Central European Journal of Energetic Materials, **2013**, *10*(1), 3-15
ISSN 1733-7178

Bomb Calorimetric Correlation Study between Chemical Structure and Enthalpy of Formation for a Linear Energetic Polyphosphazene

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Abstract: Energetic polyphosphazenes constitute a novel class of insensitive binders which potentially outperform conventional carbon-based systems in terms of their energy-densities and glass transition temperatures. To facilitate the calculation of energetic performance for these materials, we report here on the use of bomb calorimetry to determine the standard enthalpies of combustion ($\Delta_cH°$) and formation ($\Delta_fH°$) of 2,2,2-trifluoroethan-1-oxy-/2,3-dinitratopropan-1-oxy-polyphosphazene (I) as the proportion of (energetic) 2,3-dinitratopropan-1-oxy substituents (% Energetic Substitution, % ES) is varied between 31% and 78%. Similar data is presented for the parent polymer bis(2,2,2-trifluoroethan-1-oxy)-polyphosphazene (II) (% ES = 0). $\Delta_cH°$ was found to vary between -2275 kJ·mol^{-1} for the parent polymer II (% ES = 0) and -3415 kJ·mol^{-1} for I with % ES = 78. The corresponding values for $\Delta_fH°$ were -3184 kJ·mol^{-1} and -1566 kJ·mol^{-1}. These data indicate that, as expected, the polymer heats of formation become more favourable – with respect to the energetic performance of the polymer – as the percentage of energetic side chain functionalities (% ES) increases.

Keywords: PBX technology, energetic polyphosphazenes, bomb calorimetry, enthalpy of combustion, enthalpy of formation

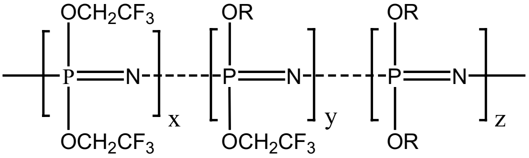
Introduction

Polyphosphazenes have been previously developed as a new category of energetic binder in order to provide improved energy-densities and glass transition temperatures (T_gs) relative to conventional carbon based polymers [1]. However, if polyphosphazenes are to be incorporated into propellant, explosive or pyrotechnic formulations their thermochemistry must be understood, in order to be able to predict performance. A key property used to assess the potential performance of new energetic ingredients in explosives is the enthalpy of formation, although other properties such as enthalpy of combustion are valuable where an external oxidant is employed, such as in composite explosives/rocket propellants and pyrotechnics.

For non-energetic polymers containing the elements C, H, O it is generally possible to calculate the enthalpy of combustion and hence formation by applying the semi-empirical techniques of oxygen consumption calorimetry and molar group additivity of the heats of formation [2, 3]. However, these methods are usually less successful for energetic polymers containing nitrogen and other hetero-atomic species and accuracy becomes significantly impaired [3]. In these cases, direct experimental measurement by bomb calorimetry is normally preferred.

The growth of the plastics industry during the last 50 years has led to a considerable amount of work on the direct thermochemical assessment of various polymeric materials. Polyacrylates [4], polystyrenes [5], polyethers [6] and poly(dimethylsiloxane) [7] are just a few examples of the non-energetic polymers that have been combusted successfully in a bomb calorimeter. Meanwhile, over the last 20 years, with the development of plastic bonded explosive (PBX) technology, a range of isocyanate-curable, carbon-based energetic binders [8] has also been thermochemically assessed by bomb calorimetry [9].

The present study has focussed on the calorimetric appraisal of 2,2,2-trifluoroethan-1-oxy-/2,3-dinitratopropan-1-oxy-polyphosphazene (I) and its parent polymer bis(2,2,2-trifluoroethan-1-oxy)-polyphosphazene (II). I comprises a random mixed substituent polyphosphazene [10a, 11] with the structure shown in Figure 1; within this structure it is possible to vary the relative proportions of the different side chains.



$R = CH_2CH(ONO_2)CH_2ONO_2$ **I**
CH_2CF_3 **II**

Figure 1. Random structures of the energetic polyphosphazenes I.

We define % ES as the percentage of energetic (*i.e.* dinitratopropoxy) side chains present in the molecule. In the current work we have examined samples of I possessing values of % ES between 31% and 78%, together with the parent polymer II, which effectively equates to I with % ES = 0. Specifically, we have sought to establish for polymer I the nature of the relationship between the standard enthalpies of combustion and formation ($\Delta_c H^\circ$ and $\Delta_f H^\circ$) and the chemical structure, as the value of % ES is varied. This work represents the first attempt to correlate experimentally the thermochemical properties of an energetic polyphosphazene with its chemical structure and is intended to aid theoretical prediction of the performance of these materials, within a range of energetic applications.

Materials and Methods

Polymer synthesis and analysis

The synthesis of I [11] (78% ES) and II [10] have been previously described. I (% ES: 70, 65 and 31%) was prepared analogously to that of 78% ES, but using precursor (2,2,2-trifluoroethan-1-oxy-/ 2,2-dimethyl-1,3-dioxolan-4-ylmethanoxy-polyphosphazene) possessing the required degrees of substitution. All such precursors were synthesised by the same synthetic methods, but with modified amounts of sodium 2,2-dimethyl-1,3-dioxolan-4-ylmethoxide and shorter reaction times (Table 1).

Table 1. Reaction conditions for the synthesis of 2,2,2-trifluoroethan-1-oxy-/2,2-dimethyl-1,3-dioxolan-4-ylmethanoxy-polyphosphazene (precursor to I)

% ES found in final product	Sodium alkoxide: polymer II (molar ratio)	Reaction time in refluxing THF (h)
31	1:1	6
65	2:1	12
70	3:1	20
78	5:1	24

The % ES in I, required for calculating the molecular mass of the average repeat units, was measured using ^{1}H NMR spectroscopy and confirmed (one sample only, % ES = 70) by elemental CHN microanalyses (Butterworth Analytical). A summary of the empirical formulae calculated for the polymer repeat units at various values of % ES is presented in Table 2.

Table 2. Percent energetic substituent and empirical formulae for Polymer I

% ES	Unit empirical formula
0 (II)	$C_{4.00}H_{4.00}N_{1.00}O_{2.00}F_{6.00}P_{1.00}$
31	$C_{4.62}H_{5.86}N_{2.24}O_{5.72}F_{4.14}P_{1.00}$
65	$C_{5.30}H_{7.90}N_{3.60}O_{9.80}F_{2.10}P_{1.00}$
70	$C_{5.40}H_{8.20}N_{3.80}O_{10.40}F_{1.80}P_{1.00}$
78	$C_{5.56}H_{8.68}N_{4.12}O_{11.36}F_{1.32}P_{1.00}$

Bomb calorimetry of Polymers I & II and combustion product analysis

Energetic polymers are normally combusted as neat viscous liquids, without burn-rate enhancers or kindling agents [12]. Such materials typically burn very cleanly under pressurised oxygen, leaving no or negligible residue. Polymers I were assessed in this manner, whilst II was combusted in the form of a pressed powder as previously described [13]. The calorimetric measurements were obtained using a Gallenkamp ‘Autobomb CBA-305’ static adiabatic calorimeter, fitted with a Parr 1108-Cl halogen-resistant twin-valve combustion bomb. Ignition of all samples was effected electrically. The temperature increases were monitored by a Gallenkamp F25 platinum-resistance probe digital thermometer, accurate to ± 0.1 K, interfaced to an external PC which allowed online recording of temperature data (sampling interval 3 s). Initial temperatures for both calibration and measurement experiments were equilibrated to 298.0 ± 0.5 K by means of a thermostatic water bath. The calorimeter, which was calibrated using Parr thermochemical standard grade benzoic acid, had a heat equivalent

$\varepsilon = 10890 \pm 40\ \mathrm{J \cdot K^{-1}}$. The general procedures adopted to conduct the calibration of the calorimeter and the calorimetric and chemical control parts of each combustion experiment, including the selection of suitable secondary standards for nitrogen, phosphorus and fluorine, have been described previously [13]. The instrumental parameters of the techniques employed in the chemical control part of the calorimetric investigations (NMR spectroscopy, Ion chromatography and GS-MS) have also been previously described [13].

Five calorimetric experiments and two chemical control experiments were carried out for each sample [13]. All samples burned cleanly under excess oxygen (3.0 MPa), leaving virtually no residue (typically less than 1 mg from ~300 mg of initial sample, Figure 2). Whilst performing chemical analysis of the aqueous combustion products, the non-ideal combustion species monofluoro- (H_2PO_3F), difluoro- (HPO_2F_2), hexafluoro-phosphoric (HPF_6) acids and nitric (HNO_3) acid were detected, in addition to the expected ideal combustion species H_3PO_4, and HF [14].

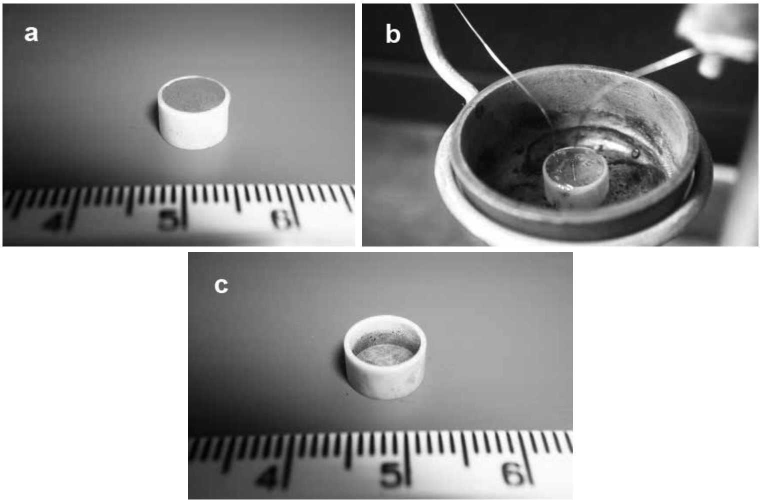


Figure 2. (a) Polymer-filled 150 µl alumina crucible; (b) Polymer-filled alumina crucible with ignition wire, inside bomb crucible; (c) Alumina crucible after combustion. [Scale shown: cm]

Since the fluorinated phosphoric acids are hydrolytically-unstable and persisted long enough in the aqueous bomb solutions to interfere with the calorimetric measurements, a new analytical method was developed to enable quantitation of each species. This allowed us to derive the general stoichiometric equation for the combustion reaction of these polymeric systems and to estimate the (small) magnitude of the corrections to standard states to be applied to the raw combustion energy values. The results of this work, including the general combustion equation for Polymers I and II, have already been reported [13].

Results and Discussion

Synthesis and combustion of Polymer I of varying % ES value

As in all bomb calorimetric experiments, structural and purity control [15] of the polymers is paramount to obtaining meaningful results. Additionally, with macromolecules the presence of end-of-chain units which are structurally different to the main chain units and/or the presence of branching along the polymer chain can also be significant sources of error. For example the measured empirical formula of GAP has been shown to vary as a function of its molecular weight, because the mass contribution of its end-units becomes significant as the molecular weight of the polymer decreases [9].

In the present work the absence of impurities in all samples was ascertained by ^1H and ^{19}F NMR spectroscopy and it was established by GPC that the molecular weights were sufficiently high to render the mass contribution of the end-groups negligible (typical Mn = 14900, Mw = 17000, corresponding to chains of approximately 60 monomer units). The empirical formulae for the repeat units in each of the four samples of Polymer I are given in Table 2, together with that for II.

Derivation of $\Delta_c H°$ and calculation of $\Delta_f H°$

The procedure adopted to derive the standard enthalpies of combustion ($\Delta_c H°$) and formation ($\Delta_f H°$) from the raw bomb energy data was identical for all samples. As a general example, we report only the calculations for Polymer I (% ES = 70). The balanced equation for the exhaustive ideal combustion reaction of Polymer I (% ES = 70) derived from the empirical formula of its monomeric unit may be written [14] as:

$$C_{5.40}H_{8.20}N_{3.80}O_{10.40}F_{1.80}P_{1.00} + 3.05\ O_2 + (nH_2O) \rightarrow 5.40\ CO_{2(g)} + 3.20\ H_2O_{(l)} +$$
$$+ 1.90\ N_{2(g)} + 0.5\ P_2O_{5(s)}\ (\rightarrow 1.00\ H_3PO_{4(aq)}) + 1.80\ HF_{(aq)}$$

This expression excludes consideration of the energies of formation and hydrolysis of HNO_3, H_2PO_3F, HPO_2F_2 and HPF_6, for which thermochemical correction is normally applied during evaluation of the standard internal energy of combustion (Table 3) [13]. (HPF_6 was only observed for samples with % ES = 0 and 31.)

Table 3. Thermochemical corrections for the formation and hydrolysis of monofluoro- and difluorophosphoric acids applied to the measured internal energy values of Polymer I (% ES = 70)

Measured value of -Δ_cU ($J\cdot g^{-1}$) §	HPO_2F_2 formed (mmol) from 1 g sample	H_2PO_3F formed (mmol) from 1g sample	HPF_6 formed (mmol) from 1g sample	Energy (-ΔU) contributed by hydrolysis of HPO_2F_2 (J)	Energy (-ΔU) contributed by hydrolysis of H_2PO_3F (J)	Total energy correction applied to measured -Δ_cU (J)	Final correctedvalue of -$\Delta_cU°$ ($J\cdot g^{-1}$)
9220±160	0.264	1.204	0	3.7	18.4	22.1	9240*±160

§ The small energy term associated with the formation of HNO_3 has been accounted for previously [13].

* Rounded to 3 significant figures

$\Delta_cH°$ is derived from the standard internal energy of combustion ($\Delta_cU°$) by application of Eq. 1 [15] which assumes the ideal gas law to apply at the typical oxygen bomb pressure (3.0 MPa):

$$\Delta_cH° = \Delta_cU° + \Delta nRT \tag{1}$$

where ΔnRT is the compression energy or 'work' term and Δn is the difference between the gaseous moles of products and reactants, R is the universal gas constant and T is the absolute temperature. Thus, for the above example:

$$\Delta n = +5.40 + 1.90 - 3.05 = +4.25 \text{ mol}$$
$$\text{and } \Delta nRT = (+4.25)(\text{mol}) \times 8.314\ (J\cdot mol^{-1}\cdot K^{-1}) \times 298.15\ (K) = +10.5 \text{ kJ}$$

From Table 3, with the estimated monomer unit molecular mass = 357.9, the corrected, molar, standard internal energy of combustion (with the uncertainty interval taken as twice the standard deviation of the mean) was:

$$\Delta_cU° \text{ Polymer I (\% ES = 70)} = -9240 \pm 160\ J\cdot g^{-1} = -3307 \pm 57\ kJ\cdot mol^{-1}$$

from which the standard enthalpy of combustion is calculated:

$\Delta_c H°$ (Polymer I (%ES = 70%) = - 3307 + (+ 10.5) = - 3296 ± 57 kJ·mol^{-1} = -9209 ± 160 J·g^{-1}

where the units of $\Delta_c H°$ and $\Delta_f H°$ (kJ·mol^{-1} and J·g^{-1} respectively) relate to the average repeat unit of the polymer.

Finally, using the latest CODATA values [16] (Table 4) for the standard enthalpies of formation of the ideal products of reaction (after secondary reaction with water), the $\Delta_f H°$ for Polymer I (% ES = 70) can be calculated as follows:

$\Delta_f H°$ Polymer I (% ES = 70) = | $\Sigma\Delta_f H°$ (products) – $\Delta_c H°$ Polymer I (% ES = 70) | = - {(5.40 × 393.51) + (3.20 × 285.83) + (1.90 × 0) + (1.80 × 335.35) + (1.00 × 1299.0)} – (- 3296) = -4942.2 + 3296 = -1646 kJ·mol^{-1} = -4599 J·g^{-1}.

Table 4. CODATA formation enthalpy values of key combustion products

Ideal combustion product	$-\Delta H°_{f(298.15\ K)}$ / kJ·mol^{-1}
$CO_{2\ (g)}$	393.51 ± 0.13
$H_2O_{\ (l)}$	285.83 ± 0.04
$N_{2\ (g)}$	0
$H_3PO_{4\ (aq)}$	1299.0 ± 1.5
$HF_{\ (aq)}$	335.35 ± 0.65

Propagation of the uncertainties associated with the $\Delta_f H°$ values of the products of reaction to the main uncertainty associated with the $\Delta_c H°$ value can be shown to be negligible if compared to the main calorimetric uncertainty interval by application of Equation 2 to the standard enthalpy terms summated, where $\delta\Delta_f H°x$ is the absolute standard deviation associated with the value $\Delta_f H°x$:

$$\delta\left(\Delta_f H°_{Polymer\ I}\right)=\left[\left(\delta\Delta_f H°_{CO_2}\right)^2+\left(\delta\Delta_f H°_{H_2O}\right)^2+\left(\delta\Delta_f H°_{H_3PO_4}\right)^2+ \right.$$
$$\left. + \left(\delta\Delta_f H°_{HF}\right)^2+\left(\delta\Delta_c H°_{Polymer\ I}\right)^2\right]^{0.5} \tag{2}$$

By application of Eq. 2, the propagation of error due to the uncertainty intervals associated with the CODATA values can be calculated as: = 57.02 kJ·mol^{-1}.

The final value of $\Delta_f H°$ may therefore be expressed as:

$\Delta_f H°$ Polymer I (% ES = 70)= -1646 ± 57 kJ·mol^{-1} = -4599 ± 160 J·g^{-1}

The standard enthalpies of combustion ($\Delta_cH°$) and hence formation ($\Delta_fH°$) of the other samples were derived in the same manner.

For the sake of completeness we report in Table 5 the thermochemical corrections applied to the raw combustion energy data for the fluorinated phosphoric acids detected during the combustion of the non-energetic starting material, Polymer II (effectively Polymer I, % ES = 0). This sample generated, in addition to HPO_2F_2 and H_2PO_3F, significant amounts of HPF_6. The magnitude of the additional correction to account for the formation of this extra species, which is reversed in sign to that of the other fluorinated acids [17], is also very small when compared to the total bomb energy change value.

Table 5. Thermochemical corrections to account for the formation and hydrolysis of monofluoro-, difluoro- and hexafluoro-phosphoric acids, applied to the measured Δ_cU values of II

Measured value of $-\Delta_cU$ ($J\cdot g^{-1}$) §	HPO_2F_2 Formed (mmol) from 1 g sample	H_2PO_3F Formed (mmol) from 1g sample	HPF_6 Formed (mmol) from 1g sample	Energy ($-\Delta U$) contributed by hydrolysis of HPO_2F_2 (J)	Energy ($-\Delta U$) contributed by hydrolysis of H_2PO_3F (J)	Energy ($-\Delta U$) contributed by hydrolysis of HPF_6 (J)	Total energy correction applied to measured $-\Delta_cU$ (J)	Final corrected value of $-\Delta_cU°$ ($J\cdot g^{-1}$)
9340±210	1.063	1.254	0.520	15.0	19.2	-16.7	17.5	9360±210

§ The small energy term associated with the formation of HNO_3 has been accounted for previously [13].

Without the addition of water to the bomb prior to the experiment, combustion of II should generate fluorine gas, because this is known to form (in the absence of water vapour) during the combustion of highly-fluorinated compounds which do not contain hydrogen (*e.g.* hexafluorobenzene and octafluorotoluene [18, 19]). Given that each empirical monomer unit contains only four hydrogen atoms with which to form HF, an excess of two fluorine atoms per unit is theoretically available to contribute to the formation of fluorinated carbon and/or phosphorus based gaseous species [13].

In order to gain more insight into the combustion stoichiometry of II, a sample was combusted without the addition of any water. Qualitative analysis of the exhaust gases by GC-MS failed to detect either fluorine gas or any of the fluorinated gaseous species predicted above. However, water vapour (traces) was detected in the bomb exhaust, so it is assumed that any F_2 produced reacted rapidly with water to yield aqueous HF (also detected) and oxygen.

In view of these results, it was assumed that (a) no gaseous fluorinated carbon and/or phosphorus species had formed, (b) the hydrogen in the monomer unit was converted to water, (c) the fluorine in the monomer unit was initially converted to $F_{2(g)}$ which then reacted with water (whether adventitious, formed in the reaction and/or added to the bomb at the outset) to give $HF_{(aq)}$ and $O_{2(g)}$. One mole of polymer would therefore liberate 3 moles of fluorine gas which would react with water to give 1.5 moles of $O_{2(g)}$ which also contributes towards the total volume increase of the bomb process and hence upon the final calculation of the work term, ΔnRT.

$C_{4.00}H_{4.00}N_{1.00}O_{2.00}F_{6.00}P_{1.00} + 5.25O_{2(g)} \rightarrow 4.00CO_{2(g)} + 0.5N_{2(g)} + 2H_2O_{(l)}$
$+ 3F_{2(g)} + 0.5\ P_2O_{5(s)}\ (\rightarrow 1.00H_3PO_{4\,(aq)})$
and
$3F_{2(g)} + 3H_2O_{(l)} \rightarrow 6HF_{(aq)} + 1.5O_{2(g)}$
$\Delta n = +\,4.00 + 0.5 + 1.5 - 5.25 = +0.75$ mol
$\Delta nRT = (+0.75)\ (\text{mol}) \times 8.314\ (\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \times 298\ (\text{K}) = +\ 1.86$ kJ

From bomb calorimetry, the corrected $\Delta U°_c = -\ 9360 \pm 210\ \text{J}\cdot\text{g}^{-1}$
$= -\ 2275 \pm 51\ \text{kJ}\cdot\text{mol}^{-1}$
and since the work term is 1.86 kJ, the enthalpy of combustion is given by:
$\Delta_cH° = -\ 2275 + (+1.86) = -\ 2273 \pm 51\ \text{kJ}\cdot\text{mol}^{-1} = -9354 \pm 210\ \text{J}\cdot\text{g}^{-1}$

Finally, using the CODATA values of the enthalpy of formation for the ideal combustion products,

$\Delta_fH°_{\text{II, (298.15 K)}} = -\{(4.00 \times 393.51) + (1.5 \times 0) + (2.00 \times 285.83) + (0.5 \times 0) + (6.00 \times 335.35) + (1.00 \times 1299.0)\} - (-2273) =$
$-5457 + 2273 = -3184 \pm 51\ \text{kJ}\cdot\text{mol}^{-1} = -13102 \pm 210\ \text{J}\cdot\text{g}^{-1}$

Table 6 presents a summary of the Δ_cU-derived $\Delta_cH°$ and $\Delta_fH°$ values for I at different %ES values, while Figure 3 shows a plot of $\Delta_cH°$ and $\Delta_fH°$ against % ES. Figure 3 confirms the anticipated correlation between the enthalpies of combustion and formation of I and its % ES. These data show that as the % ES increases so too does the enthalpy of combustion, whilst the enthalpy of formation exhibits decreasing exothermicity. The latter feature indicates that enthalpies of detonation should increase with % ES, whilst the former feature suggests that high values of % ES could be energetically advantageous, even when using an external oxidant (*e.g.* in composite propellant applications).

Table 6. $\Delta_cH°$ and $\Delta_fH°$ (expressed in both $kJ \cdot mol^{-1}$ and $J \cdot g^{-1}$) of Polymer I with different % ES values. (At % ES = 0, Polymer I = Polymer II)

% ES	$-\Delta_cH°$ ($kJ \cdot mol^{-1}$)	$-\Delta_cH°$ ($J \cdot g^{-1}$)	$-\Delta_fH°$ ($kJ \cdot mol^{-1}$)	$-\Delta_fH°$ ($J \cdot g^{-1}$)
0	2275 ± 51	9360 ± 210	3184 ± 51	13102 ± 210
31	2616 ± 41	8871 ± 140	2135 ± 41	7277 ± 140
65	3018 ± 37	8630 ± 105	1900 ± 37	5433 ± 105
70	3296 ± 57	9209 ± 160	1646 ± 57	4599 ± 160
78	3415 ± 85	9201 ± 230	1566 ± 85	4219 ± 230

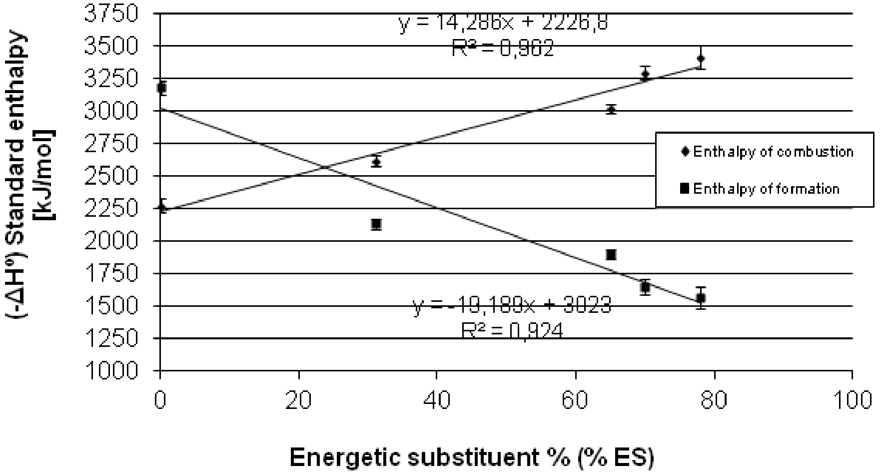


Figure 3. Cartesian plot of $\Delta_cH°$ and $\Delta_fH°$ of Polymer I as a function of Polymer % ES value, showing error bars.

Conclusions

Standard enthalpies of combustion and formation have been determined for samples of Polymer I with % ES in the range of 31% to 78%. Similar determinations on Polymer II have provided data representing the bounding case for Polymer I with % ES = 0. A clear correlation has been demonstrated between both the enthalpies of combustion and formation for I and its degree of substitution by energetic functionalities. Thus, as % ES increases, so too does the enthalpy of combustion, whilst the heat of formation demonstrates reducing exothermicity. These data indicate that – as might intuitively be expected – high values of % ES are likely to facilitate the most favourable energetic properties in formulations containing I.

Acknowledgements

We thank Dr David Duncan (AWE) for the provision of GPC data.

References

[1] Golding P., Trussell S.J., Energetic Polyphosphazenes – a New Category of Binders for Energetic Formulations, *National Defense Industrial Association **2004** Insensitive Munitions and Energetic Materials Technology Symposium*, San Francisco, California, 15th-17th November; Golding P., Trussell S. J., Enhanced Energetic Polyphosphazenes, *National Defense Industrial Association **2006** Insensitive Munitions and Energetic Materials Technology Symposium*, Bristol, 24th-28th April.

[2] Walters R.N., Hackett S.M., Lyon R.E., Heats of Combustion of High Temperature Polymers, *Fire Mater.*, **2000**, *24*, 245-252.

[3] Walters R.N., Molar Group Contributions to the Heat of Combustion, *Fire Mater.*, **2002**, *26*(3), 131-145.

[4] Girdhar H.L., Peerzada G.M., Handoo D., Specific Enthalpies of Combustion of Some Acrylic Polymers, *Fuel*, **1985**, *64*(7), 1011-1013.

[5] Ribeiro da Silva M.A.V., Cabral J.I.T., Experimental Study on the Thermochemistry of 5-Nitroindole and 5-Nitroindoline, *J. Chem. Thermodyn.*, **2009**, *41*, 355-360.

[6] Andruzzi F., Barnes D.S., Plesch P.H., Enthalpy of Polymerization of Endo-2-methyl-7-oxabicyclo[2.2.1]heptane, *Makromol. Chem.*, **1975**, *176*(7), 2053-2057.

[7] Sanden R., Determination of the Heat of Formation of Poly(dimethysiloxane), Int. Jahrestatung Fraunhofer – Institut Fuer Treib- und Explosivstoffe, *17th Anal. Prop. Explos. Chem. Phys. Methods*, **1986**, 65/1-65/13.

[8] Desai H.J., Cunliffe A.V., Hamid J., Honey P.J., Stewart M.J., Amass A.J., Synthesis and Characterisation of α,ω-Hydroxy and Nitrato Telechelic Oligomers of 3,3-(Nitrato-methyl)methyl Oxetane (NIMMO) and Glycidyl Nitrate (GLYN), *Polymer*, **1996**, *37*(15), 3461-3469.

[9] Diaz E., Brousseau P., Ampleman G., Prud'homme R.E., Heats of Combustion and Formation of New Energetic Thermoplastic Elastomers Based on GAP,

PolyNIMMO and PolyGLYN, *Propellants Explos. Pyrotech.*, **2003**, *28*(3), 101-106.

[10] (a) Allcock H.R., Maher A.E., Ambler C.M., Side Group Exchange in Poly(organophosphazenes) with Fluoroalkoxy Substituents, *Macromolecules*, **2003**, *36*(15), 5566-5572; (b) Montague R.A., Matyjaszewski K., *J. Am. Chem. Soc.*, **1990**, *112*(18), 6721-6729.

[11] Golding P., Trussell S.J., *Novel Energetic Polyphosphazenes Useful for Explosive Binding*, Patent application **2006**, WO 032882A-1.

[12] Schmiddt R.D., Manser G.E., Heats of Formation of Energetic Oxetane Monomers and Polymers, *32nd Int. Annu. Conf. ICT*, Karlshrue, Germany, **2001**, 140-1 to 140-8.

[13] Bellamy A.J., Contini A.E., Golding P., Oxygen Combustion Calorimetry of Samples Containing Phosphorus and Fluorine: Formation of Fluorinated Phosphoric Acids as Non-ideal Combustion Species, *Combust. Sci. Technol.*, **2008**, *180*, 2103-2126.

[14] Bellamy A.J., Contini A.E., Golding P., Trussell S.J., Bomb Calorimetric Study of a Series of Energetic Linear Polyphosphazenes, *New Trends Res. Energ. Mater., Proc. Semin., 8th*, Pardubice, Czech Republic, **2005**, 134-141.

[15] *Experimental Thermochemistry*, (Rossini F.D., Ed.), Interscience Publishers, New York, **1956**.

[16] Cox J.D., Wagman D.D., Medvedev V.A., *CODATA Key Values for Thermodynamics*, Hemisphere Publishing Corporation, New York, **1989**.

[17] Contini A.E., Calorimetric Investigations of a Series of Energetic Polyphosphazenes, *PhD Thesis*, Cranfield University, **2005**. Document available online at https://dspace.lib.cranfield.ac.uk/handle/1826/2997.

[18] Krech M., Price S.J.W., Yared W.F., Determination of the Heat of Formation of Octafluorotoluene and Calculation of D[C_6F_5-F] – D[C_6F_5-CF_3], *Can. J. Chem.*, **1973**, *51*(22), 3662-3664.

[19] Krech M., Price S.J.W., Yared W.F., Determination of the Heat of Formation of Hexafluorobenzene, *Can. J. Chem.*, **1972**, *50*(18), 2935-2938.