The Influence of Molecular Weight on Explosive Hazard

Kason Bala and Peter Golding

Energetic Polyphosphazenes – a new category of binders for energetic formulations

Peter Golding and Stephen J Trussell

Bomb calorimetric study of a series of energetic linear polyphosphazenes

Anthony J. Bellamy, Alessandro E. Contini, Peter Golding and Stephen J. Trussell

PERFORMANCE VERSUS HAZARD

IM Requirements: High Performance/Low Hazard

Inverse Relationship Typical

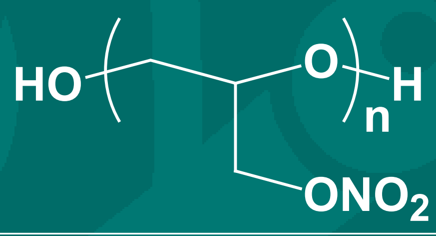
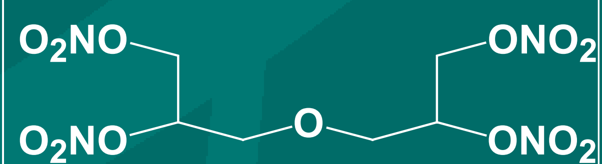
Mitigation Techniques:

- Micronisation
- Coating (PBXs)
- Dilution (Energy Loss)

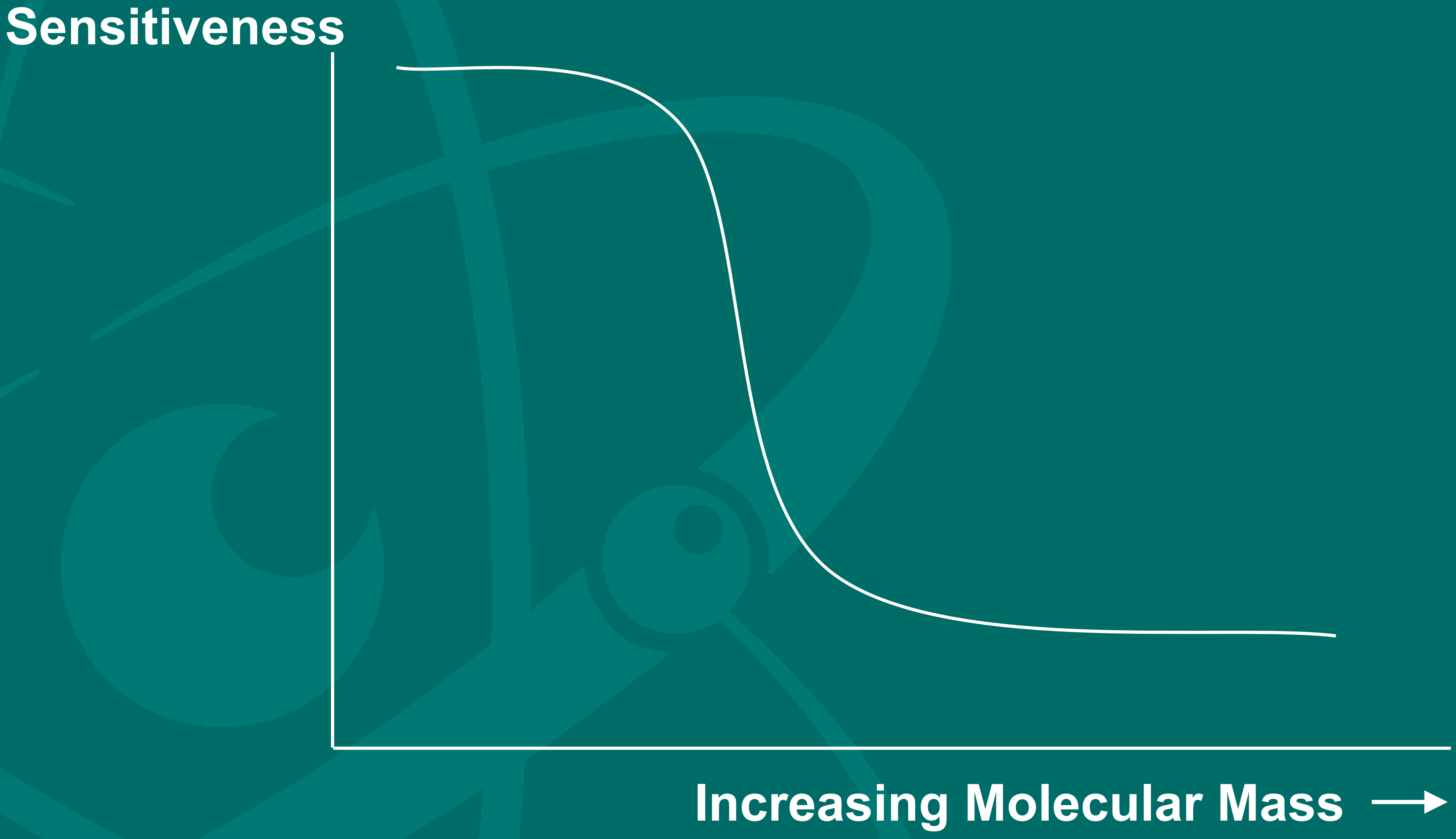
Key Influences on Hazard:

- Chemical Stoichiometry (Oxygen Balance)
- Chemical Structure
- Physical Morphology

COMPARATIVE HAZARD DATA

Name	Structure	Impact Sensitivity (N m)	EMTAP Test No 8 (cm)	O.B. (%)
Glycidyl nitrate		2	4.1	-60.5
DEGDN		1.5	11.8	-40.8
PolyGLYN			>126	-60.5
Diglycerol tetranitrate		1.5	18.7	-18.5

HYPOTHETICAL RELATIONSHIP BETWEEN SENSITIVENESS AND MOLECULAR MASS



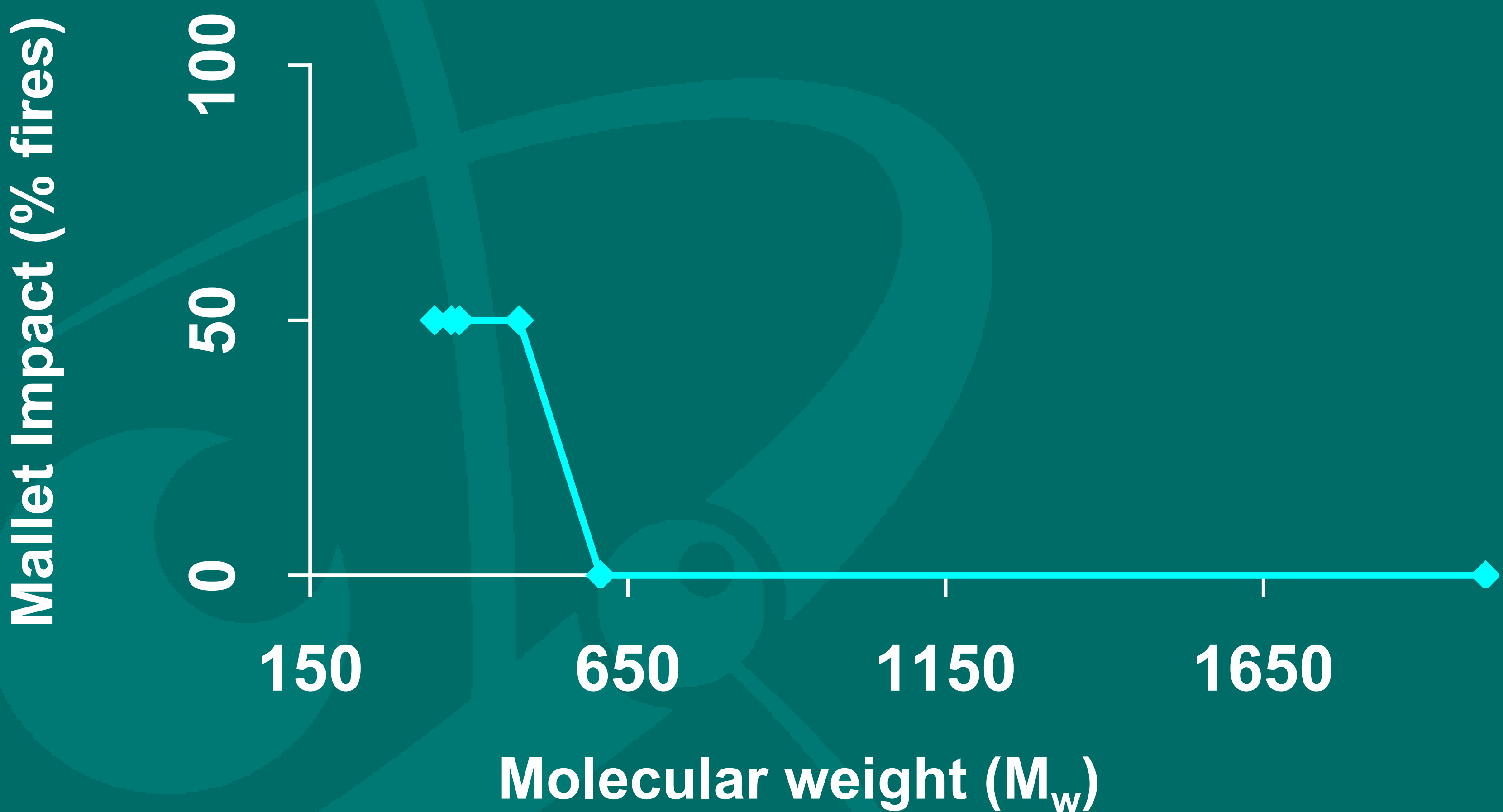
GLYN OLIGOMERS

Product Distribution Oligomer size, n	HPLC Ratio (%)	Average Molecular Weight (M_W)
2	100	346
2:3	83:17	372
2:3:4	81:14:5	385
2:3:4:5	42:33:19:6	479
2:3:4:5:6:7	12:36:24:16:8:4	607
polyGLYN	-	~2000

SMALL-SCALE HAZARD TEST DATA

Product Distribution Oligomer size, n	M_W	Mallet Impact (Steel/Steel) (%)	Hot Plate (300°C)	EMTAP Test No 8, Median Height (cm)
Glycidyl nitrate	119	Volatile	Volatile	4.1
2	346	50	Flame	18.7
2:3	372	50	Flame	
2: 3:4	385	50	Flame	
2:3:4:5	479	50	Flame	
2:3:4:5:6:7	607	0	Charring	
polyGLYN	~2000	0	Charring	Out of range

SMALL-SCALE HAZARD DATA



HAZARD DIFFERENCES BETWEEN SMALL MOLECULES AND POLYMERS - POSSIBLE CAUSES

Volatility

Ease of generation of small fragments

Number of degrees of freedom

Energetic Polyphosphazenes – a new category of binders for energetic formulations

Peter Golding and Stephen J Trussell

PLASTIC BONDED EXPLOSIVES (PBXs)

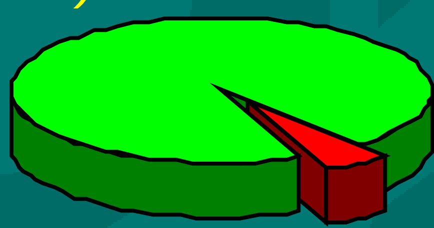
Crystalline Filler + Polymeric Binder + Additives

Filler Provides Energy

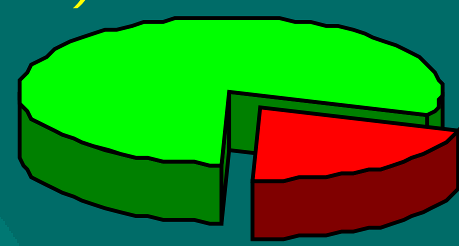
Binder Provides Shape/Robustness

& Desensitises Most Explosives

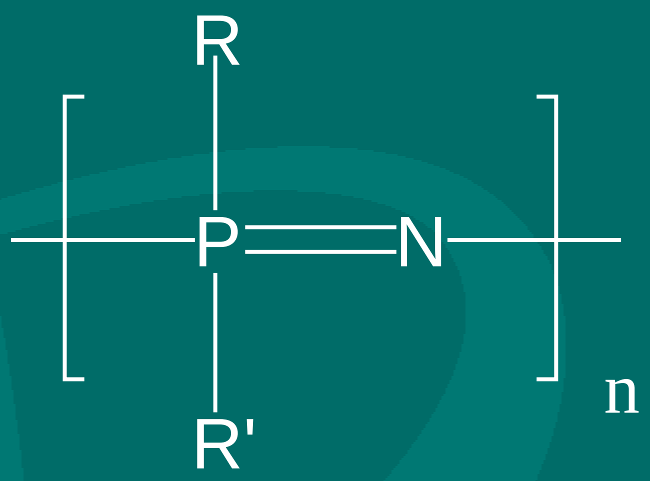
Traditional Inert Binder



Energetic Binder



POLYPHOSPHAZENES



ADVANTAGES

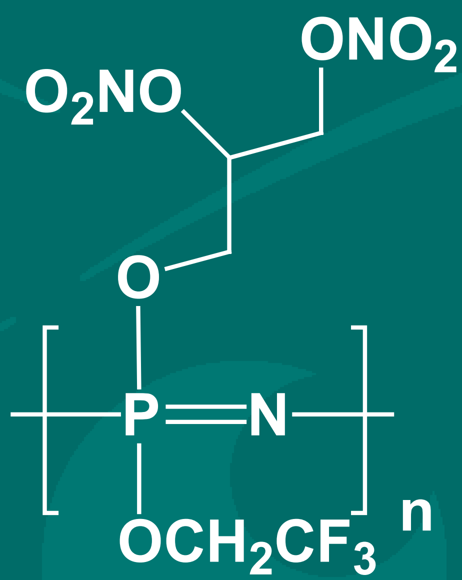
Can be dense

Can have low T_gs

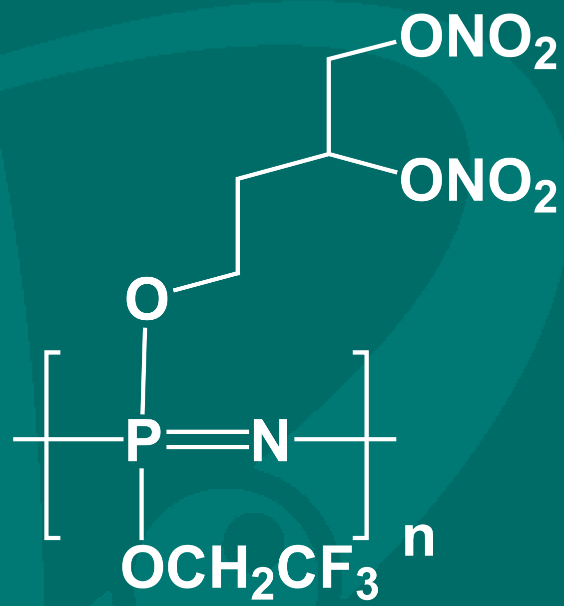
Potential synthetic flexibility

Chemical and thermal stability

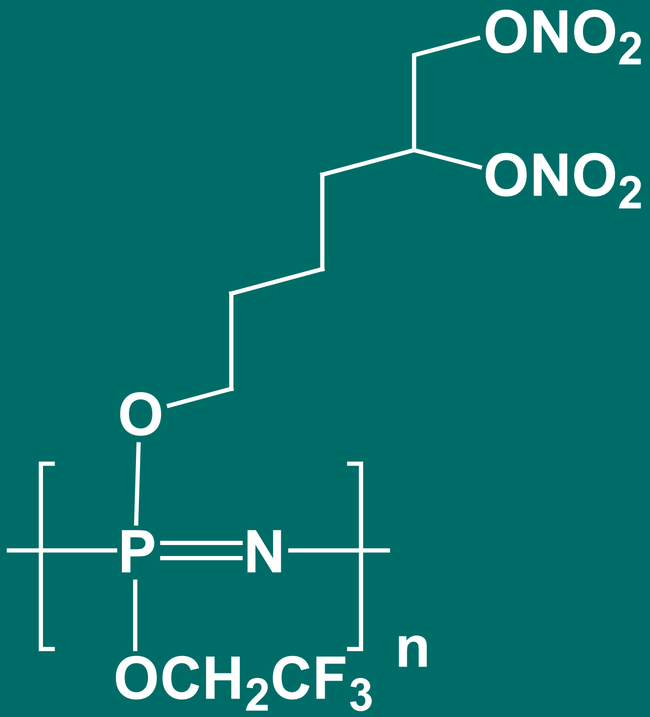
NITRATE ESTER FUNCTIONALISED POLYPHOSPHAZENES SYNTHESISED AT AWE



C3 PPZ

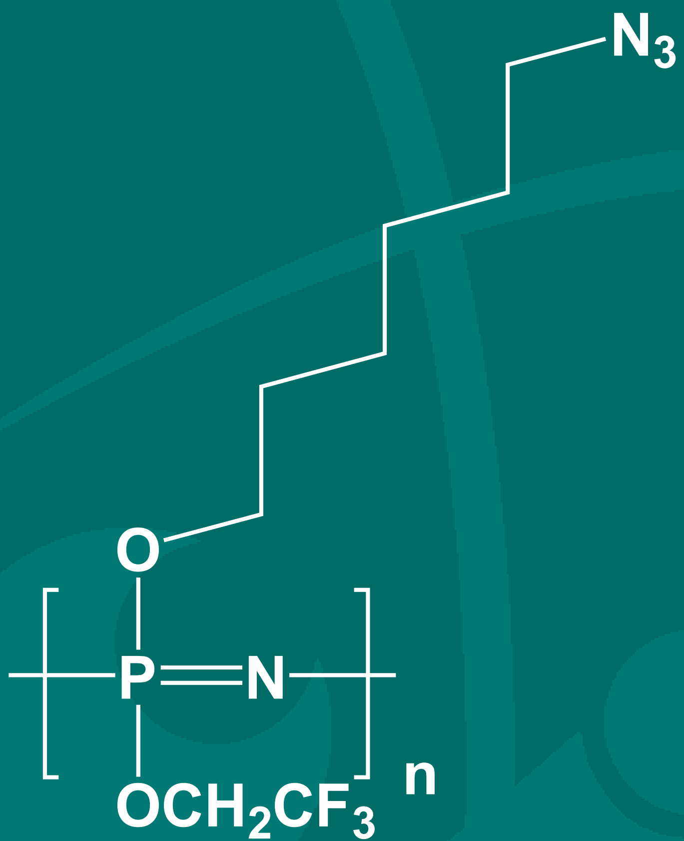


C4 PPZ

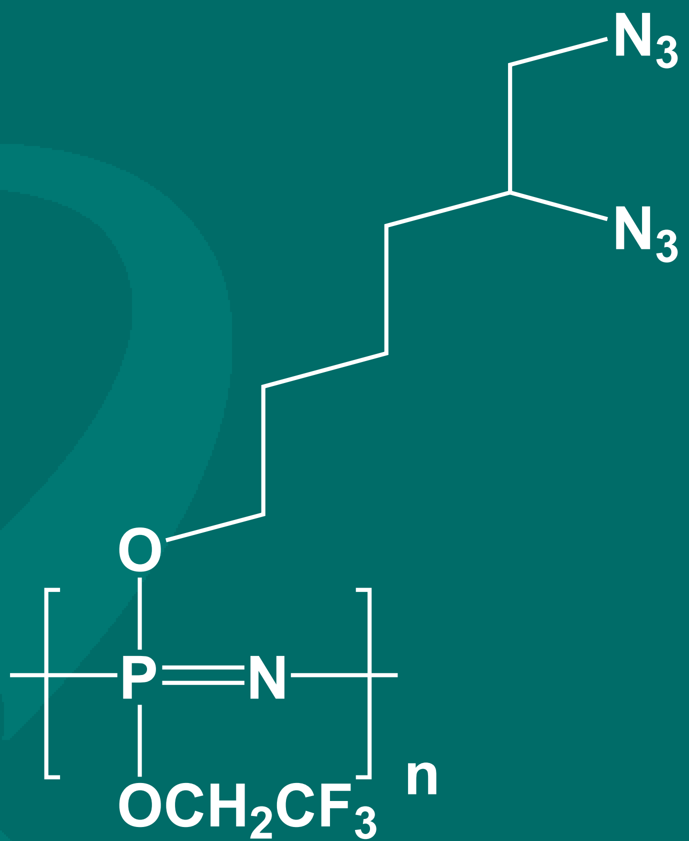


C6 PPZ

AZIDE FUNCTIONALISED POLYPHOSPHAZENES SYNTHESISED AT AWE

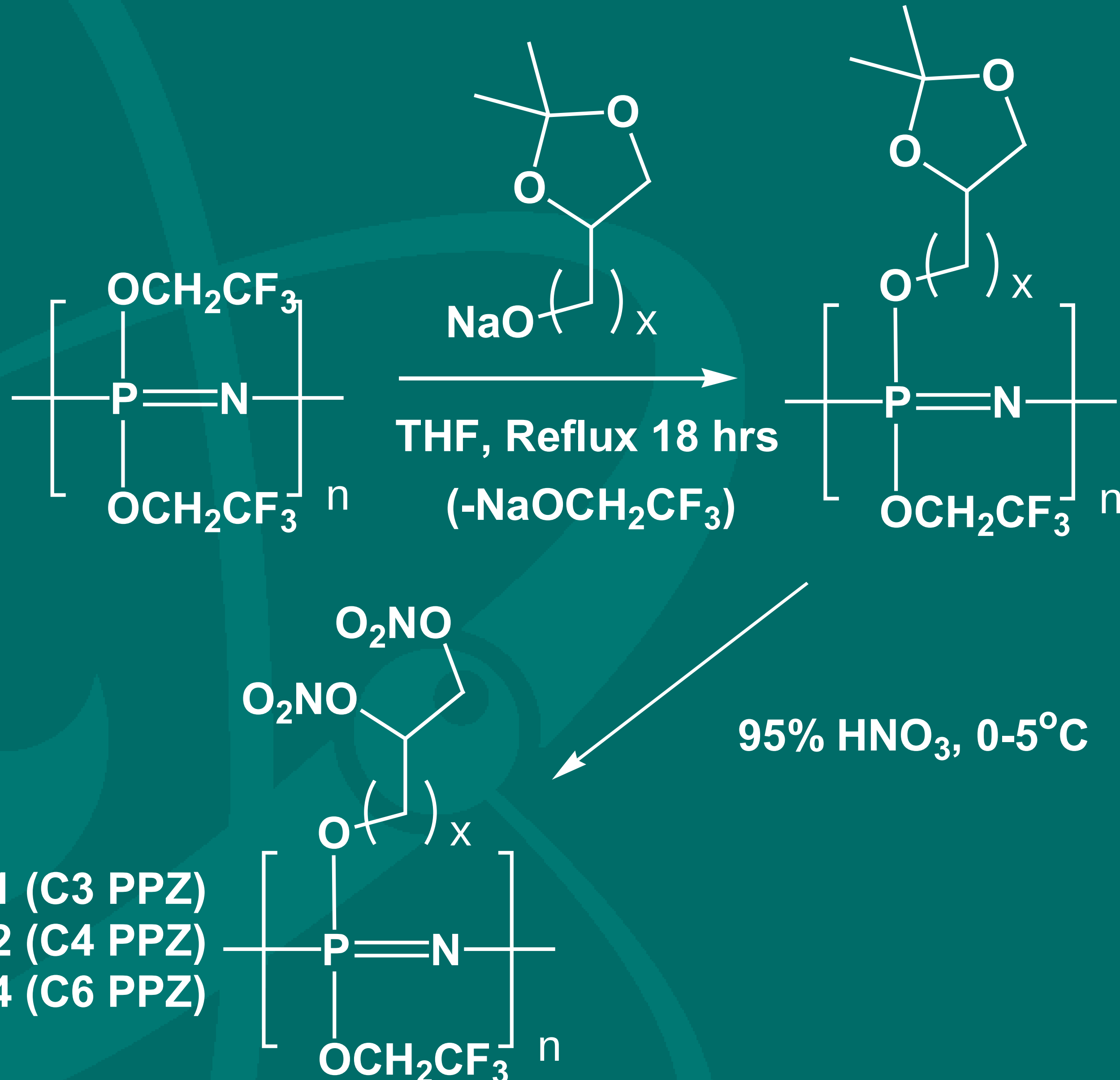


C6 Mono-N_3 PPZ



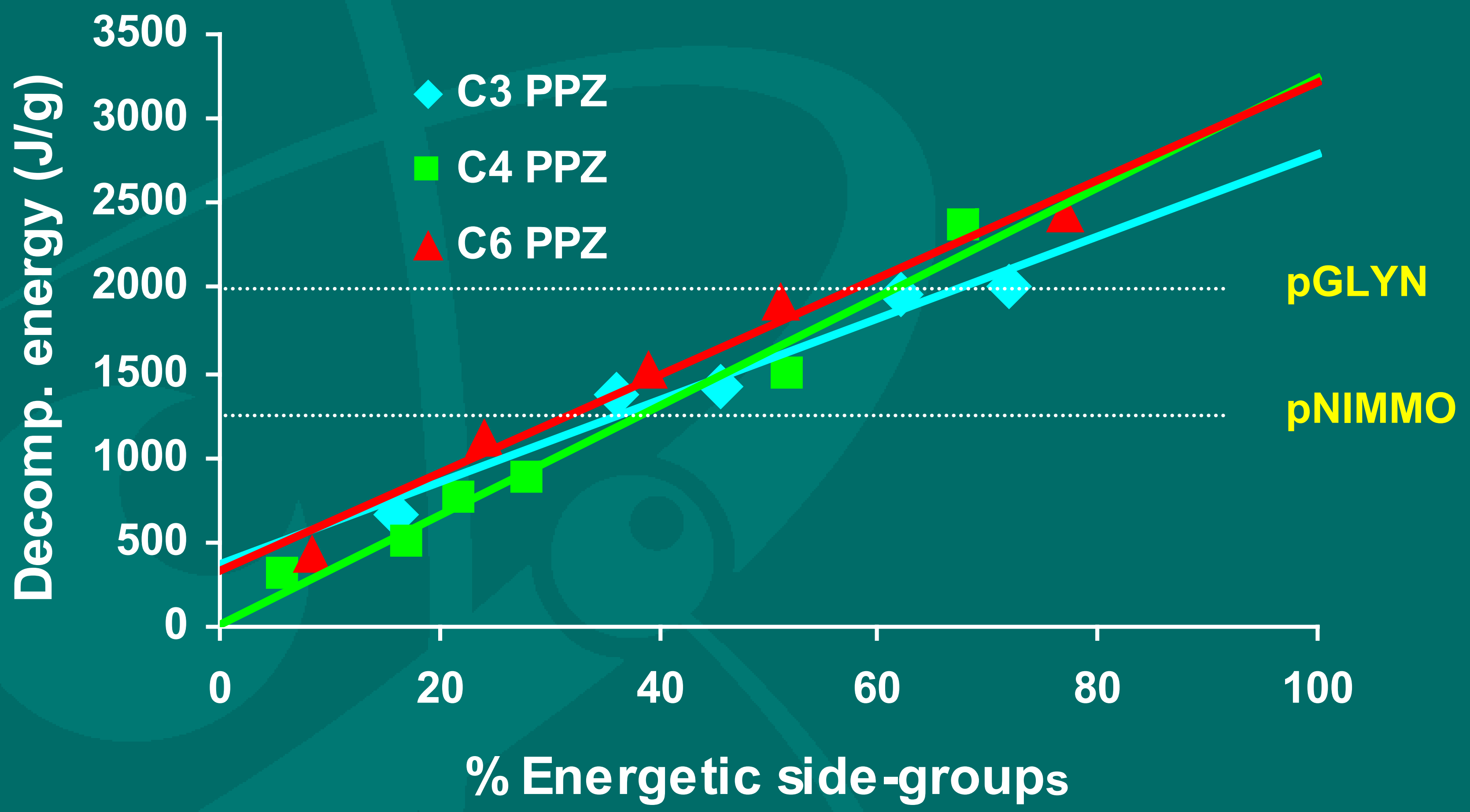
C6 Di-N_3 PPZ

SYNTHESIS OF NITRATE ESTER FUNCTIONALISED POLYPHOSPHAZENES

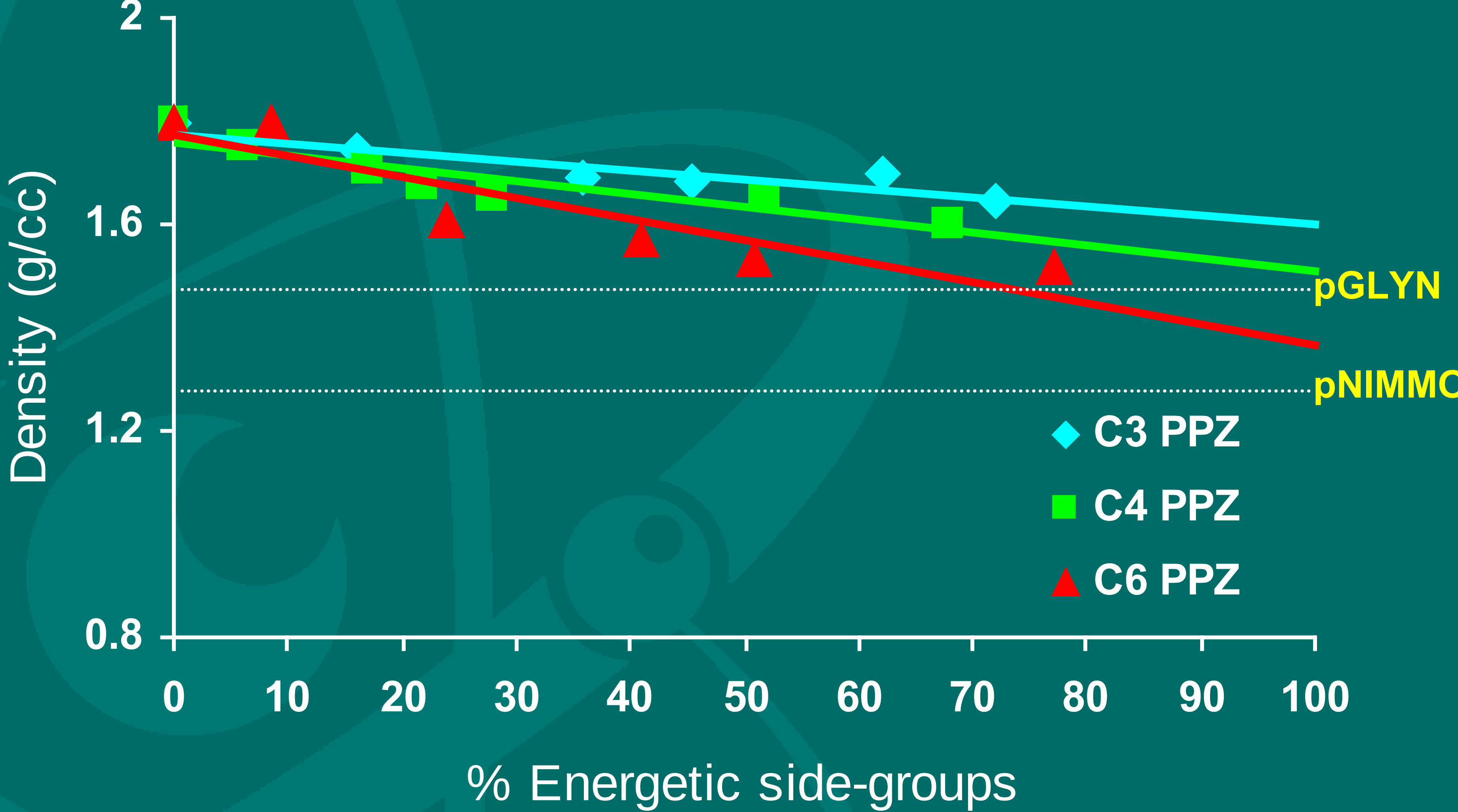


x = 1 (C3 PPZ)
x = 2 (C4 PPZ)
x = 4 (C6 PPZ)

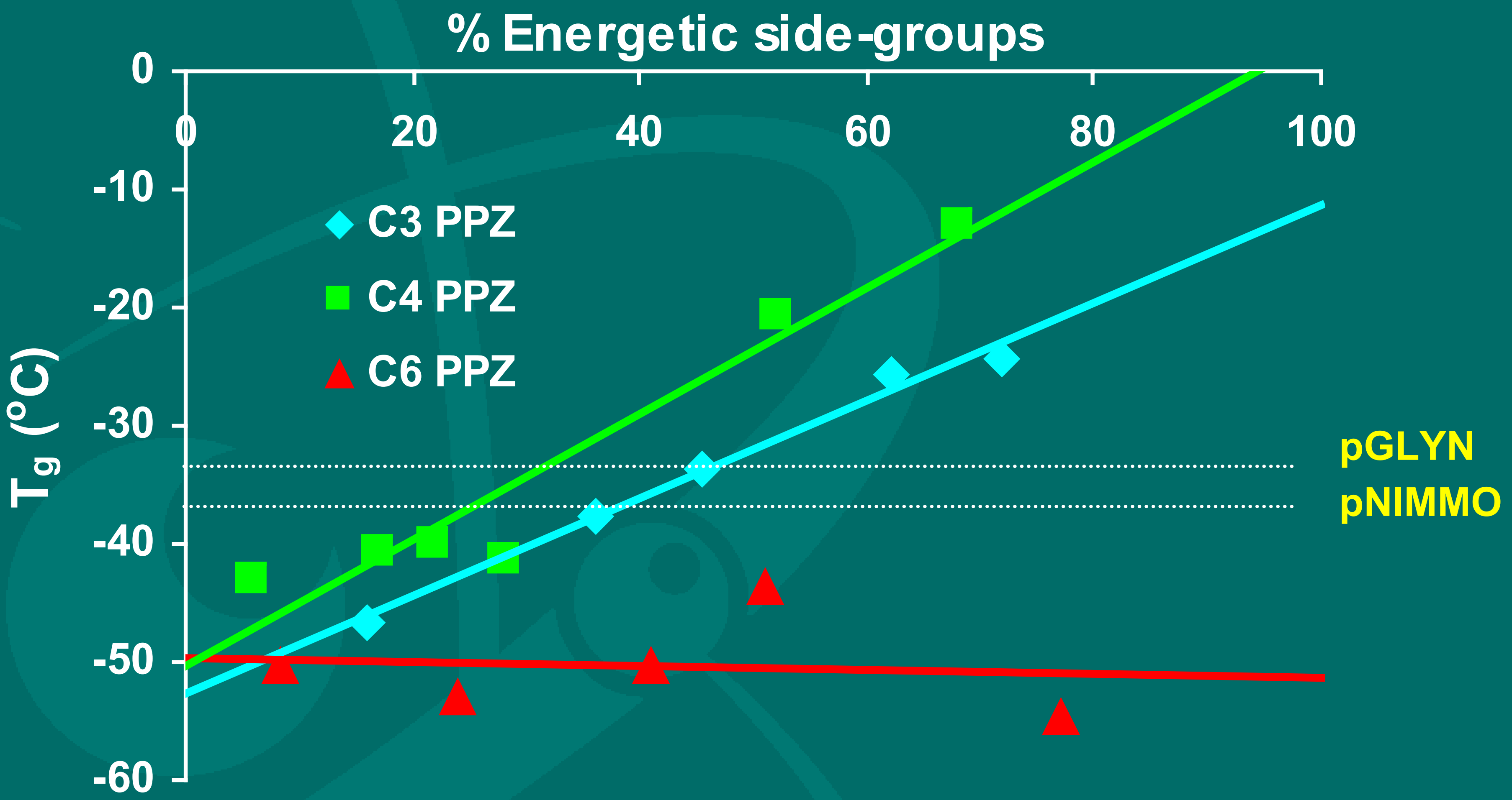
DECOMPOSITION ENERGIES OF NITRATE ESTER FUNCTIONALISED POLYPHOSPHAZENES



DENSITY VALUES OF NITRATE ESTER FUNCTIONALISED POLYPHOSPHAZENES



GLASS TRANSITION TEMPERATURES OF NITRATE ESTER FUNCTIONALISED POLYPHOSPHAZENES



COMPARATIVE PHYSICAL DATA FOR NITRATE ESTER FUNCTIONALISED POLYMERS

Material	% Energetic side-groups	Density (g/cm^3)	T_g (ºC)	Decomp. Energy (DSC) (J/g)	Energy Density (J/cm^3) [% higher than pGLYN]
C3 PPZ	72	1.65	-25	2020	3330 [14]
C4 PPZ	68	1.60	-13	2370	3790 [30]
C6 PPZ	77	1.52	-55	2430	3690 [26]
PolyGLYN	-	1.46	-30	2000	2920
PolyNIMMO	-	1.26	-33	1300	1640

HAZARD TEST DATA FOR C6 PPZ CONTAINING 70% NITRATE ESTER FUNCTIONALISED SIDE-GROUPS

HAZARD TEST	RESULTS/OBSERVATIONS
Mallet impact (steel on steel)	0% fires
Mallet friction (steel on steel)	0% fires
Electric spark	No ignitions at 4.5J
Flame	Burns quietly, requires high temperatures to ignite. Sintered char residue
DSC	Large exotherm, onset at 186°C

FORMULATION WITH POLYPHOSPHAZENES

Intended for pressable systems

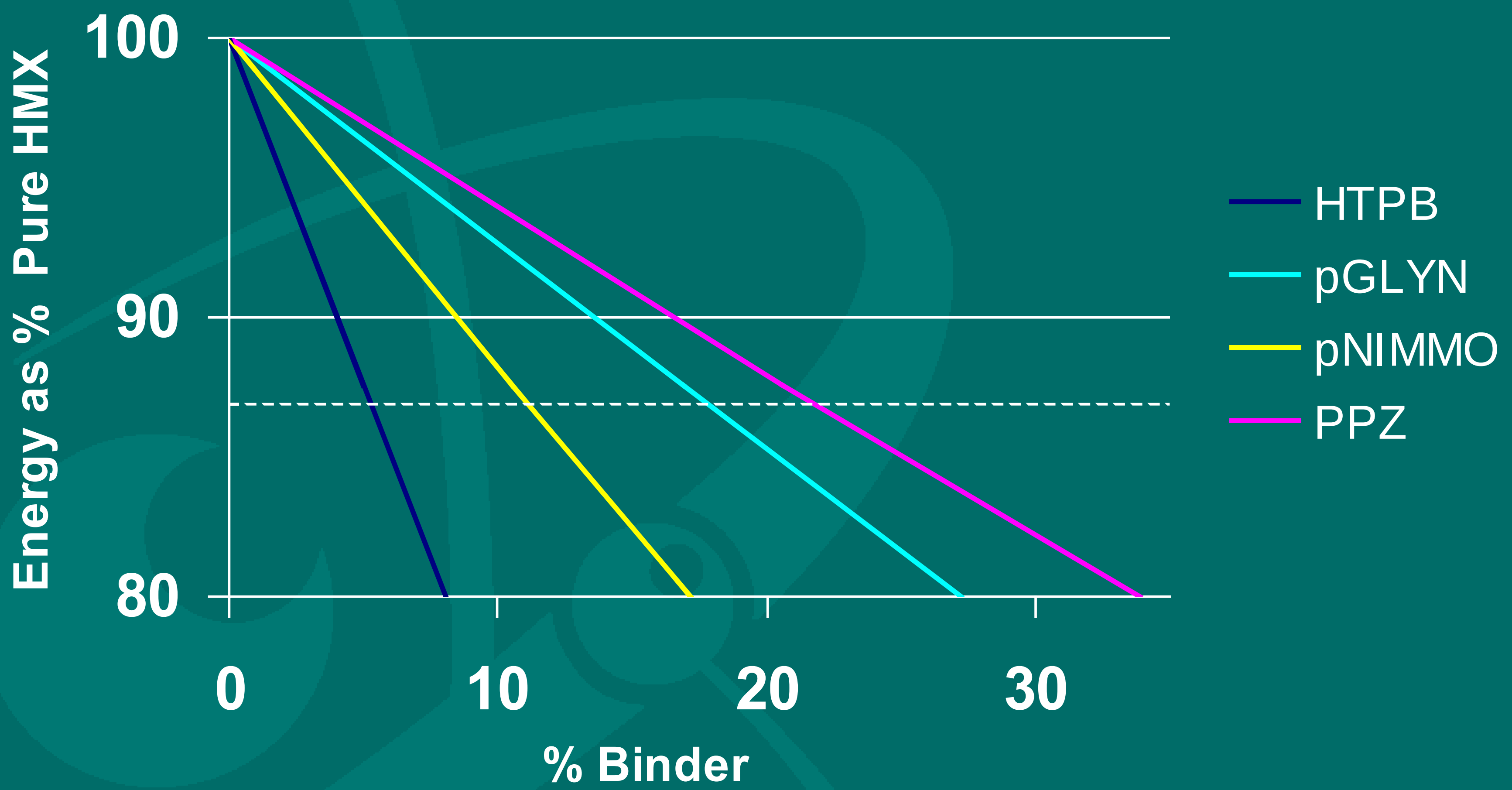
Very promising binder properties

Preliminary experiments with: HNS, HMX, TATB & FOX-7

Miscible with polyGLYN

Lowers Tg of polyGLYN

INFLUENCE OF BINDER ON PERFORMANCE



Bomb calorimetric study of a series of energetic linear polyphosphazenes

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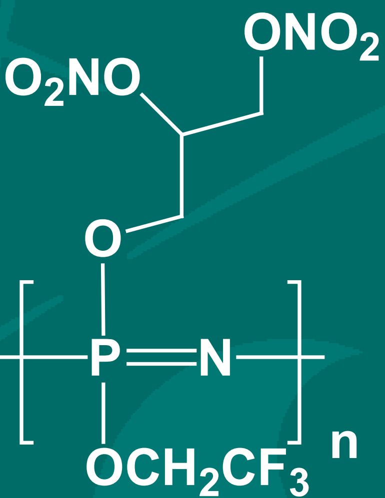
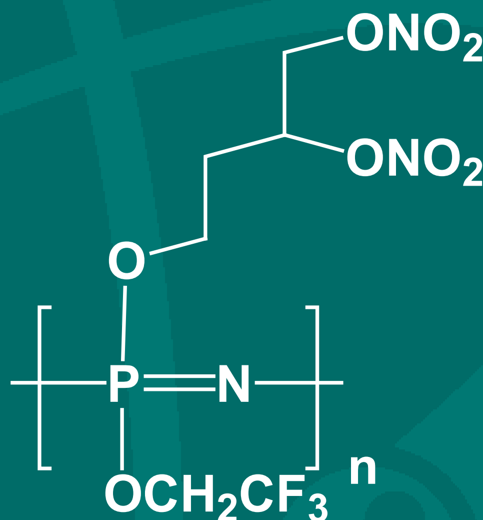
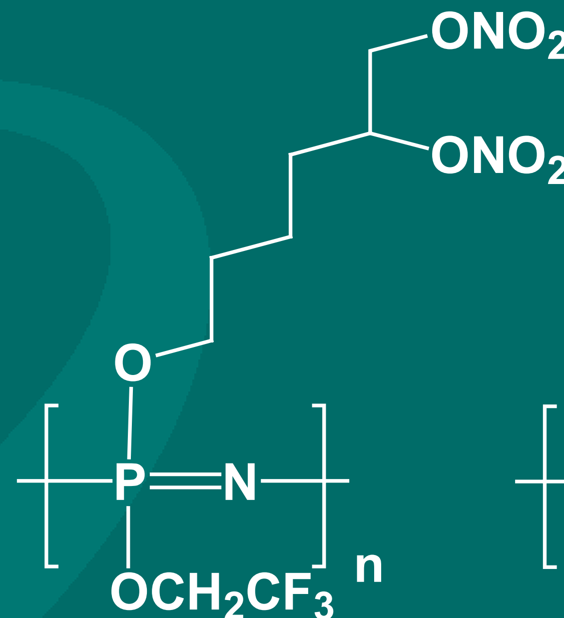
NITRATE ESTER FUNCTIONALISED POLYPHOSPHAZENES USED FOR BOMB CALORIMETRY EXPERIMENTS



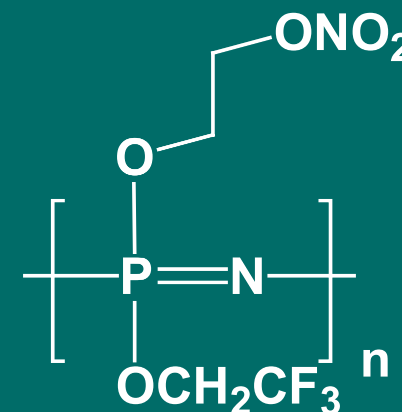
C3 PPZ



C4 PPZ



C6 PPZ



C2 Mono PPZ

MEASURED VALUES OF INTERNAL ENERGY OF COMBUSTION (ΔU_c)

Energetic Polymer	% Energetic Side Group Substitution	ΔU_c ($J\ g^{-1}$)
C2-Mononitrato PPZ	76	-10520 ± 1.7%
C3-Dinitrato PPZ	31	-8880 ± 1.6%
	65	-8640 ± 1.2%
	70	-9220 ± 1.7%
C4-Dinitrato PPZ	59	-10890 ± 1.5%
	61	-11250 ± 0.9%
C6-Dinitrato PPZ	50	-13910 ± 3.7%
	51	-14450 ± 1.2%

PRODUCTS OF COMBUSTION CHEMISTRY

Internal Combustion Energy

Ideal Products:

$C_{5.4} H_{8.2} O_{10.4} N_{5.2} F_{1.8} P_{1.0} + O_2 =$

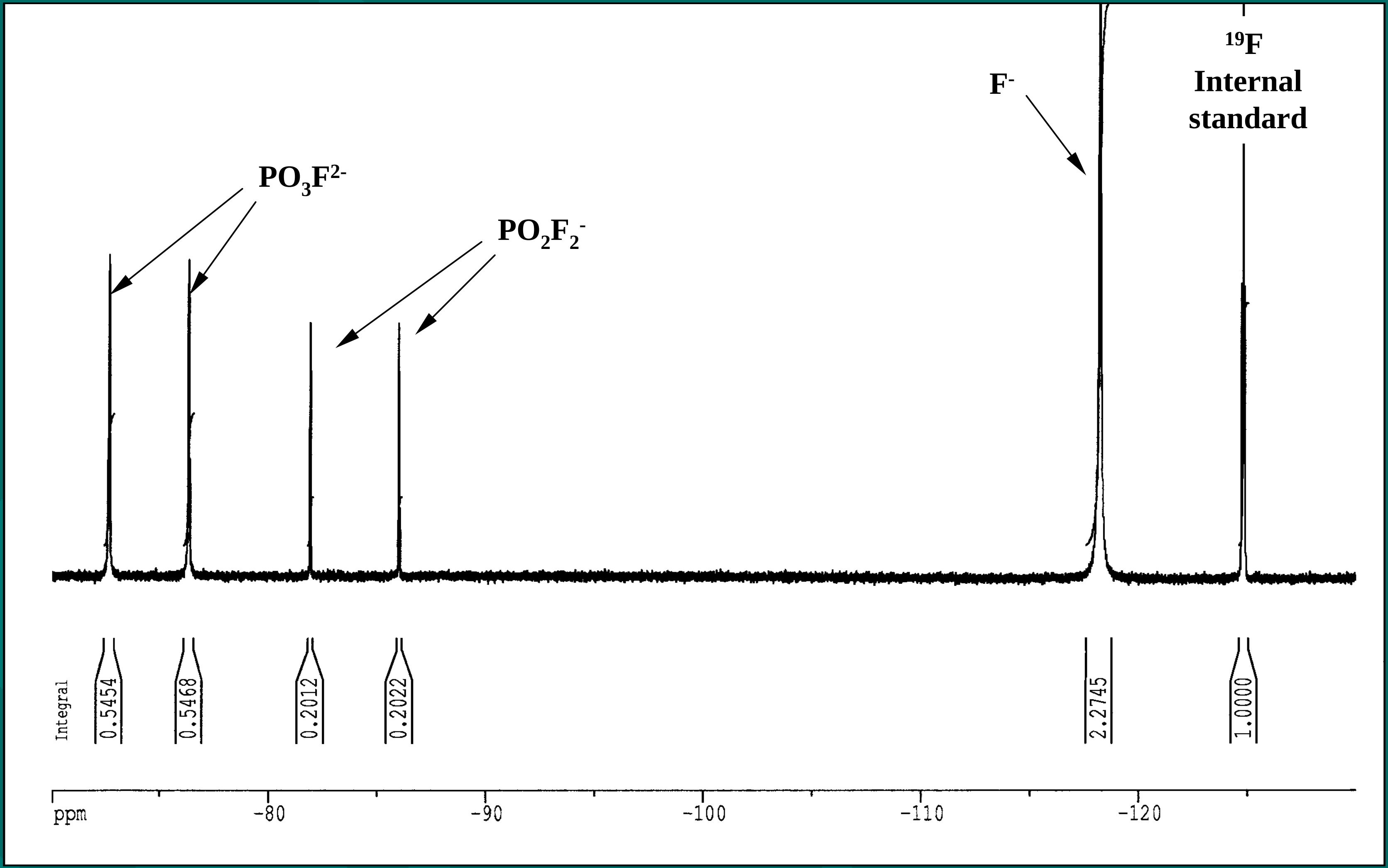
$CO_2 + H_2O + N_2 + HF + H_3PO_4$

In reality: + other products e.g. HNO_3 (so corrections applied)

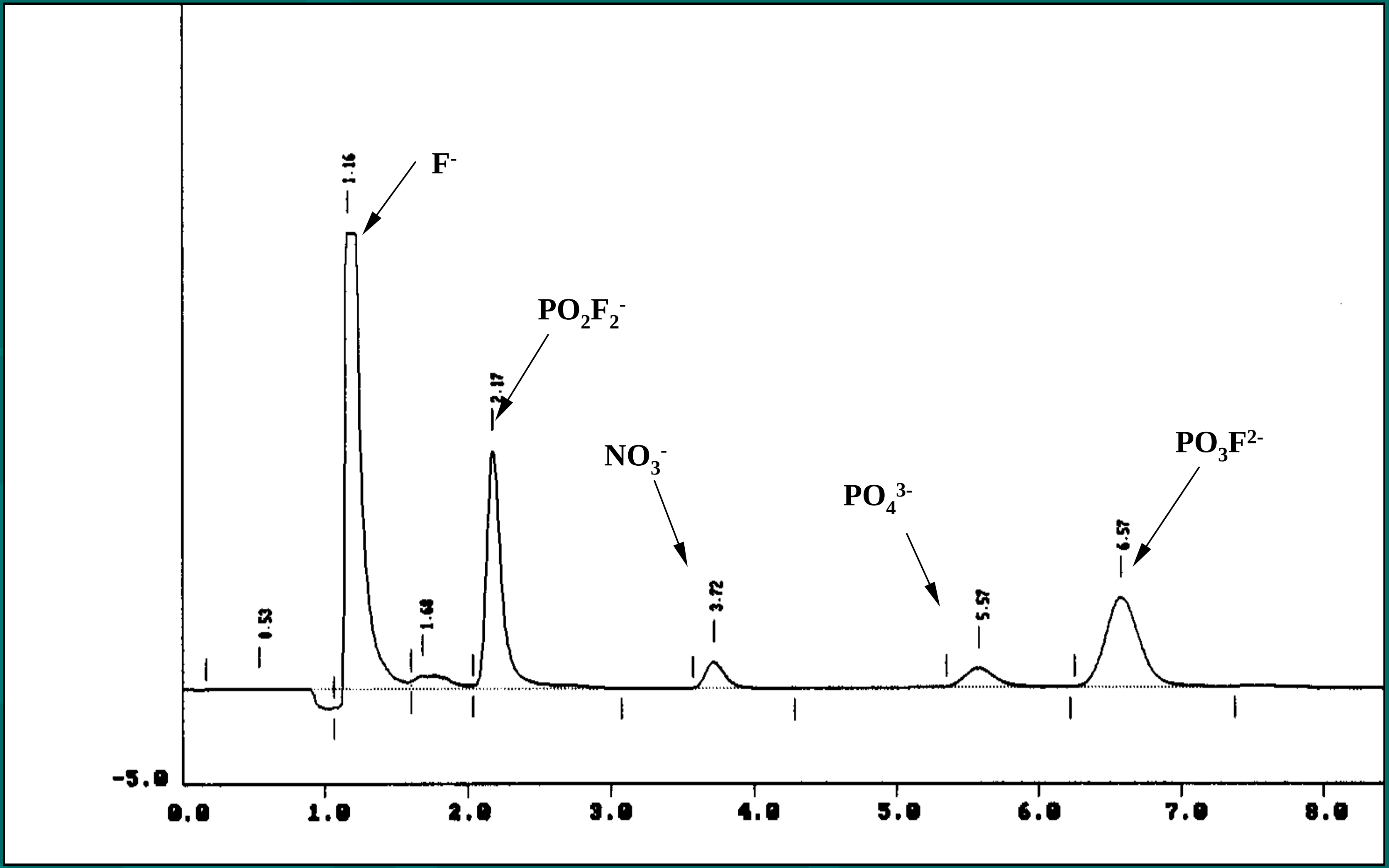
What happens to F and P?

Some options: CF_4, Fluorophosphoric acids, Polyphosphoric acid species

TYPICAL ^{19}F NMR SPECTRUM OF UNDILUTED, BUFFERED BOMB SOLUTION



TYPICAL ION CHROMATOGRAM OF DILUTED, BUFFERED BOMB SOLUTION



POLYPHOSPHAZENES: TRUE PRODUCTS OF COMBUSTION

Standard Products:-

CO_2, H_2O, N_2, HF, H_3PO_4

Non-Standard Products:-

HNO_3, H_2PO_3F, HPO_2F_2, HPF_6 (sometimes)

No Evidence For:-

Polyphosphoric acids, their fluorinated analogues or CF_4

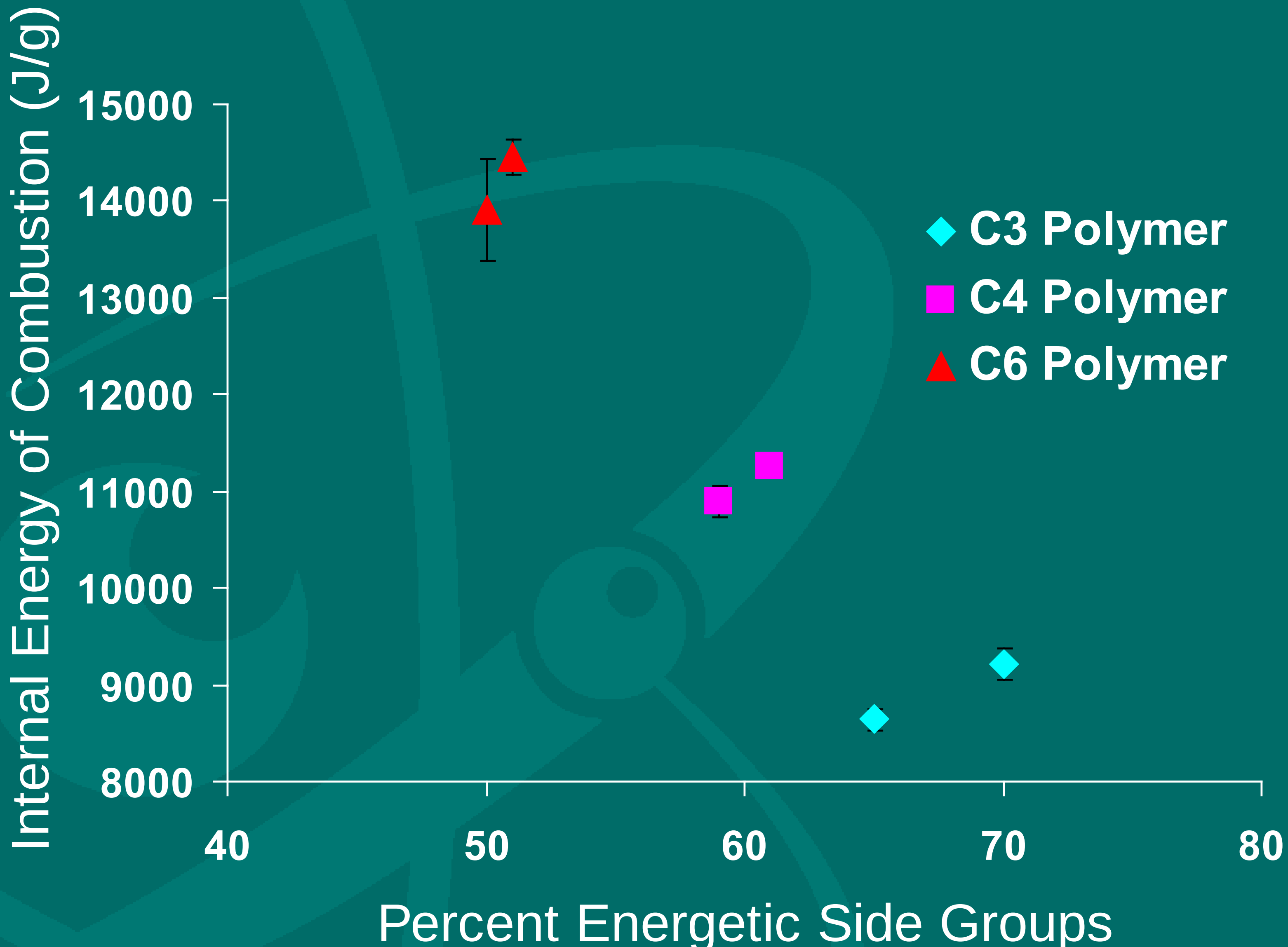
Hence: stoichiometric combustion equation constructed

STANDARD ENTHALPY OF COMBUSTION (ΔH°_c) AND STANDARD ENTHALPY OF FORMATION (ΔH°_f)

Energetic Polymer	% ES*	ΔH°_c (Jg^{-1})	ΔH°_c ($KJ\ mol^{-1}$)	ΔH°_f (Jg^{-1})	ΔH°_f ($KJ\ mol^{-1}$)
C2-Mononitrato PPZ	76	-10520 ± 180	-2670 ± 46	-5719 ± 180	-1451 ± 46
C3-Dinitrato PPZ	31	-8880 ± 140	-2612 ± 41	-6974 ± 140	-2052 ± 41
	65	-	-	-	-
	70	-9190 ± 160	-3290 ± 57	-4496 ± 160	-1609 ± 57
C4-Dinitrato PPZ	59	-	-	-	-
	61	-11250 ± 100	-4043 ± 36	-4512 ± 100	-1621 ± 36
C6-Dinitrato PPZ	50	-	-	-	-
	51	-14460 ± 180	-5338 ± 66	-4106 ± 180	-1516 ± 66

** ES = Energetic side-group substitution*

MEASURED INTERNAL ENERGY OF COMBUSTION VERSUS PERCENT ENERGETIC SIDE GROUPS



CONCLUSIONS (ALL 3 PAPERS)

- Polymerisation may be a useful tool to reduce hazard

  - in molecules and hence PBXs (solids loading)

- Full utilisation needs enhanced energy-density polymers

  - polyphosphazenes show promise

- Good progress achieved on combustion chemistry of energetic polyphosphazenes

- Existing products are not optimised

Expect a series of new products with steadily improving properties