl group in the alpha position with respect to the oxygen atom of the ester group: COO-CH-CH_3. The model suggests that the specific location of the methyl group destabilizes the ester function leading to a very high degradation rate and then to a high HRC. This finding is also supported by the low degradation temperature of these two polymers: pHRR is observed at 310 and 390°C respectively for PHB and PLA, in comparison to 410-430°C for other polyesters, and even 450°C for PET.

Another exception concerns a copolymer (ethylene-co-ethyl acrylate-co-maleic anhydride) but the content of maleic anhydride is quite negligible (2 wt%). The reason for this exception is not understood and needs more exploration.

The main exception corresponds to various polymers containing phosphonate groups. Indeed, phosphorus is a well-known charring promoter and its efficiency depends on its environment. It has previously been observed that the contributions of a phosphonate group calculated using a first series of molecules was not satisfactory for those also containing COO groups [11]. In such molecules, the experimental HRC was systematically lower than the calculated value. The highest deviation was observed when the ratio COO/phosphonate was equal to 2.

It is possible to calculate a contribution to THR for the phosphonate group which is satisfactory for all 16 phosphonate-based polymers (see Figure 13). This means that in these polymers, phosphonate is unable to promote the formation of a thermally stable char. If the phosphonate group is only present as a pendant group in these polymers, its location may limit its ability to promote charring.

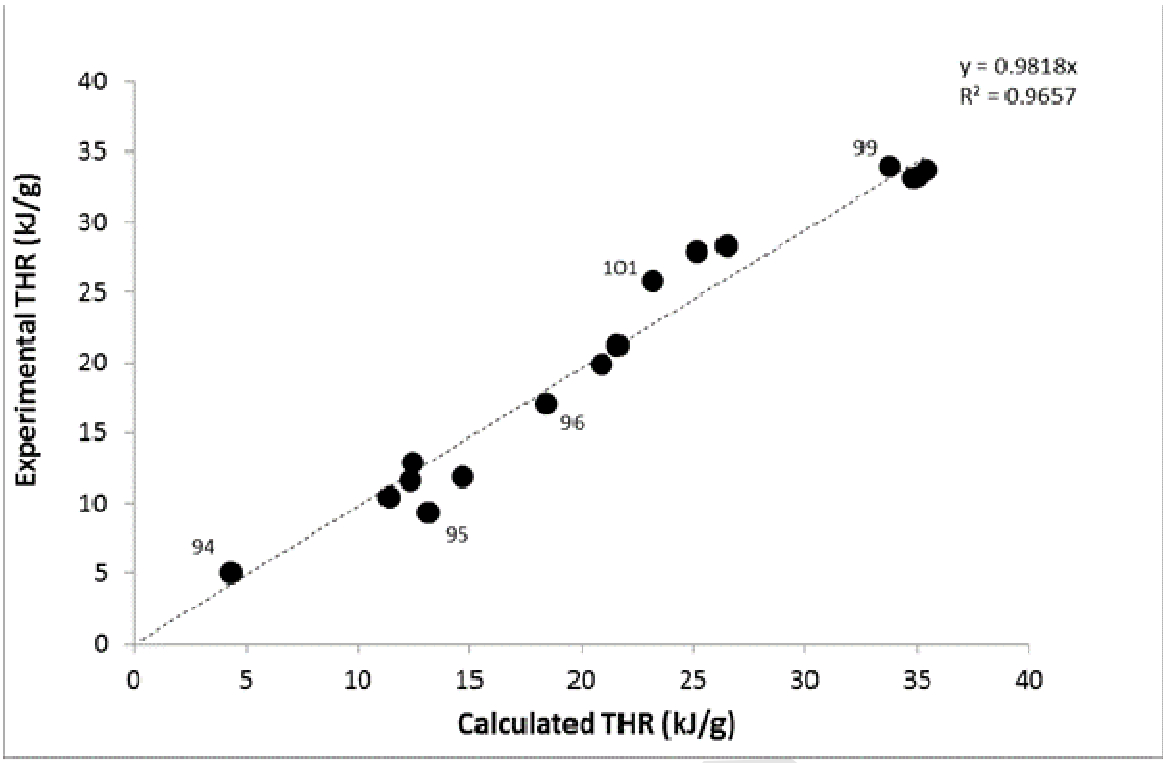


Figure 13 – Experimental versus calculated THR for 16 phosphonate-based polymers (labels correspond to polymers numbered in table 1)

Nevertheless, it is not possible to choose a contribution to HRC that is satisfactory for all polymers considered. It may be assumed that in some polymers, the phosphonate group can interact with other groups present in the macromolecule, leading to a low HRC. But in other polymers, it can be expected that no interaction occurs and then it would be possible to calculate properly the contributions of the phosphonate group. Such a possibility would be particularly interesting because it would be possible to identify the structures in which phosphonate interacts with its environment by comparison between the calculated and experimental HRC.

There are several methods for approaching the calculations of the contributions of the phosphonate group. All of them are somewhat arbitrary. A first method is to choose the contribution to HRC of phosphonate group so that calculated HRC of polymers are systematically higher or equal to the experimental ones. Another method (followed in this work) is to choose the contribution to HRC from the contribution to THR according to the tendency observed in Figure 9. Indeed, a quite good correlation is found between the contributions to HRC and to THR for most of groups. For a contribution to THR close to -5 kJ/g as for phosphonate group, the contribution to HRC should be around -100 J/g.K. It is noteworthy that this value is also in agreement with the first method proposed above: all experimental HRC are lower or equal (but never higher) than the calculated values.

The experimental versus calculated HRC values for the 16 polymers considered using a contribution to HRC equal to -100 J/g.K for the phosphonate group are plotted in Figure 14. It can be observed that a good correlation between both values is found for about 12 polymers. None of these 16 polymers exhibit experimental HRC much higher than the calculated ones. On the contrary four polymers exhibit experimental HRC significantly lower than calculated ones (91, 96, 101 and 102). A

very interesting observation may be noted for two of them: HPM1 (101), HPM2 (102). They have a structure similar to HPM3 (103). Only the groups bonded to the phosphonate group change: methyl, ethyl or phenyl. The calculated HRC of the three polymers are close to 600 J/g.K. While HPM1 and HPM2 exhibit much lower experimental HRC, HPM3 (phenyl groups bonded to the phosphonate group) has an experimental HRC much higher and close to the calculated one. The phenyl groups may inhibit the efficiency of the phosphonate group to reduce the heat release rate through interactions with the chemical environment. This effect may be related to the higher thermal stability of the phenyl group.

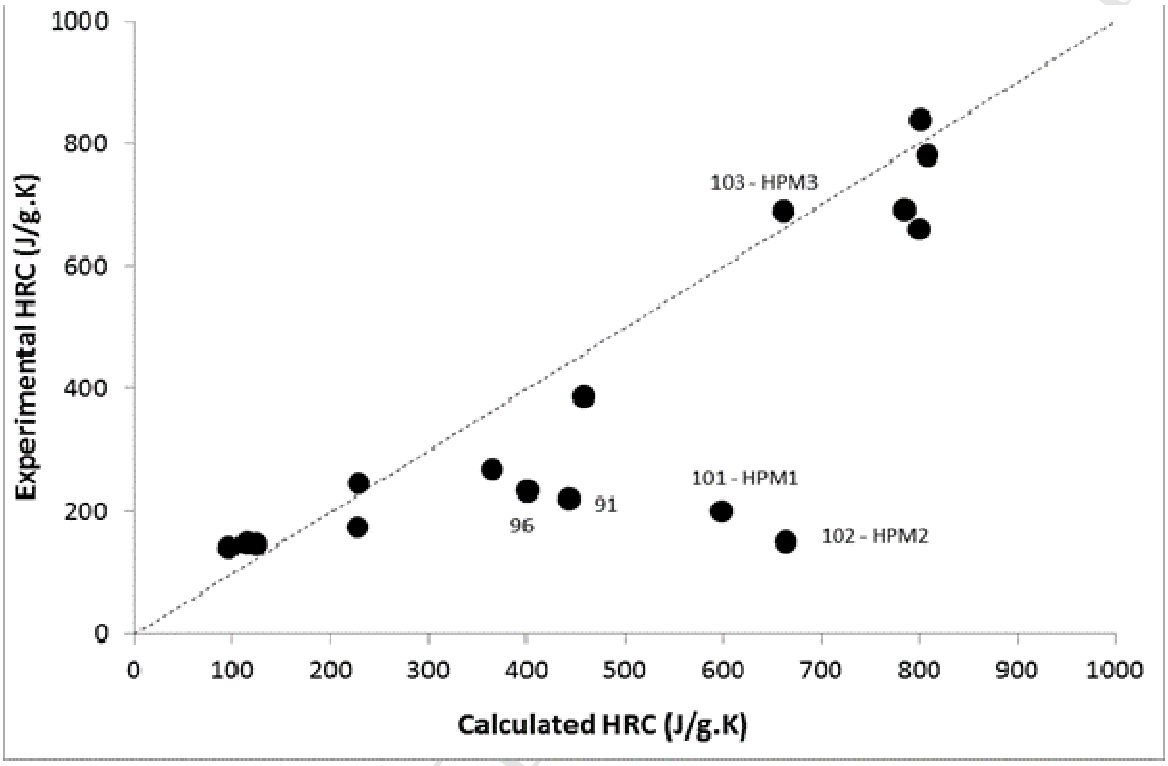


Figure 14 – Experimental versus calculated HRC for 16 phosphonate-based polymers

Contributions to THR: Second database

A second database with a reduced number of groups has been generated for the calculation of THR. Only 15 groups were considered. For example C, CH, CH_2 and CH_3 groups are collected. Similarly all COO groups (ester, acetate, acrylate and carboxylic acid) and most of halogenated groups are grouped together. Figure 15 shows the calculated THR obtained with this second database. It is obvious that the correlation between the calculated and experimental THR remains very satisfying.

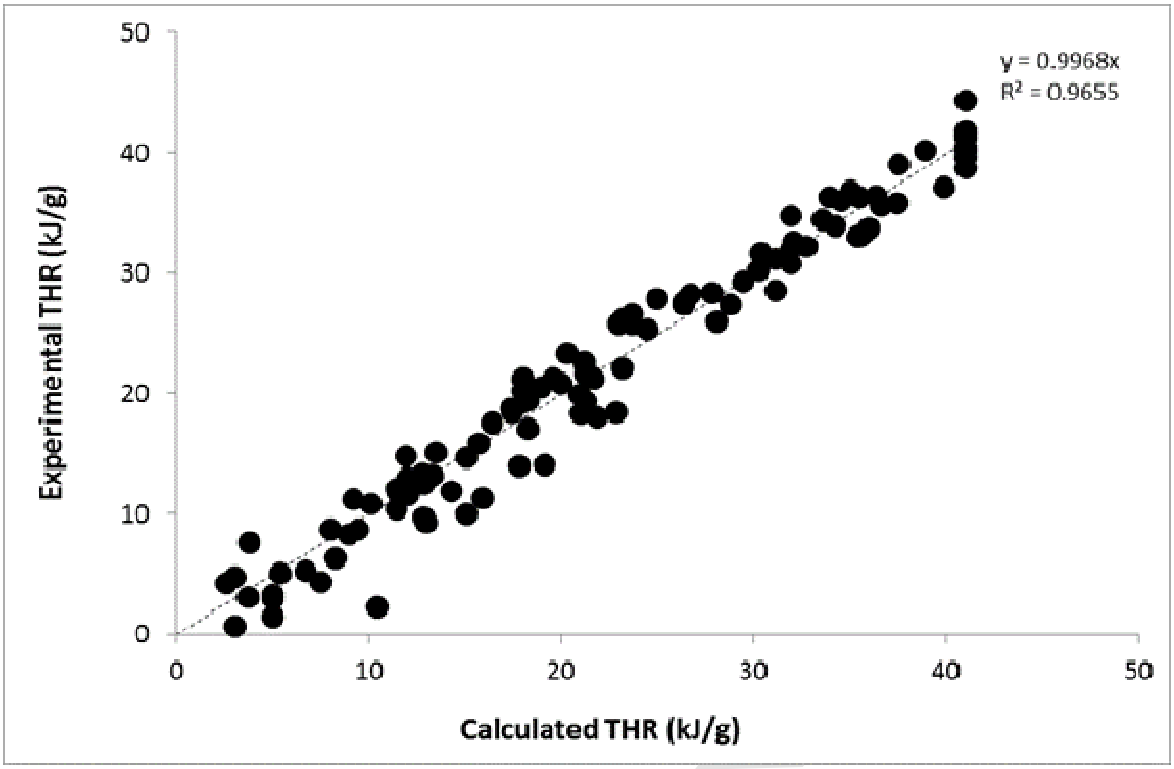


Figure 15 – Experimental versus calculated THR of 107 polymers according to the second database

Conclusions

This work proposes a new database of group contributions using a step-by-step method. Some guidelines were developed for the choice of fragment groups. Considering all the polymers studied (excluding 8 exceptions) THR and HRC can be estimated with a mean error of only 16% and 28% from a database of 31 groups. In particular, THR can be estimated with good accuracy from only 15 groups for all polymers without noticeable exception.

The groups can be compared to identify those exhibiting the lowest contributions to THR and/or HRC. Such an approach also allows an assessment of the consistency of the proposed model.

Some polymers exhibit HRC much lower or higher than the calculated ones and can be considered as exceptions. Such a significant difference between experimental and calculated values permits the identification of some interesting structures or functional groups. In particular a specific structure of some polyesters exhibiting a CH_3 group in alpha position with respect to the oxygen atom of the ester group appears to be significantly detrimental and leads to a very high HRC. A method for the calculation of the contribution of the phosphonate group has been proposed since this group seems to interact with its chemical environment in many cases. Consequently, some phosphonate-based polymers exhibit lower HRC than expected and this observation makes easier the identification of these interactions.

We hope that this work represents a major step towards the development of a method which will permit the prediction of the flame retardancy properties of macromolecular structures.

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Highlights

Flammability of polymers is calculated using a Van Krevelen approach.

The contributions to HRC and THR are calculated for 31 groups.

Some exceptions, such as, phosphorus-containing polymers, are identified.

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