Phosphazenes as Fire Retardants in Aircraft Interiors

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Outline

- **Why Phosphazenes for Fire Retardance?**
- **Fire-proofing Polyurethanes**
- **Block and Graft Copolymers for Fire-Resistant Blends with Commercial Organic Polymers**
  - **Block copolymers**
  - **Polystyrene with pendent phosphazene units**
  - **Fire-resistant polynorbornenes by ROMP**
  - **Cyclolinear polyalkenes by ADMET**
  - **Polymers with phosphate side groups**
- **Conclusions and Future Directions**

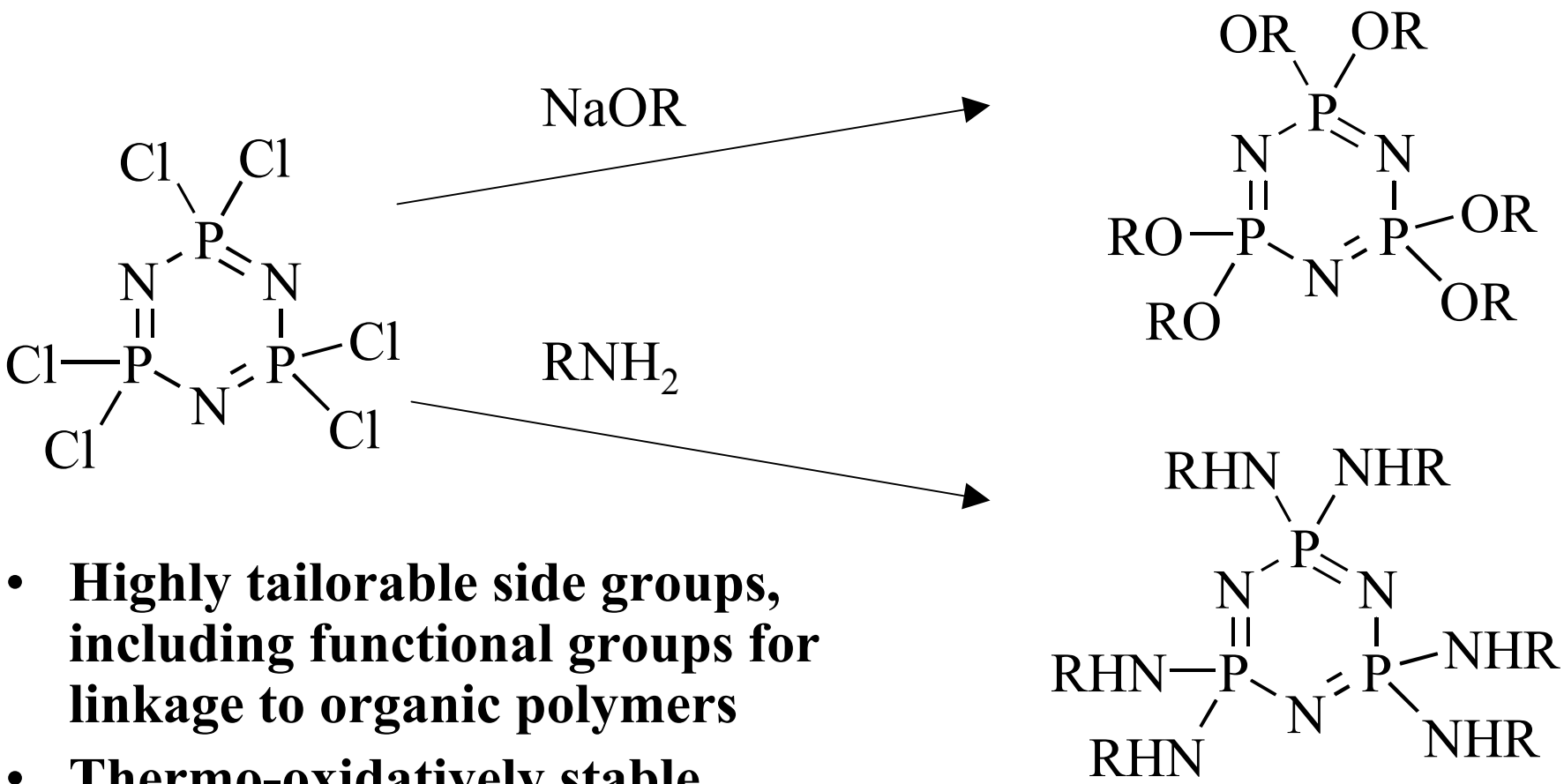
Why Polyphosphazenes?

- **Side groups and skeletal architecture easily tailorable – wide range of properties**
- **Function through vapor and/or condensed phase fire retardance mechanisms**
- **Phosphorus plus nitrogen increases char yield**

Three Types of Phosphazene Structures for Fire Retardance

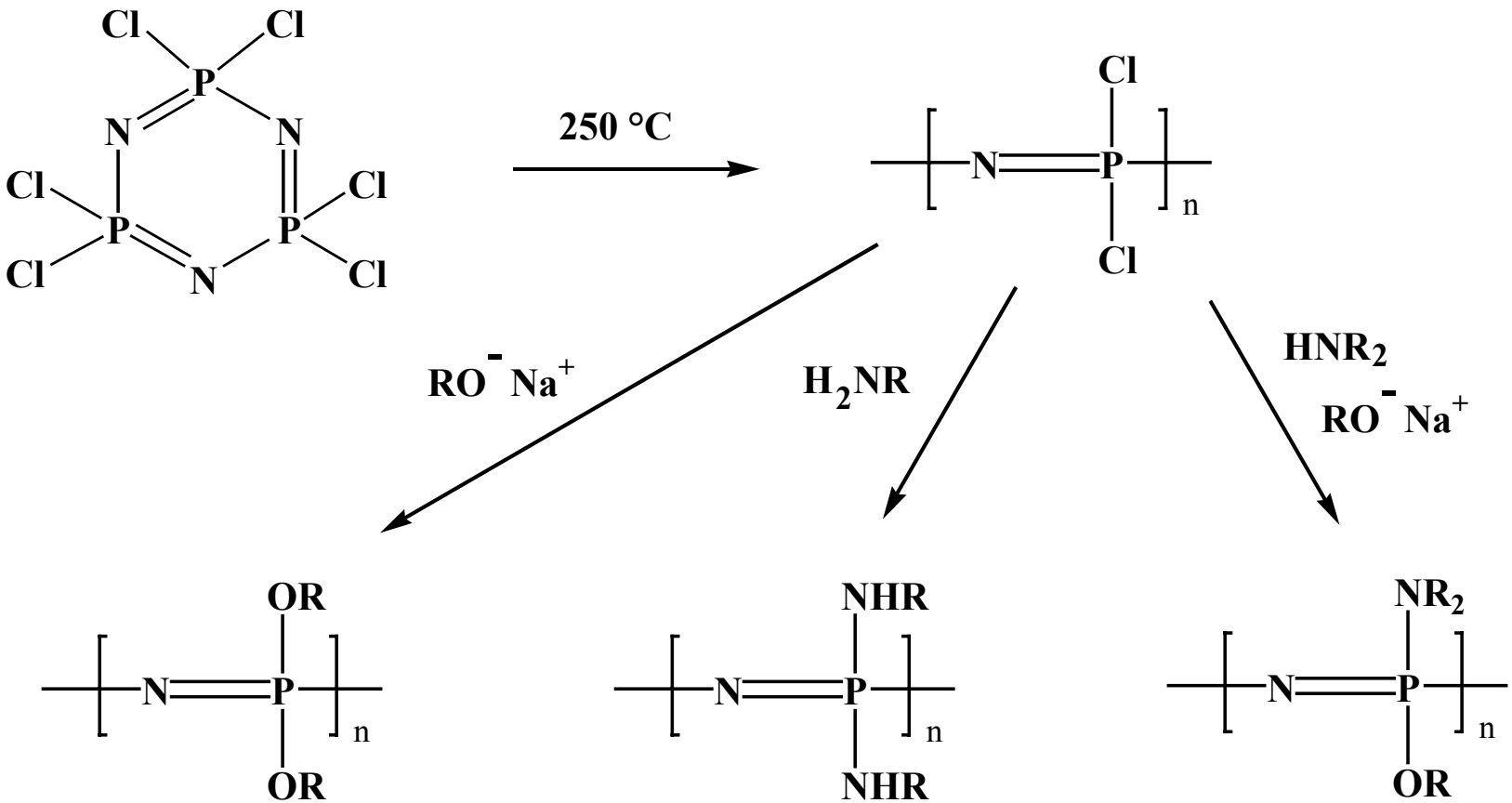
- **Cyclic, small-molecule phosphazenes covalently bonded to an organic polymer**
- **Linear, high polymeric phosphazenes**
  - **Stand-alone use**
  - **Blends with conventional polymers**
- **Block Copolymers**

Small-Molecule Cyclic Phosphazenes

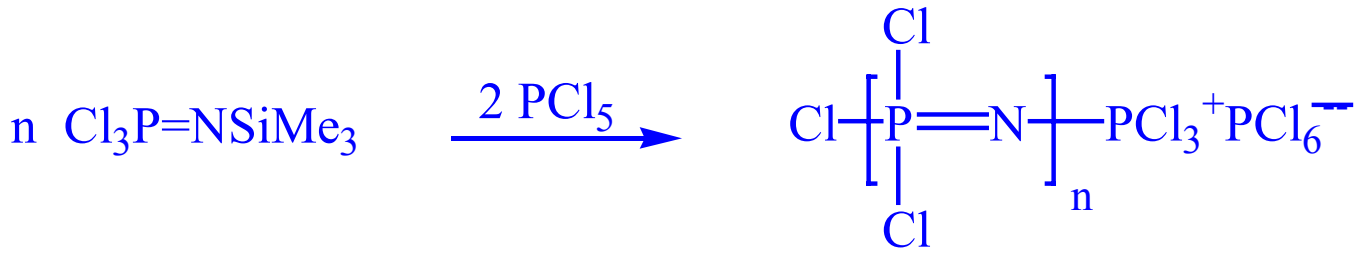


- **Highly tailorable side groups, including functional groups for linkage to organic polymers**
- **Thermo-oxidatively stable**
- **Applications include use as additives, pendent functionalities, monomers for cyclolinear polymers**

Polyphosphazene Synthesis



Living Cationic Polymerization

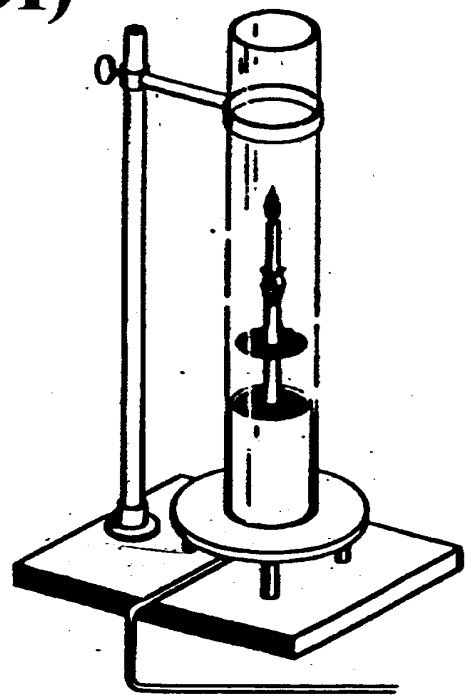


- **Polymerization of phosphoranimines**
- **Molecular weight control through stoichiometry**
- **Narrow polydispersities**
- **Undergoes macromolecular substitutions**
- **Living polymerization**
- **Allows for synthesis of blocks, dendrimers, grafts, etc**

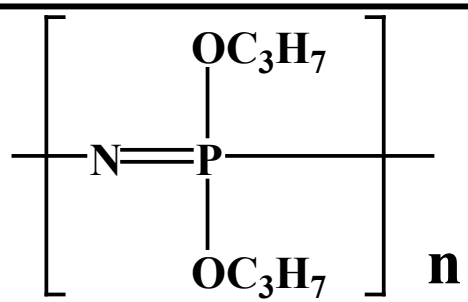
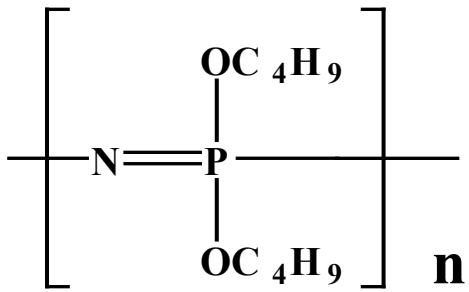
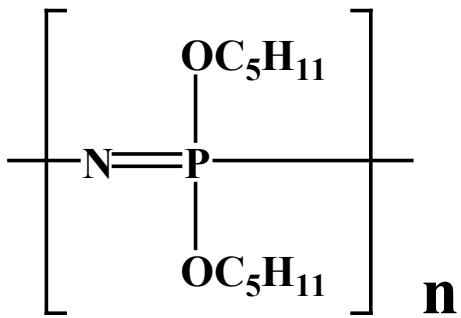
Thermal Analysis Testing

- **Thermogravimetric Analysis (TGA)**
- **Limiting Oxygen Index (LOI)**

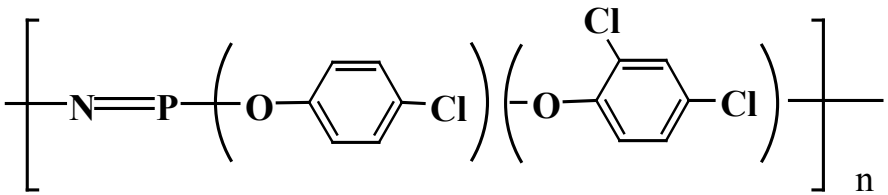
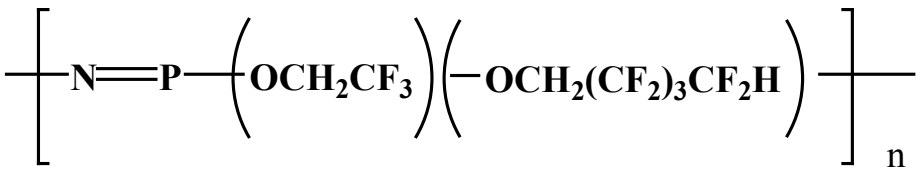
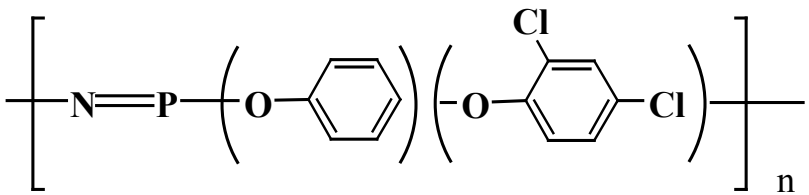
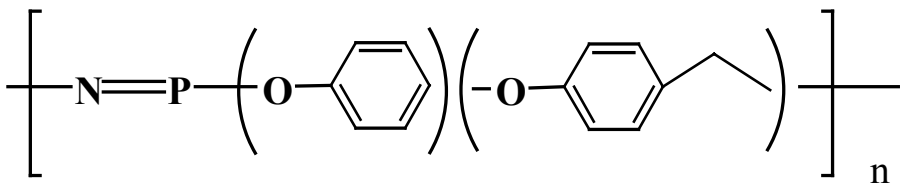
$$\text{LOI} = \frac{O_2}{(O_2) + (N_2)} \%$$



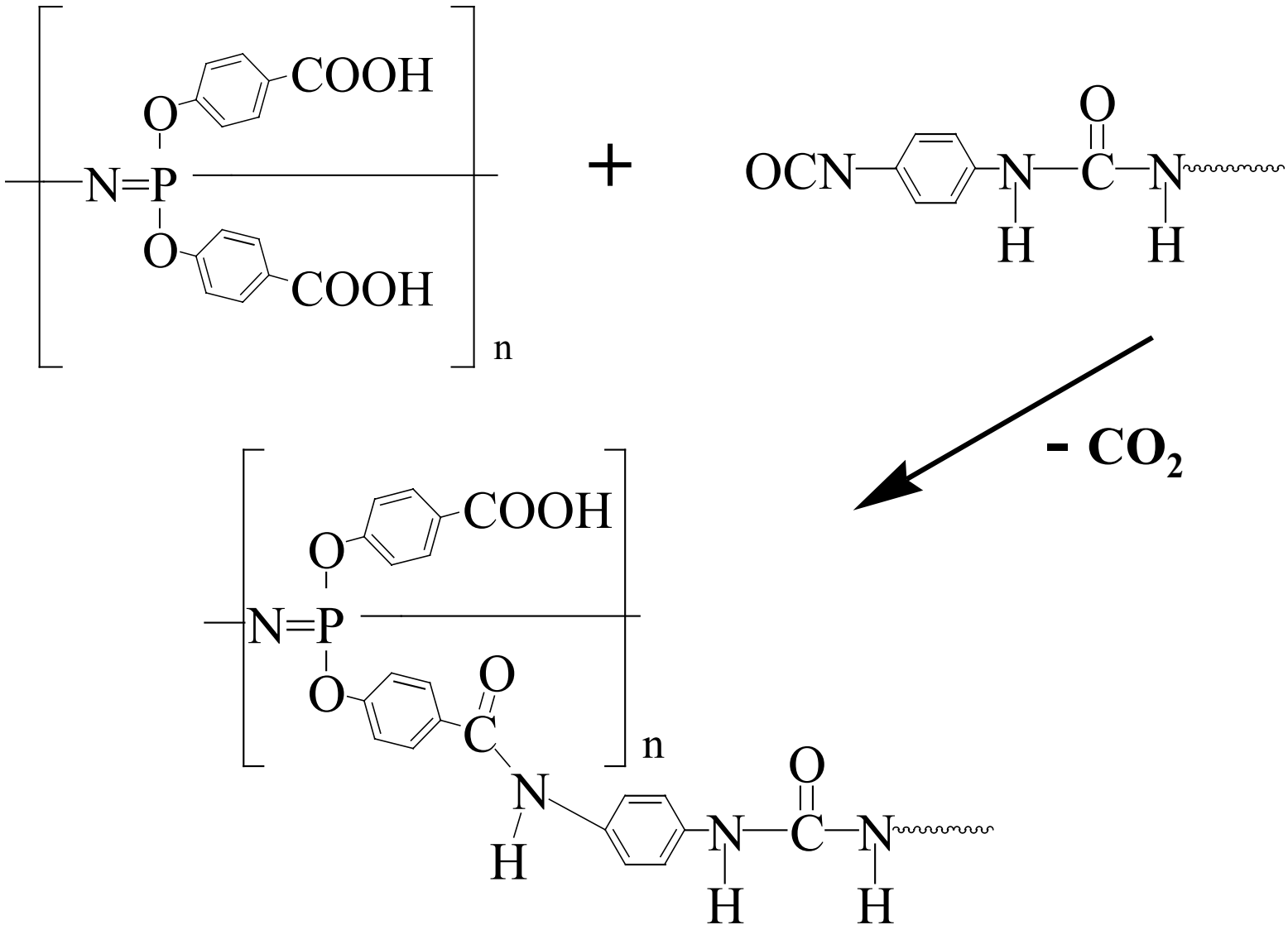
Prototype Fire Resistant Materials

Polyphosphazene	Oxygen Index (OI)
	26
	24
	18

Prototype Fire Resistant Materials

Polyphosphazene	Oxygen Index (OI)
	59
	46
	43
	32

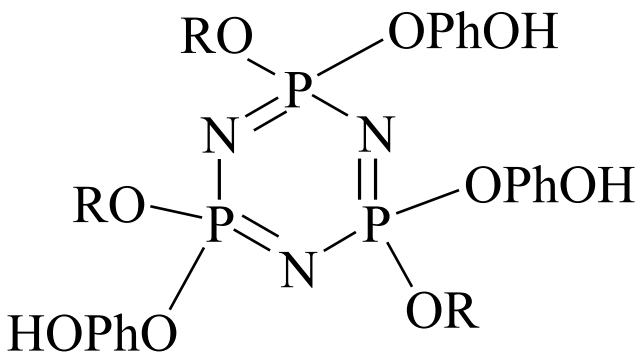
Phosphazene–Urethane Copolymers



Thermal Analysis

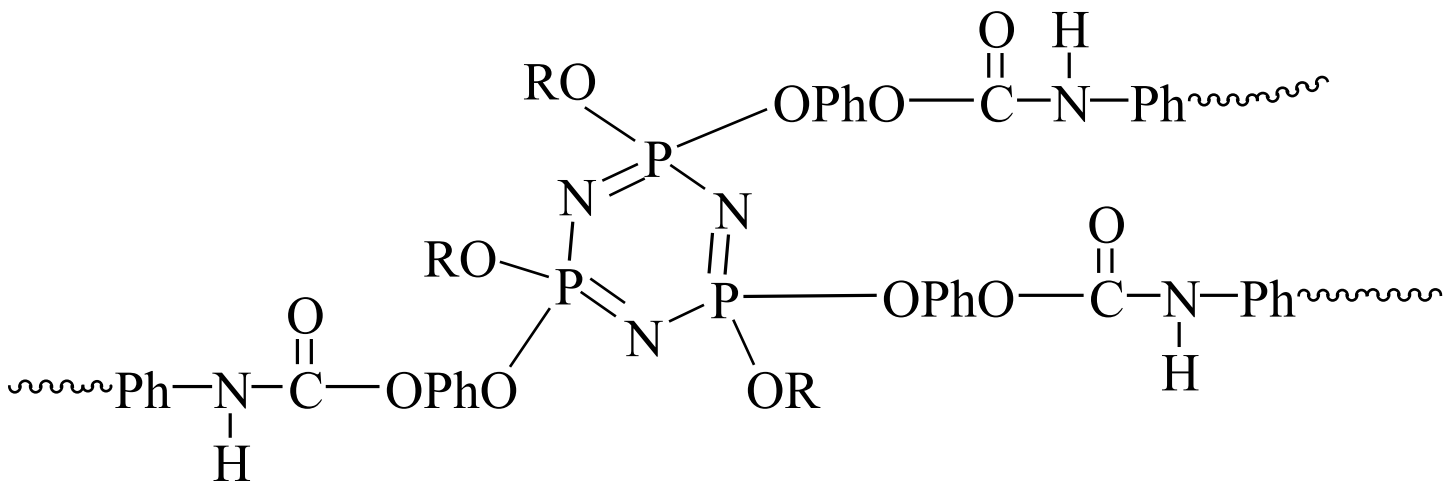
% Phosphazene	% Phosphorus	LOI	Char at 600° C
0	0	20	5
5	0.5	20	10
10	1.0	20	12
20	1.9	21.5	20
30	2.9	23	30

Cyclic Phosphazene - Polyurethane Copolymers



+ $OCNPh(OCH_2CH_2)_nPhNCO$

R = Ph, EtOEt,

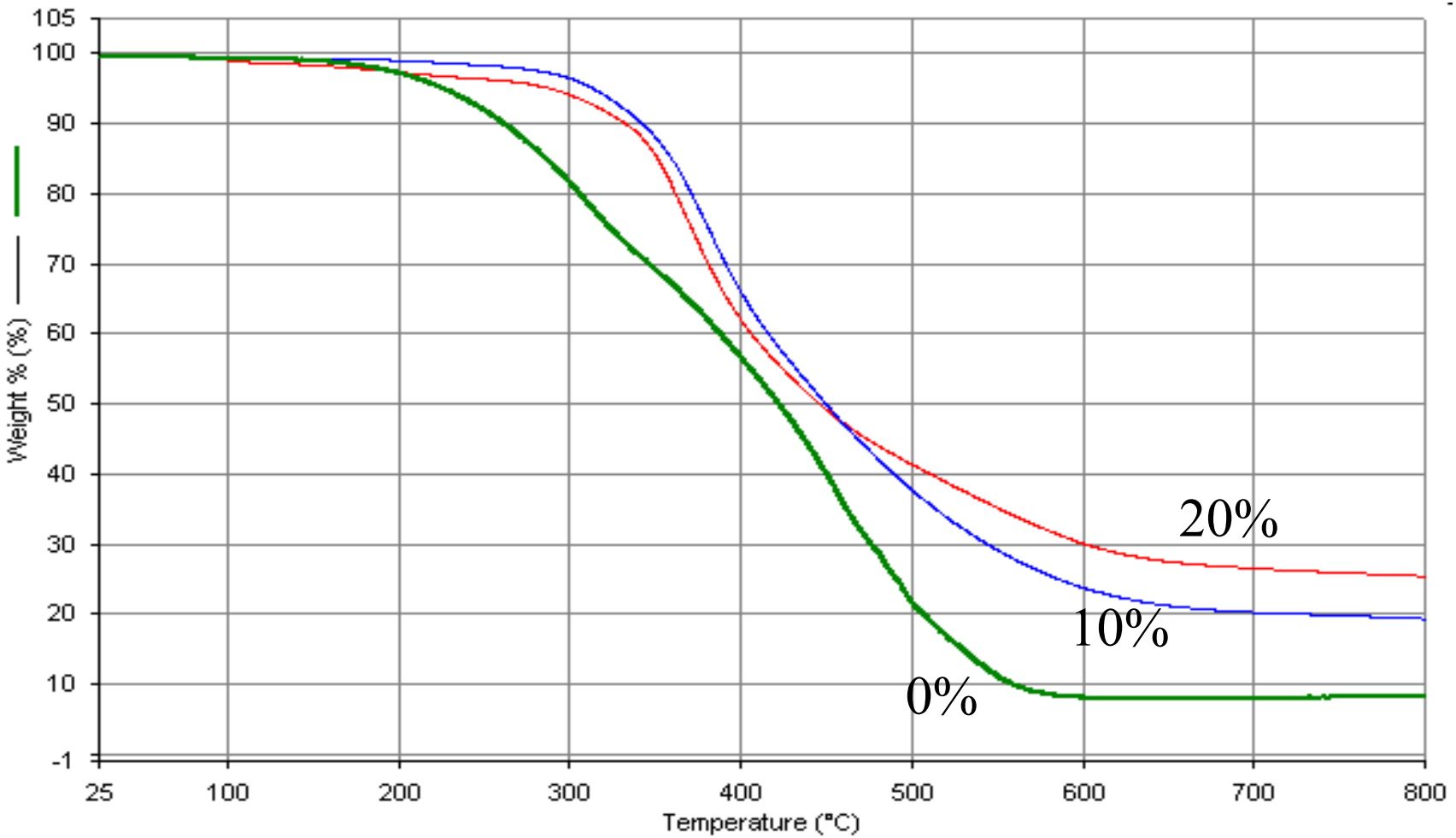


Cyclic Phosphazene-Polyurethane Copolymers

- **Increased crosslinking ability**
- **Covalently bound, non-migrating**
- **Side group tailorablity**
- **Low cost**

Thermal Analysis

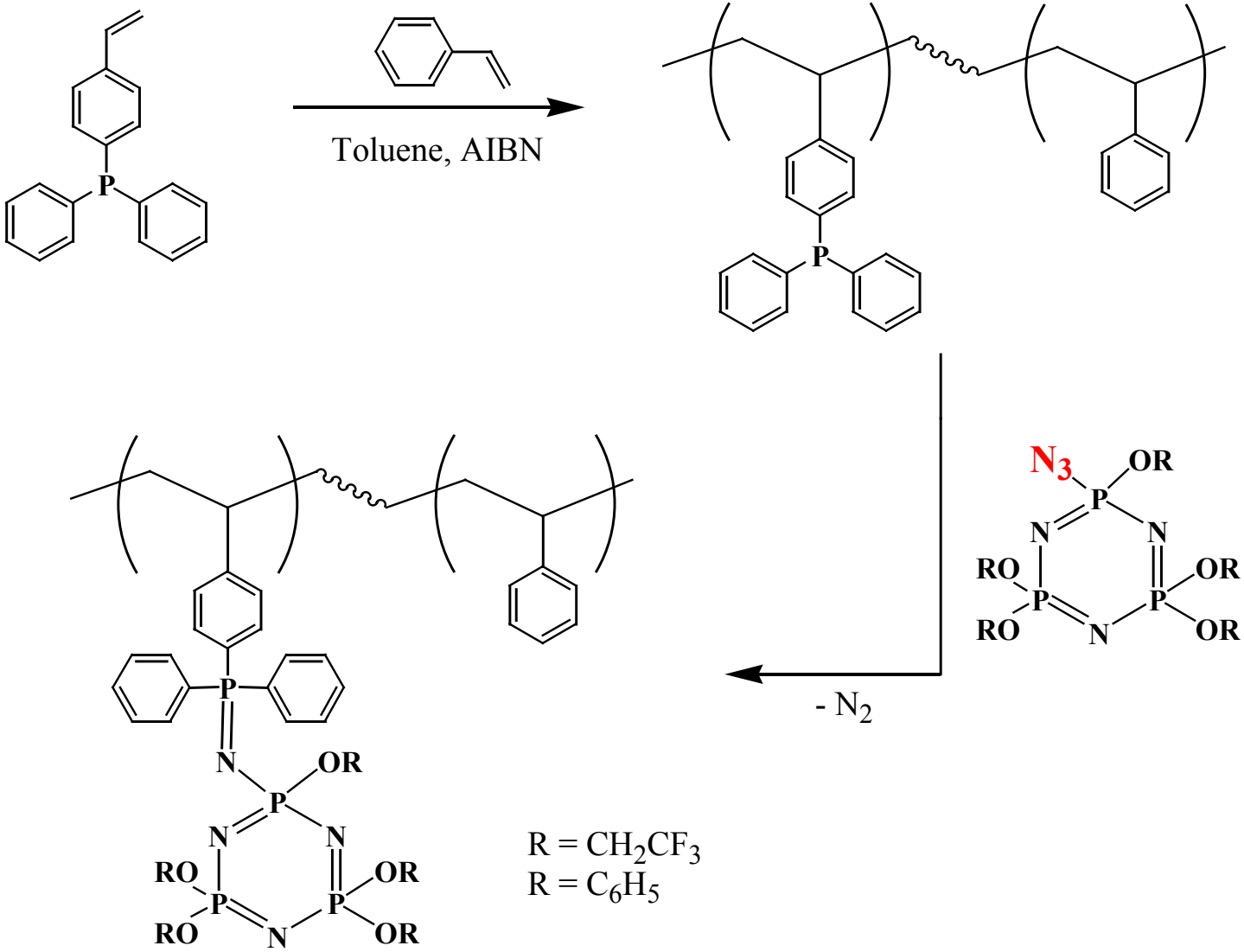
Polyurethane + $[NP(OPhOH)(OEtOEt)]_3$



Phosphinimine Chemistry

- **Phosphinimine linkage -P=N-P-**
  - **Synergistic effects**
- **Polymerization of diphenyl-p-styrylphosphine**
  - **Free radical**
  - **Anionic**
  - **Wide range of copolymers possible**
- **Tailorability of phosphazene**

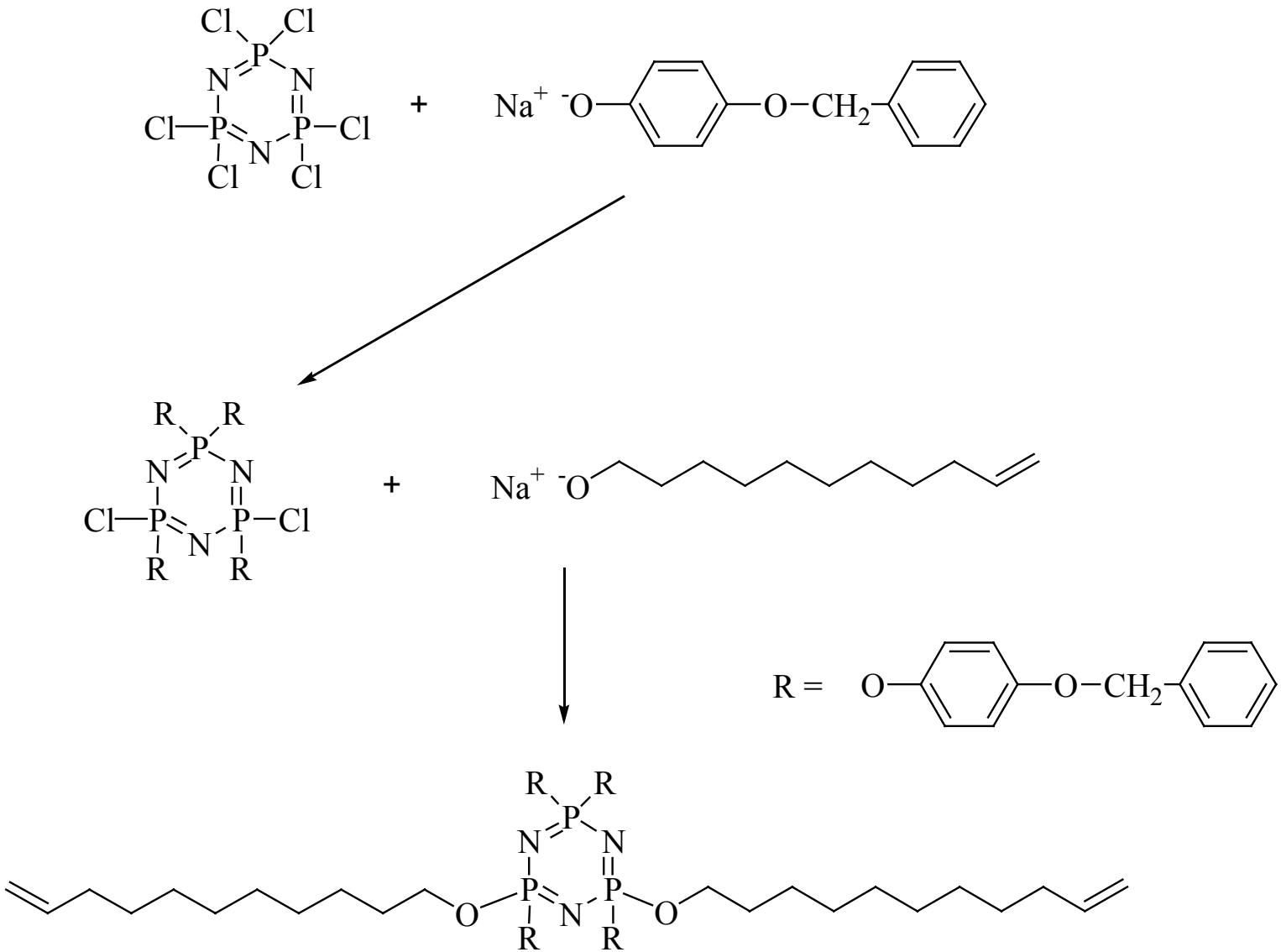
Pendent Phosphazenes



Acyclic Diene Metathesis (ADMET)

- **Intermolecular metathesis of dienes**
- **Ethylene elimination favors high polymers**
- **Catalyst selection, reaction conditions very reactivity and polymer molecular weight**

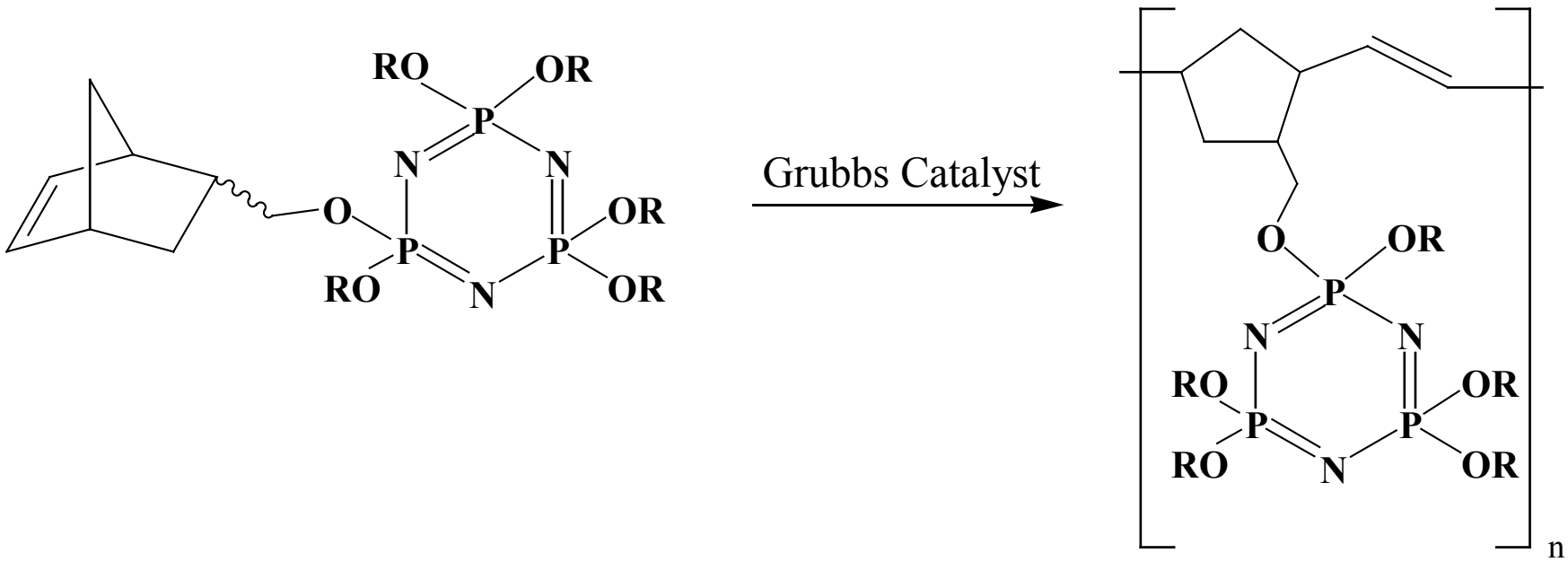
ADMET for Cyclolinear Phosohazenes



Ring Opening Metathesis Polymerization

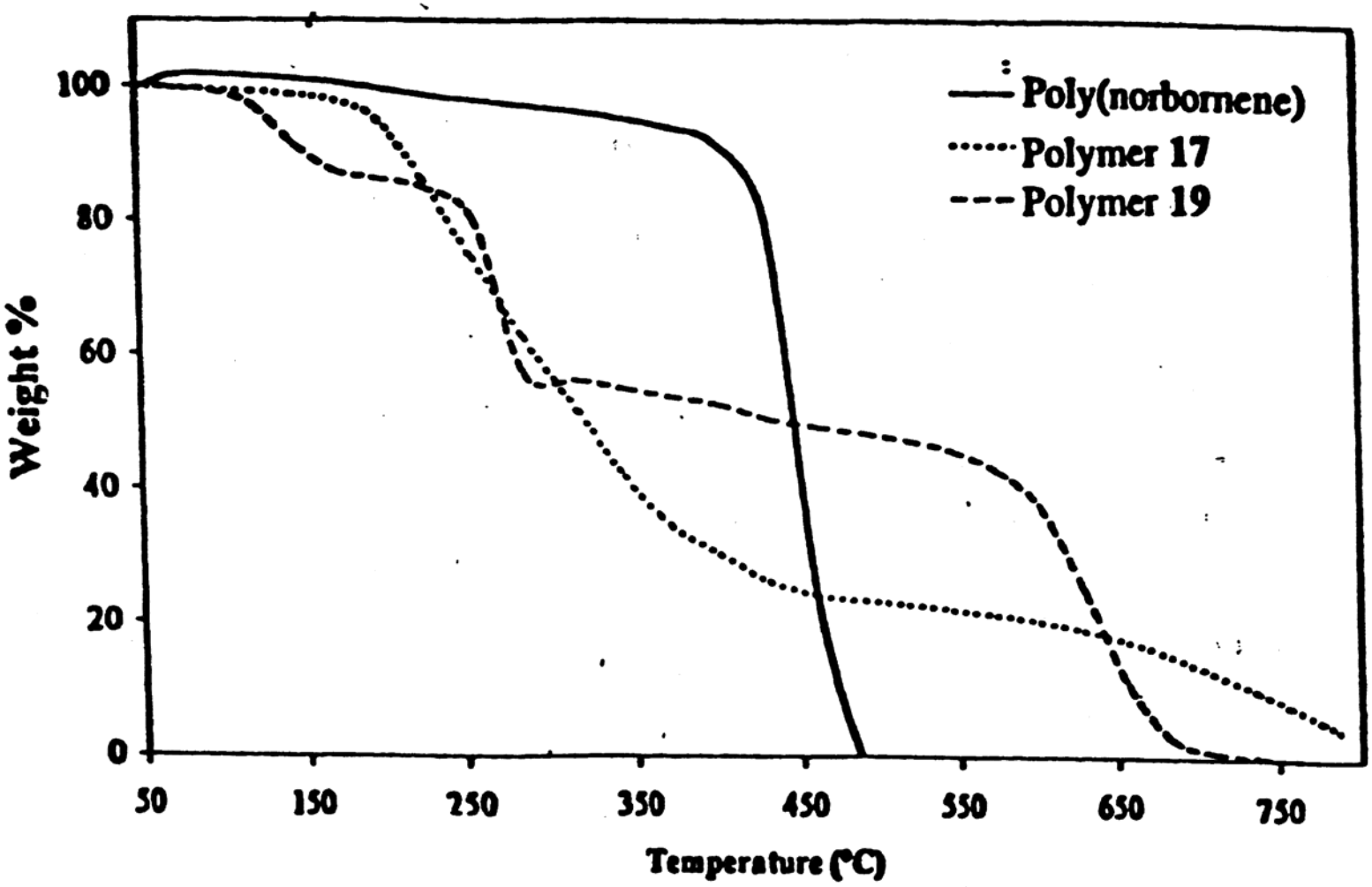
- **Ring Opening Metathesis Polymerization – ROMP**
- **Metathesis of strained cyclic olefins**
- **Living polymerization**
- **Wide range of monomers available**

Norbornene-Phosphazene Copolymers

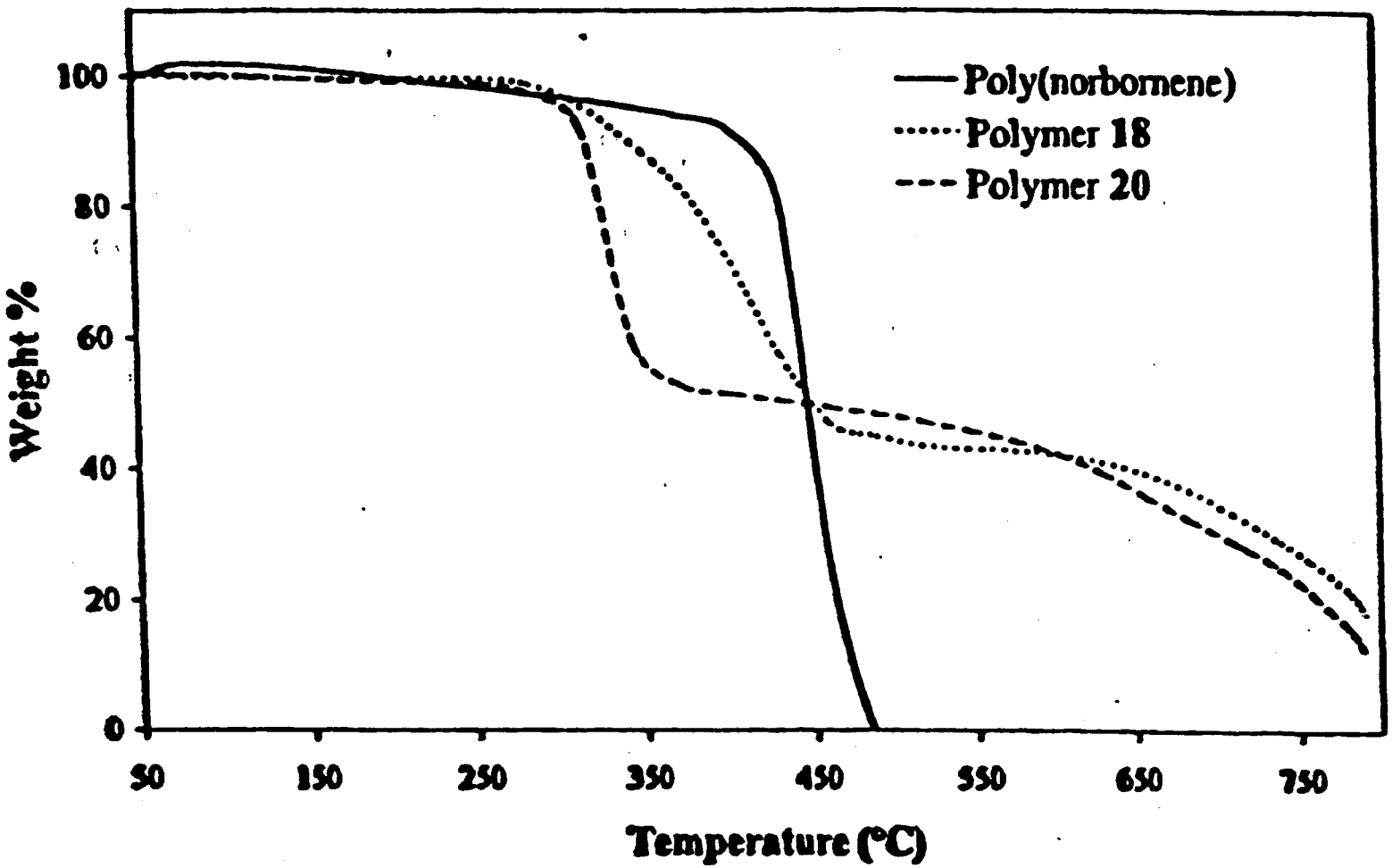


R = CF_3CH_2- **(17)**
EtOOCPh- **(18)**
CH_3CH_2- **(19)**
Ph- **(20)**

Thermal Analysis

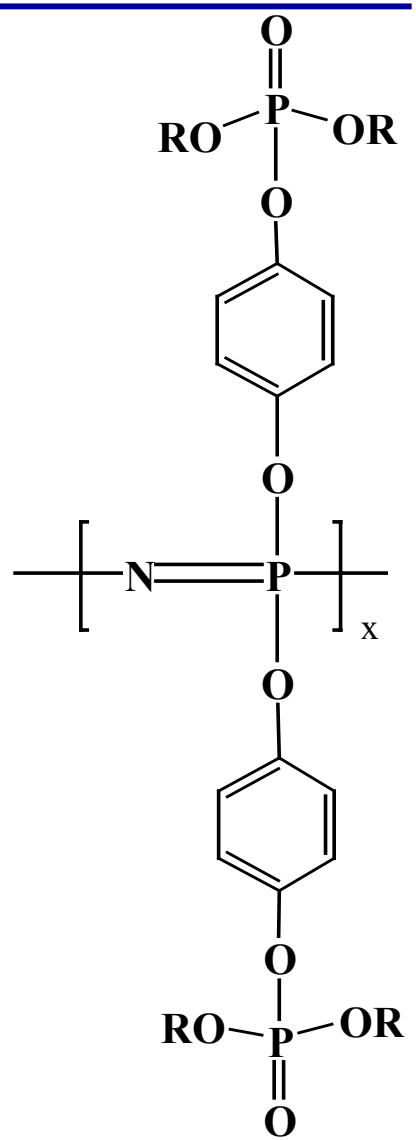


Thermal Analysis

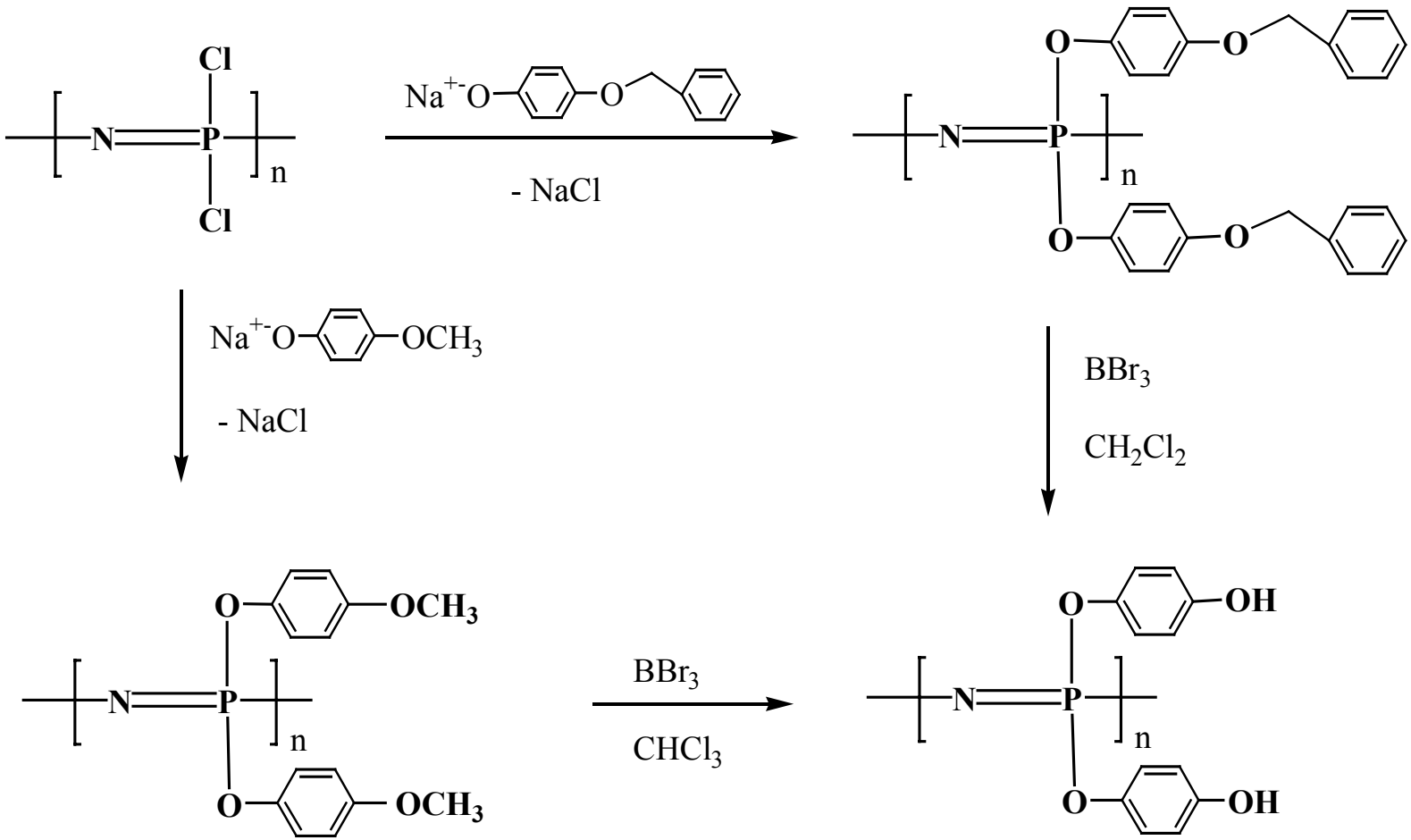


Phosphorylated Phosphazenes

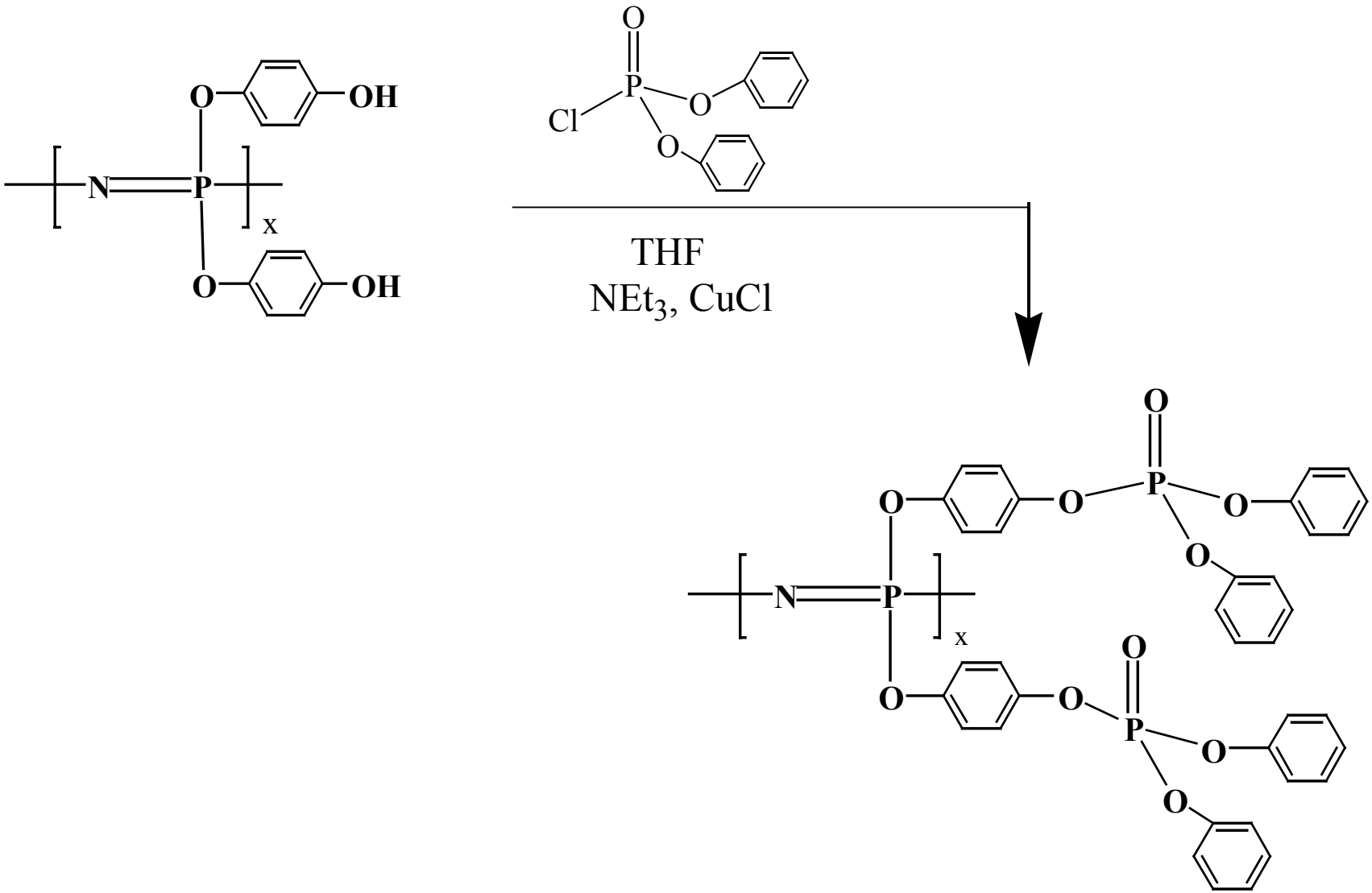
- **Improve fire resistance of polyphosphazenes**
- **Immobilize fire retardant additive onto polymer backbone**
- **Functionalize side groups with phosphate derivatives**



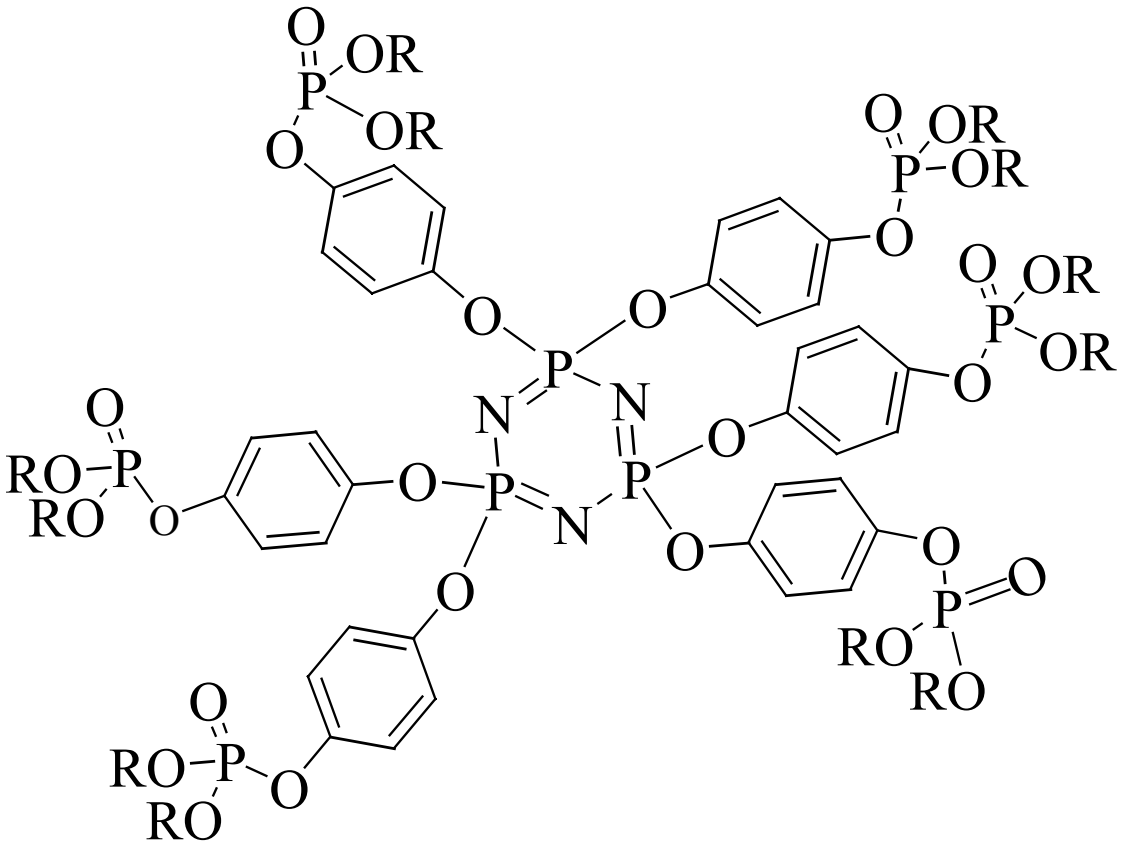
Prepolymer Synthesis



Phosphorylation



Polystyrene Additives



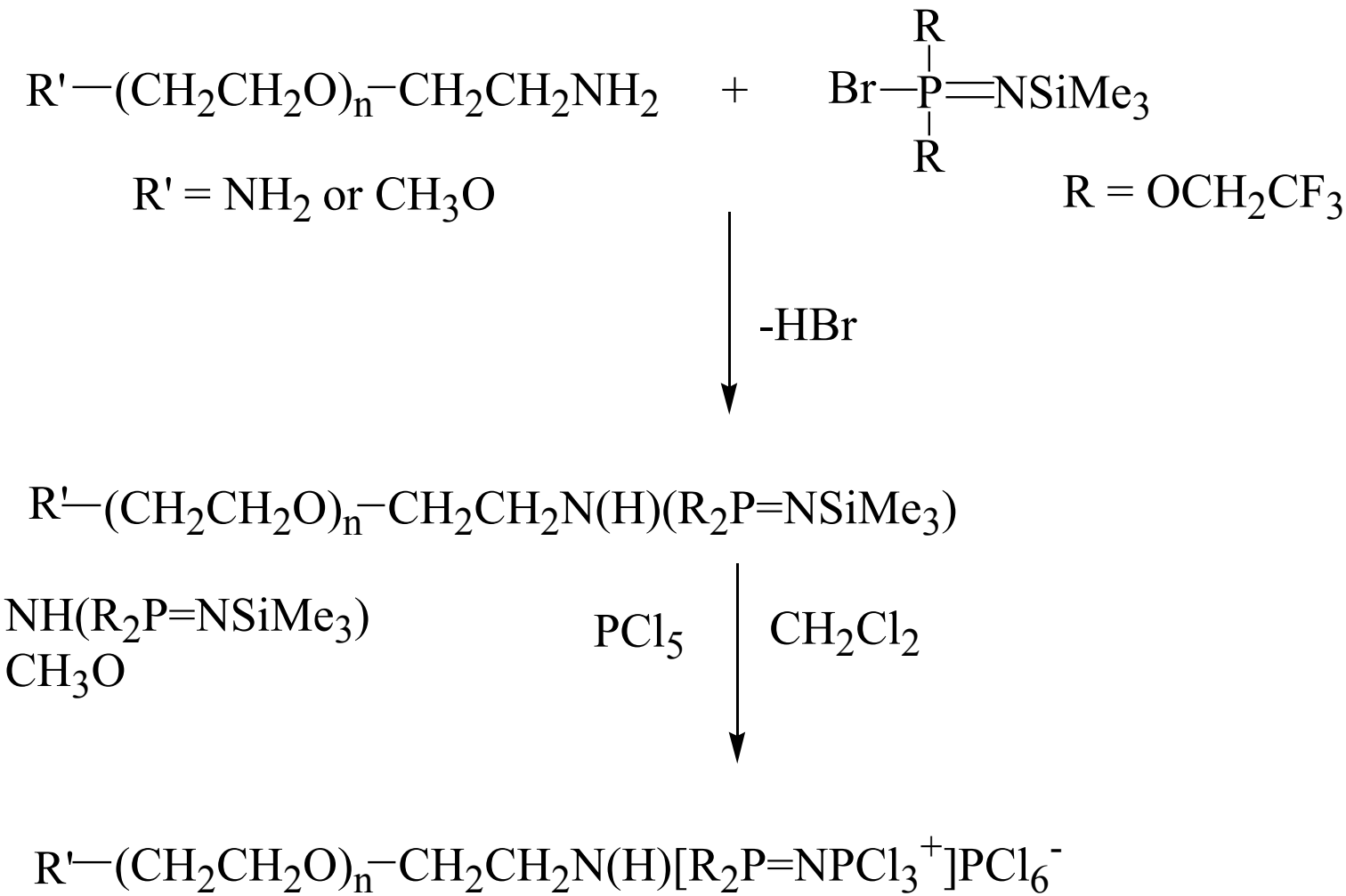
Trimer 1
R = Et

Trimer 2
R = Ph

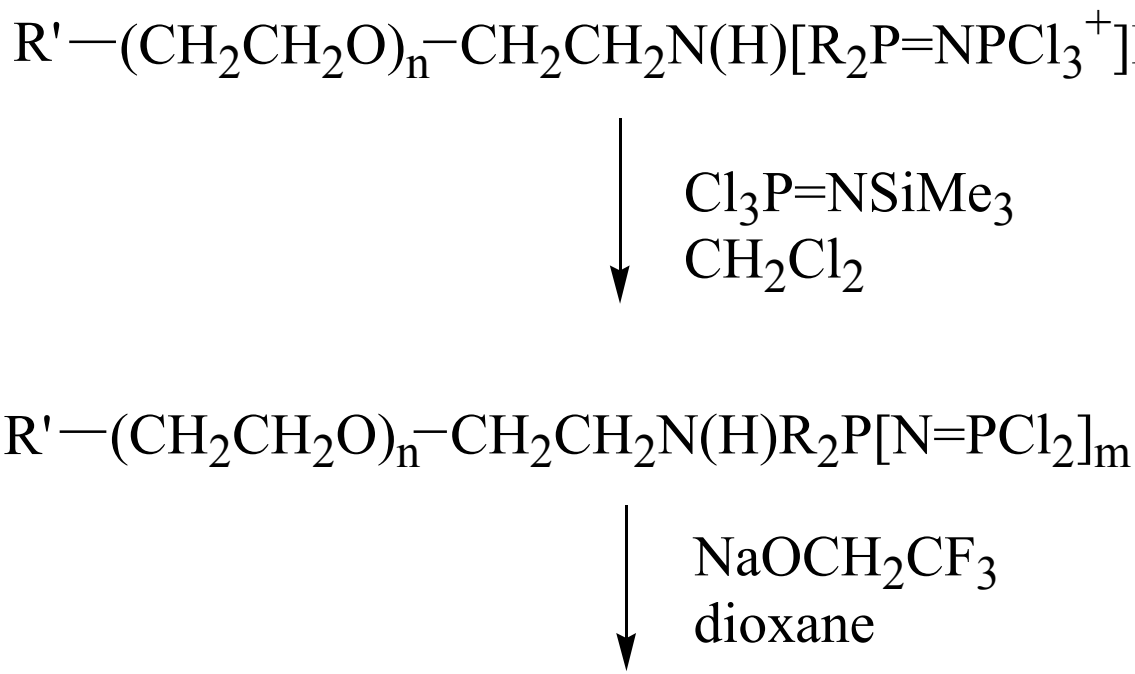
Thermal Analysis

Additive	Wt %	LOI	% Char at 500 °C
----------	0	18	1
Triphenyl Phosphate	10	22	1
	20	24	1
	30	28	2
Trimer 1 R = Et	10	19	7
	20	20	12
	30	21	17
Trimer 2 R = Ph	10	24	4
	20	26	8
	30	25	15

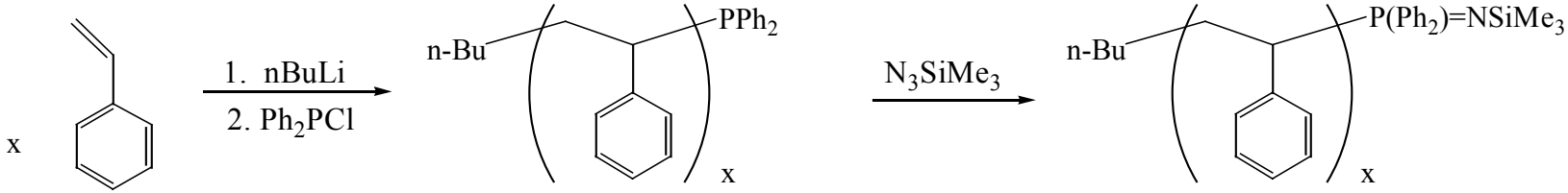
Phosphazene Poly(ethylene oxide) Block Copolymers

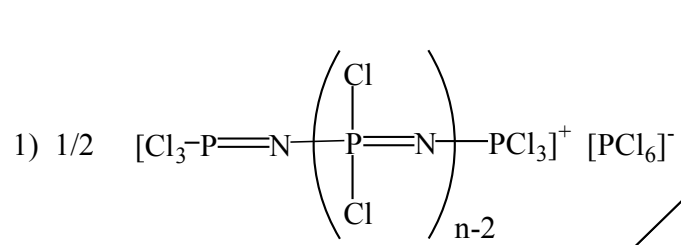


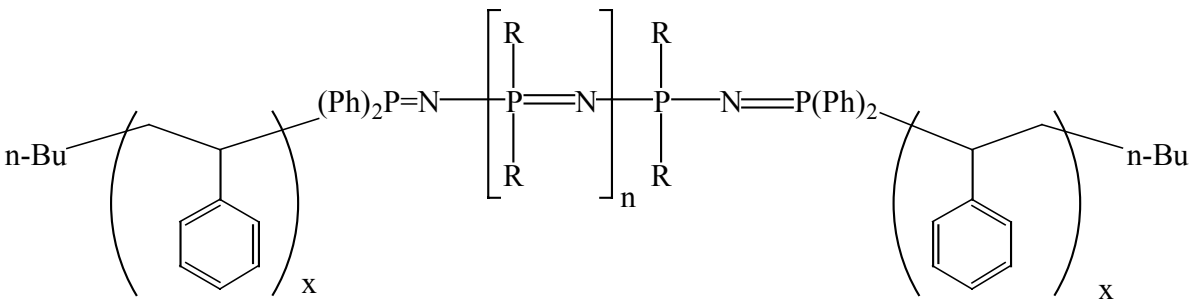
Block Copolymers, Continued



Phosphazene-Styrene Block Copolymers







R = OCH_2CF_3

Conclusions and Future Directions

- Phosphazene rings and polymer chains are highly effective fire retardant species
- They function by both vapor phase flame quenching and char formation
- A variety of options have been developed for the incorporation of phosphazene units into polymers both for stand-alone polyphosphazenes and material for blends and IPNs with normal organic polymers
- Future work will involve evaluation of the influence of the phosphazene components on physical properties and fire resistance of blends and IPNs, with a view for minimizing overall materials costs.