Thermal and flammability analyses of poly(hydroxyamide) (PHA) and its derivatives

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CUMIRP Cluster F

Outline

- Introduction
- New microscale flammability tests

  --- PCFC*, STA*(TGA/DSC), Pyrolysis GC/MS
- Thermal decomposition and flammability

  --- Poly(hydroxyamide) (PHA)

  --- Halogenated PHAs

  --- PHAs with OMe groups

  --- PHAs with different phosphate groups
- Thermal decomposition mechanisms
- Conclusions

** PCFC: Pyrolysis-combustion flow calorimeter (FAA microcalorimeter)*
** STA: Simultaneous thermal analysis (TGA/DSC)*

Fire --- A potential hazard for human life

- Annually account for more than 6,000 deaths and $10 billion in property damage.
- More stringent fire safety requirements in enclosed and inescapable applications, such as aircraft cabins, submarines, ships, subways, and high-rise buildings.

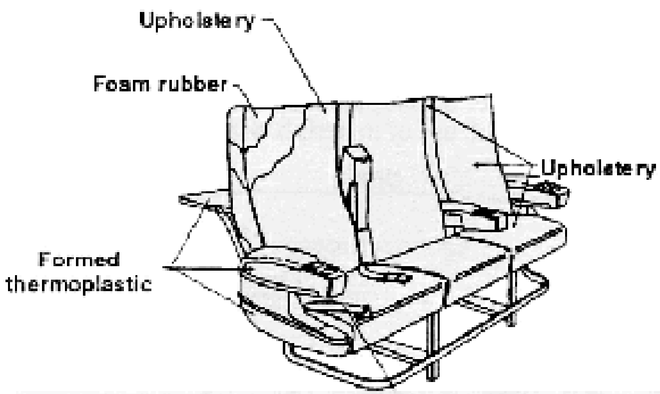
Los Angeles, 1991

Teibei, 2000

Austria, 2000

FAA long-term objectives:
"eliminate burning cabin materials as a cause of death in aircraft accidents"

Aircraft interiors contain tons of combustible polymers



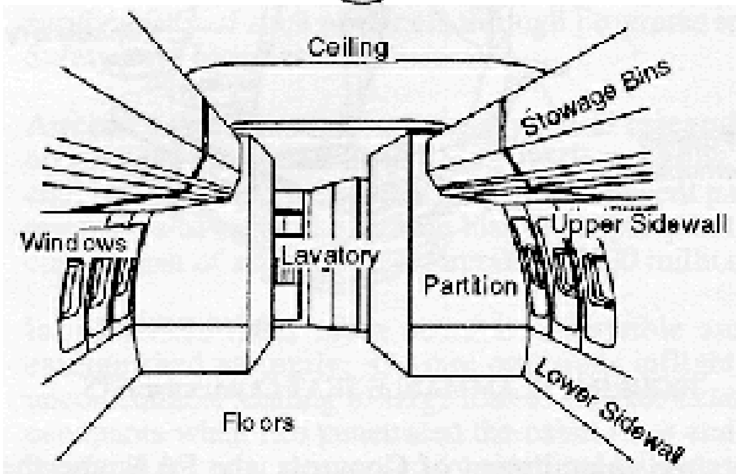


FIGURE I. FLAMMABLE CABIN COMPONENTS

FAA FIRE RESEARCH

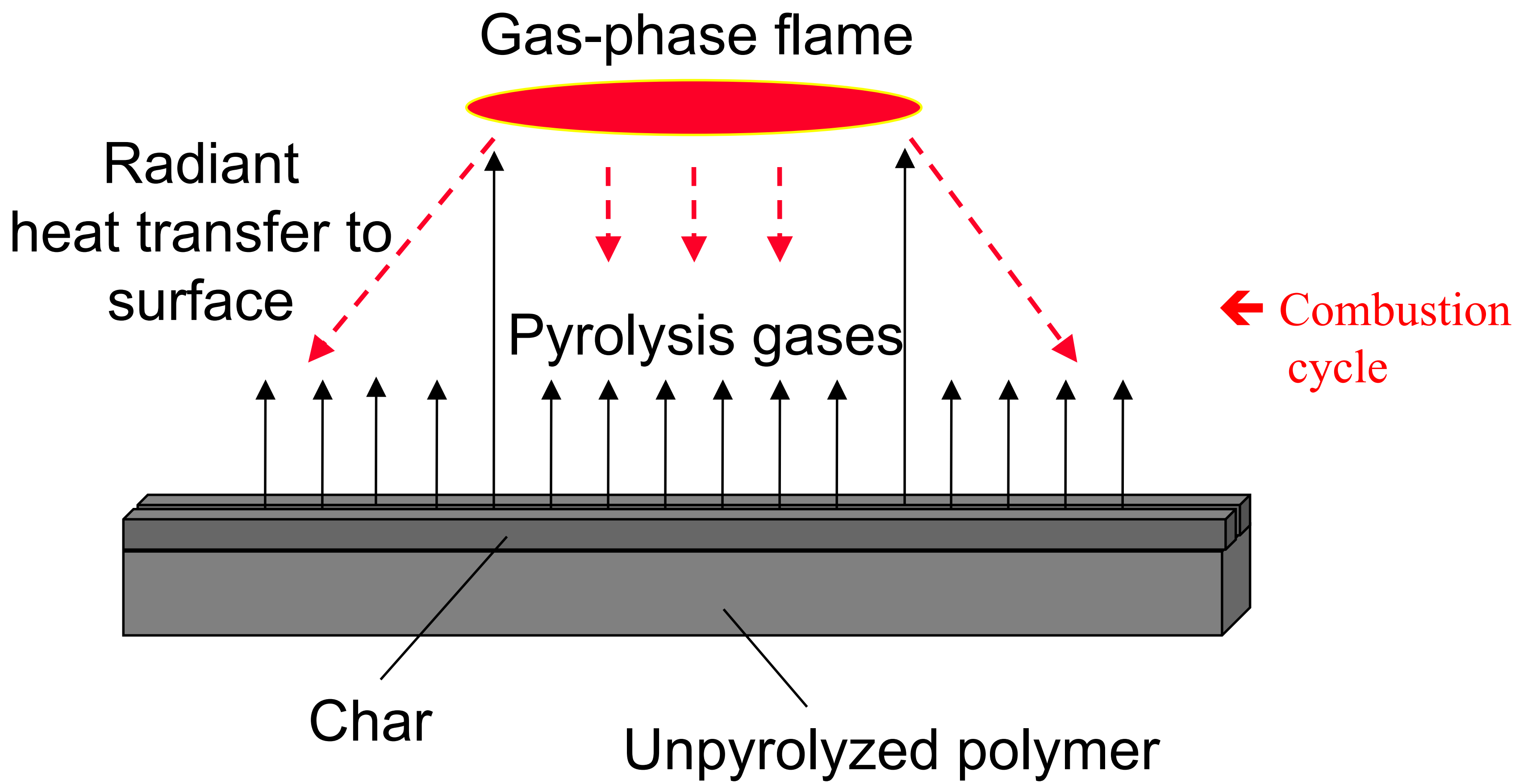
UMass CUMIRP Cluster F:
"Fire-Safe Polymers and Polymer Composites"

Objectives:

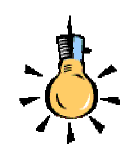
Reduce unwanted fires and extend polymer applications

- Create new tools and techniques for thermal decomposition and flammability characterization
- Establish the correlation between polymer structure, composition and macroscopic flammability
- Understand polymer decomposition chemistry and fire-resistance mechanisms
- Develop a new generation of high-performance, environmental friendly fire-resistant polymers

How to make polymer more flame resistant?



- Reduce the generation of combustible gases
- Increase char formation
- Release chemical flame suppressants (Cl, Br, P)



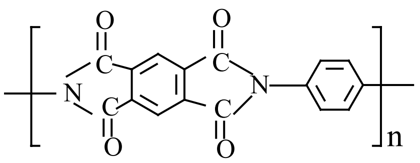
→ Flame resistance ↑

Strategies for reducing polymer flammability

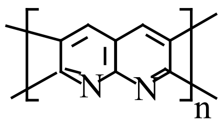
- **Inherent fire-resistant polymers**

  --- high thermal stability, low mass loss rate, low heat of combustion of pyrolysis gases, high char yield

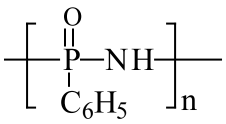
  Linear aromatic or heterocyclic polymers

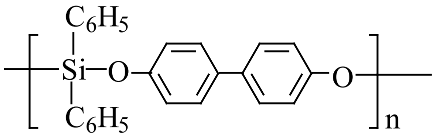


  Ladder polymers



  Semi-organic polymers





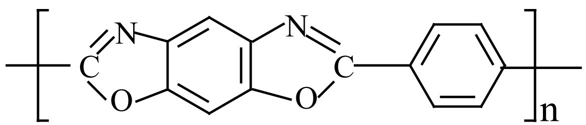
- **Structure and composition modification**

  Copolymers and blends

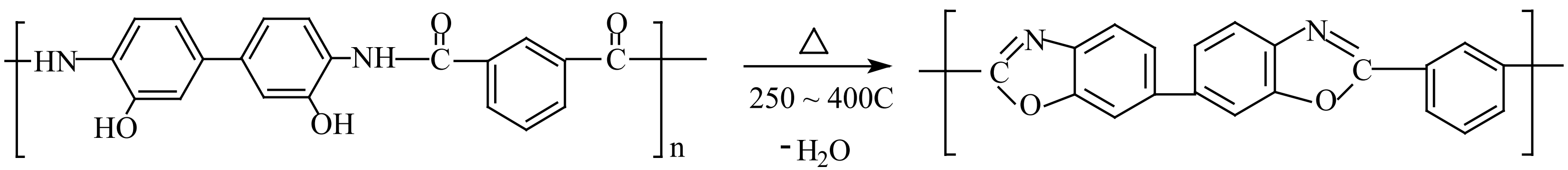
- **Flame-retardant additives**

  B, Al, P, Cl, Br, Sb, Si, N

PHA: High-performance fire-safe polymer



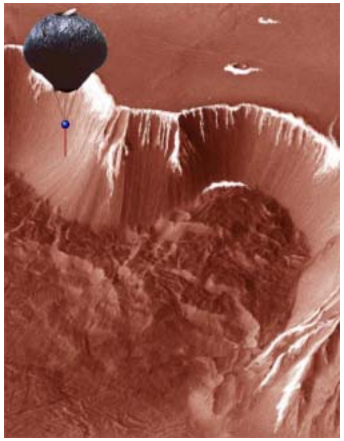
" Air Force " polybenzoxazole (PBO)



PHA

PBO

- High molecular weight, soluble and easy to process
- Large endothermic cyclization heat sink
- Simultaneous release of flame-quenching molecules
- Low heat-release rate and high char yield
- Precursor of polybenzoxazole (PBO) --- high-temperature and flame-resistant polymer



Mars aerobot
(PBO balloon)

Standard flammability tests

- Ease of ignition
- Flame spread ---- across a surface
- Fire endurance ---- penetrate a wall or barrier
- Rate of heat release
- Ease of extinction
- Smoke evolution ---- amount, rate and composition
- Toxic gas evolution ----amount, rate and composition

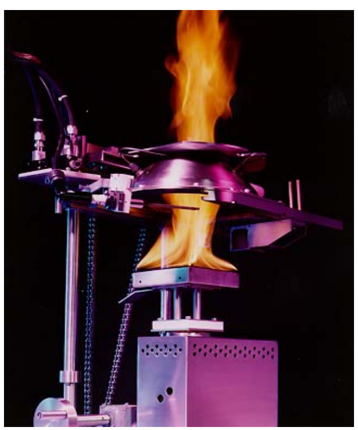
Tests most commonly used in USA:

Limiting oxygen index (LOI), UL-94 small flame test, cone calorimeter, Ohio State University (OSU) calorimeter, ASTM-E-84 Steiner Tunnel, NBS smoke chamber.

Thermal decomposition and flammability tests

Traditional:

UL-94



Cone calorimeter: 100g

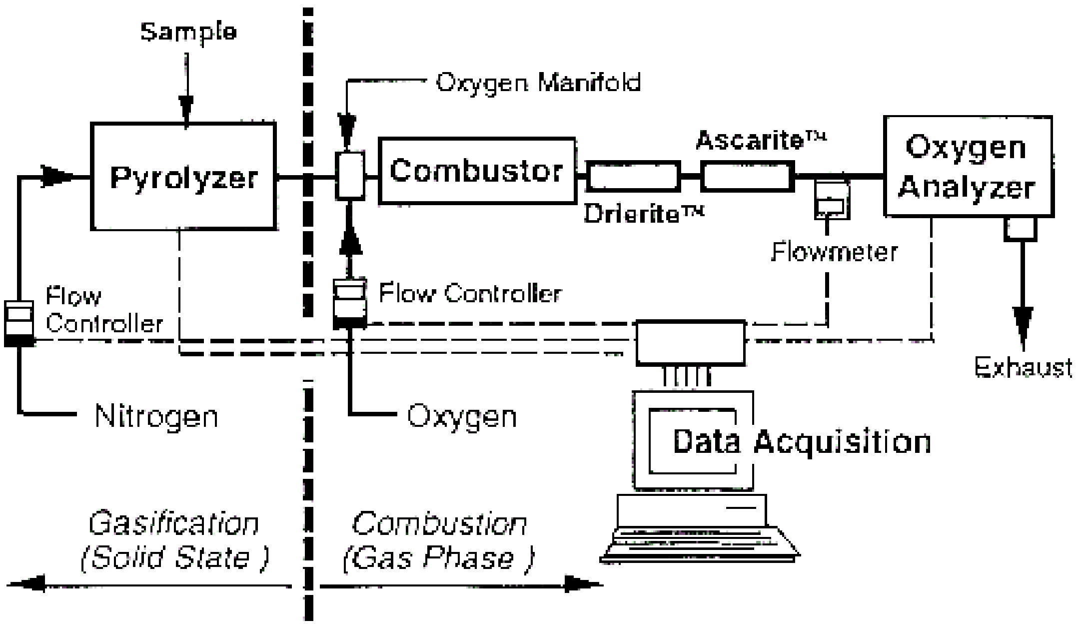
New:

PCFC (FAA): 1mg
(Flammability)

STA (TGA/DSC): 10mg
(Thermal decomposition)

Py-GC/MS: 50~300μg
(pyrolysis gases)

Pyrolysis-combustion flow calorimeter (PCFC)



Heat release capacity η_c(J/g.K):

$$\eta_c = \frac{\dot{h}_c^{\max}}{\beta} = \frac{1}{\beta}\frac{E\Delta\dot{m}_{O_2}^{\max}}{m_o}$$

$$\boxed{E = 13.1 \pm 0.7\ kJ/g\text{-}O_2}$$

$\dot{h}_c^{\max}$: Peak of heat release rate (w/g)

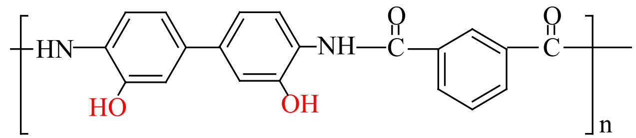
β : Heating rate (K/s)

High-throughput milligram-scale method for materials flammability research (based on oxygen consumption principle)

Lyon, R. E.; Walters, R.N. ***International SAMPE Symposium and Exhibition (Proceedings)*** *45th 2000, v45, p1721*

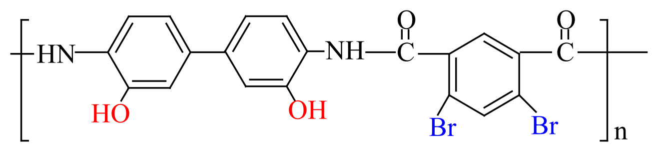
Structures of PHA and its derivatives (1)

PHA

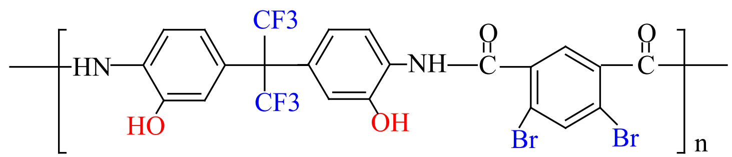


PHA-1 (-OH)

Halogenated PHAs

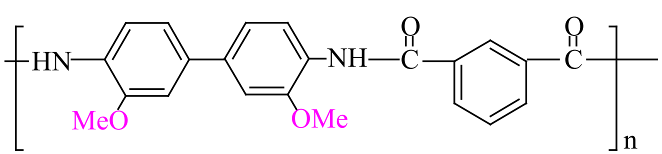


PHA-3 (-OH, m-Br)

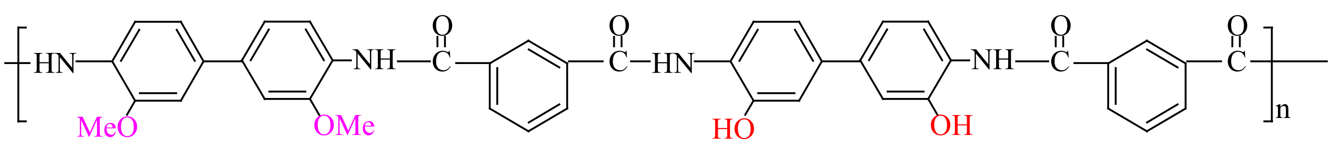


PHA-5 (-OH, -CF_3, m-Br)

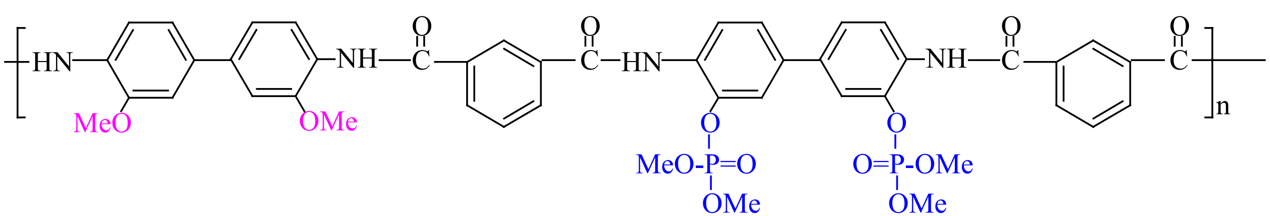
PHAs containing OMe group



PHA-7 (-OMe)

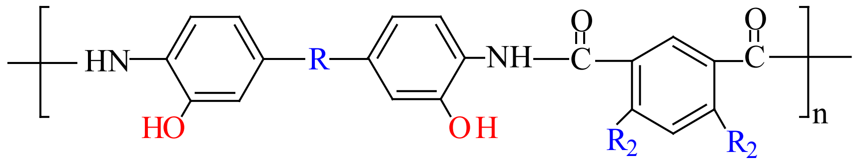


PHA-8 (-OMe, -OH)



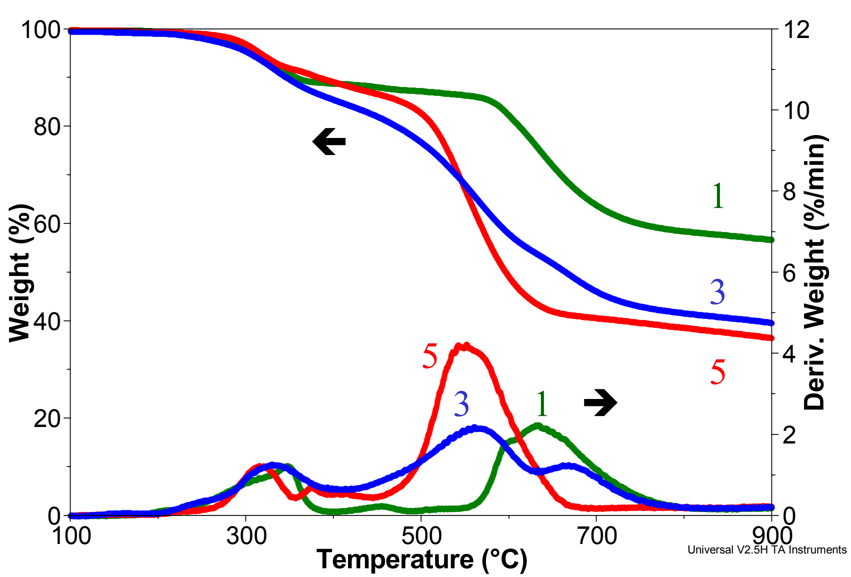
PHA-9 (-OMe, -OPO$(OMe)_2$)

Thermal decomposition of PHA and halogenated PHAs

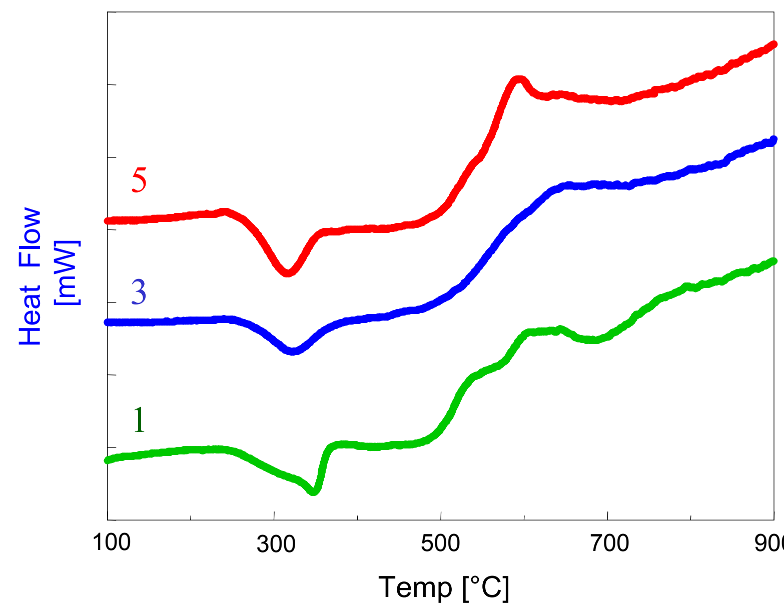


($10^{o}C/min$, N_2)

PHA-1: R_2= H; PHA-3: R_2= Br; PHA-5: R_2= Br, R= $C(CF_3)_2$



TGAs and derivative of TGAs (DTGs)

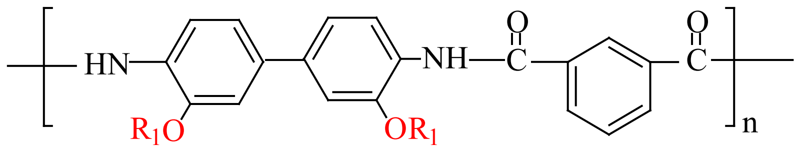


DSC curves

Two-stage

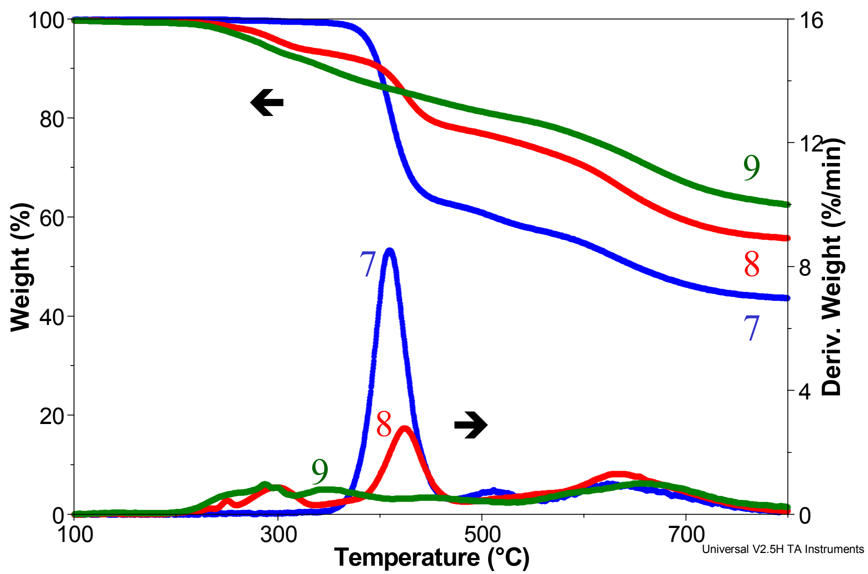
First stage: endothermic
Second stage: exothermic

Thermal decomposition of PHAs containing OMe groups

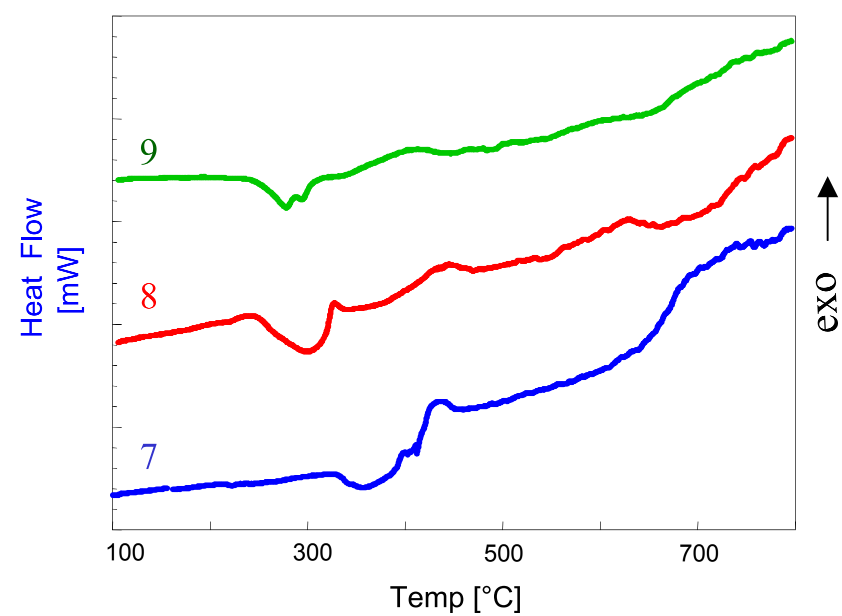


($10^oC/min, N_2$)

PHA-7: R_1= Me; PHA-8: R_1= H, Me; PHA-9: R_1= Me, $PO(OMe)_2$



TGAs and derivative of TGAs (DTGs)



DSC curves

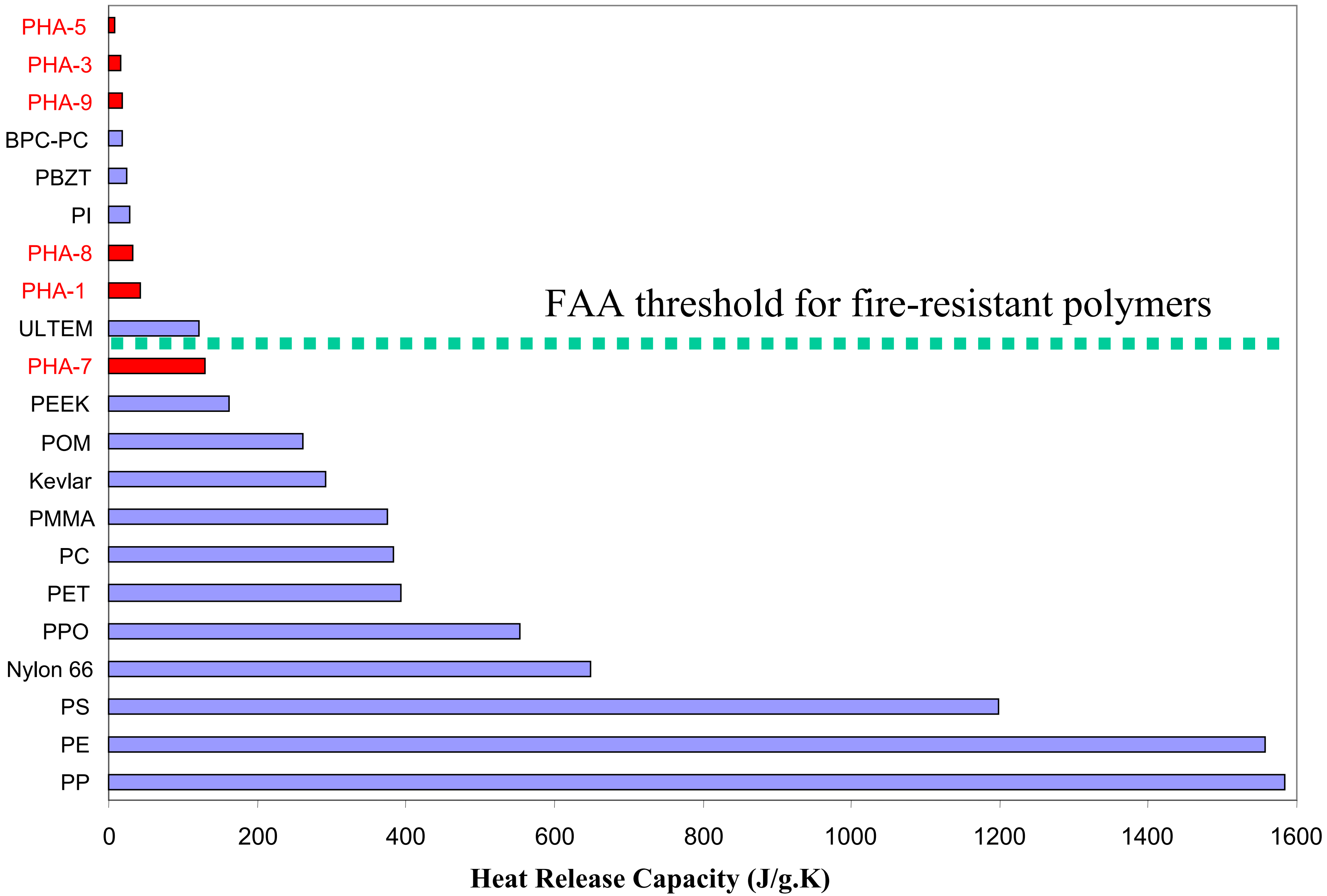
Flammability of PHAs (1)

Samples	H.R.capacity [a] (J/g.K)	Total heat [a] (kJ/g)	Peak mass loss rate [b] (x 10^3/s)	Char yield [b] (%)
PHA-7 (-OMe)	130	17	1.4	43
PHA-1 (-OH) (iso)	42	10	0.4	56
PHA-8 (-OMe,-OH)	33	11	0.5	55
PHA-9 (-OMe,-OPO($OMe)_2$)	18	9	0.2	60
PHA-3 (-OH, m-Br)	17	5	0.4	39
PHA-5 (-OH, -CF_3, m-Br)	8	3	0.7	36

(a) PCFC results. Pyrolyze at 4.3^oC/s to 930^oC.

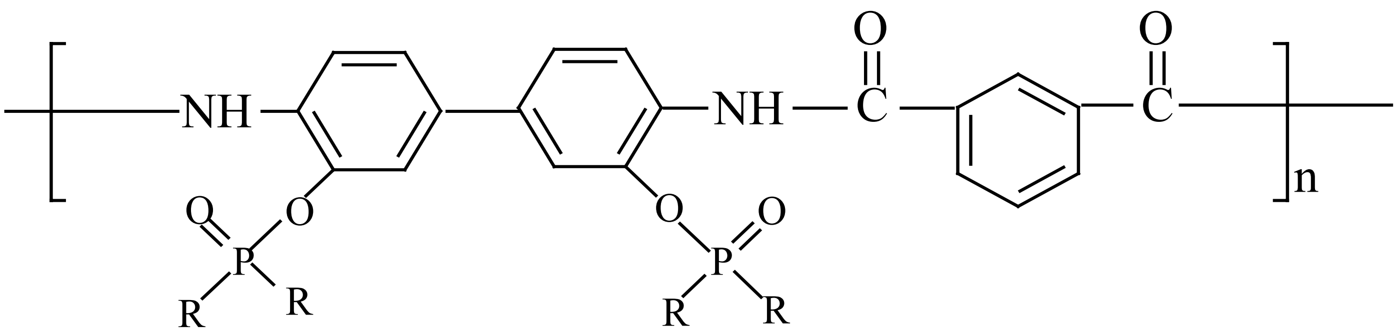
(b) TGA/DSC results. Heat at 10^oC/min to 1000^oC. Char yield is the solid residue left at 930^oC.

The flammability of polymers

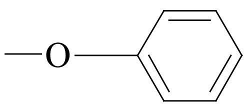


Structures of PHA and its derivatives (2)

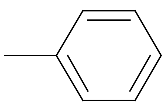
PHAs containing phosphate groups



R:



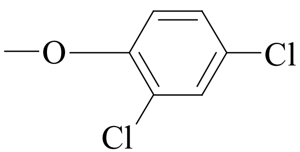
PHA-10



PHA-11

$-OC_2H_5$

PHA-12

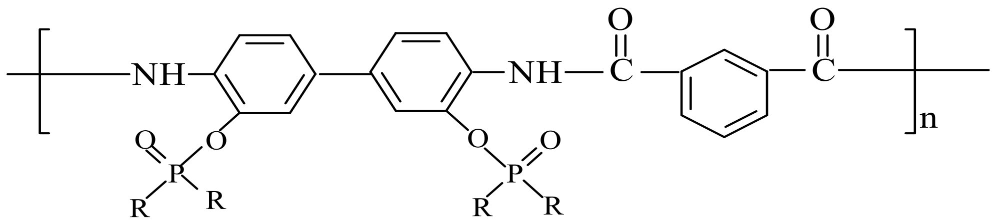


PHA-13

$-OCH_3$

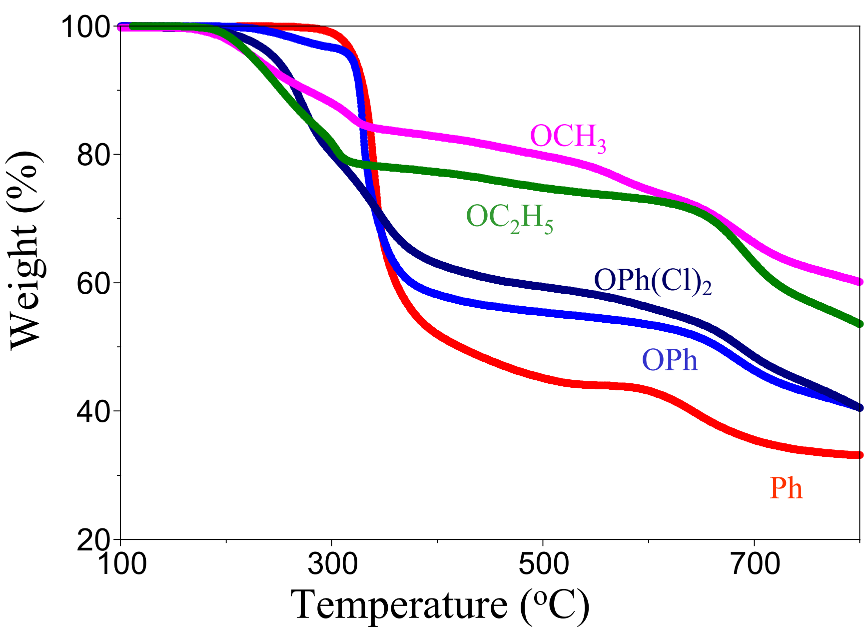
PHA-14

Thermal decomposition of phosphate PHAs

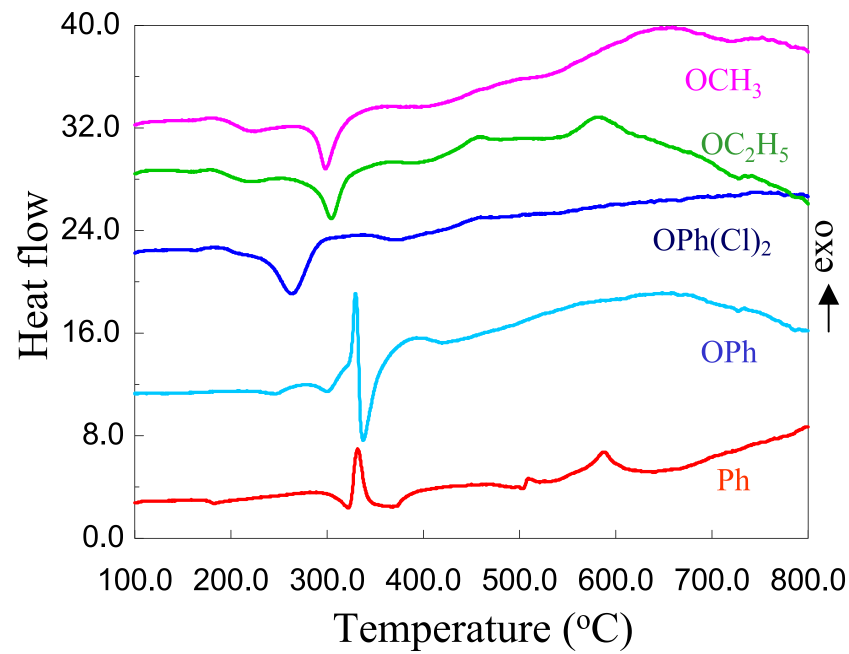


($10^{o}C/min$, N_2)

R	OPh	Ph	OC_2H_5	$OPh(Cl)_2$	OCH_3



TGA curves



DSC curves

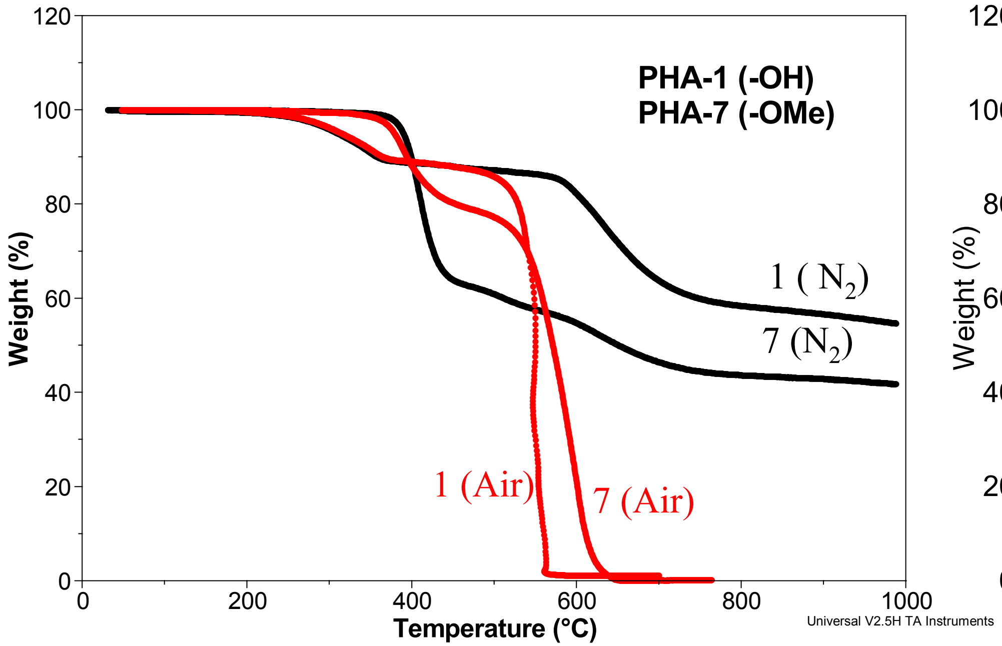
Flammability of phosphate PHAs

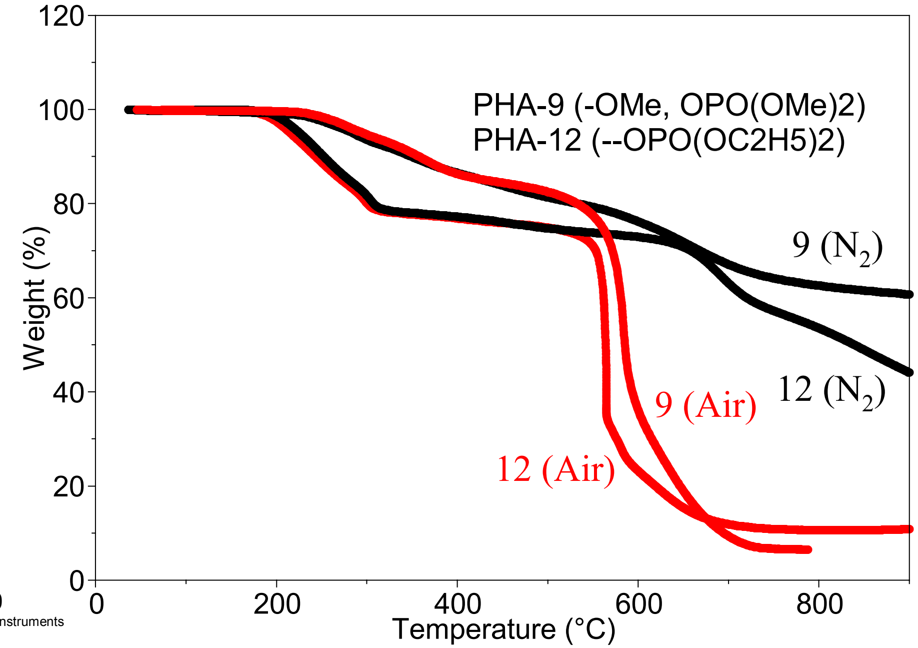
Samples	H.R.capacity [a] (J/g.K)	Total heat [a] (kJ/g)	Peak mass loss rate [b] (x 10^3/s)	Char yield [b] (%)
PHA-10 (-OPh)	340	15	3.3	36
PHA-11 (-Ph)	210	21	2.9	32
PHA-12 (-OC_2H_5)	73	9	0.4	41
PHA-13 (-$OPh(Cl)_2$)	59	8	0.6	29
PHA-14 (-OCH_3)	19	8	0.2	52

(a) PCFC results. Pyrolyze at 4.3°C/s to 930°C.

(b) TGA/DSC results. Heat at 10°C/min to 1000°C. Char yield is the solid residue left at 930°C.

Thermal oxidative stability of PHAs

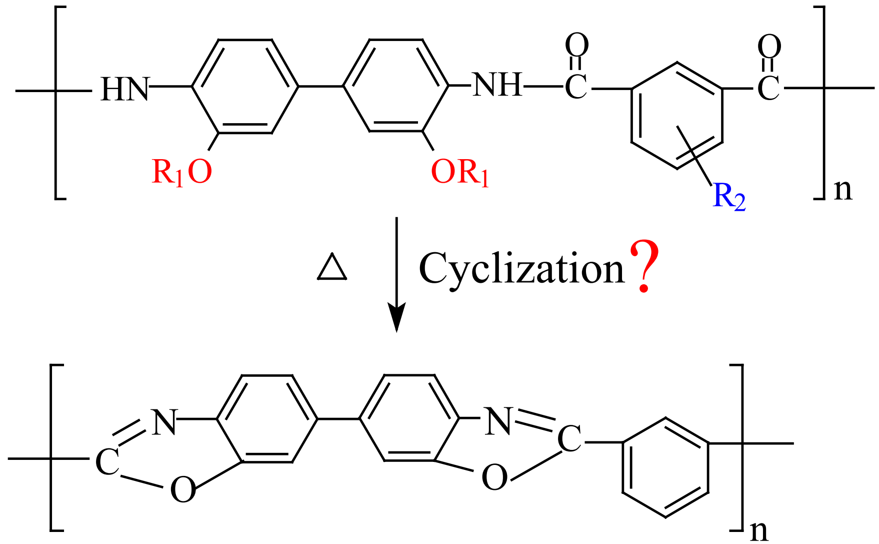




TGA curves (10°C/min)

- Oxygen: No effect on initial thermal stability
- Char: Easy to oxidize
- Phosphorus: Enhance char formation

Thermal cyclization of PHAs?



PBO

+

$\boxed{R_1OH + R_2\cdot}$

R_1OH (H_2O, CH_3OH or phosphate)

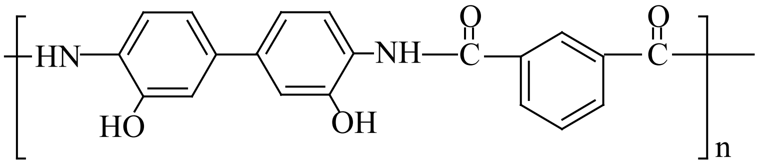
+

$R_2\cdot$ (Br· and other flame-quenching molecules)

R_1 = H, CH_3, $PO(OPh)_2$, $POPh_2$, $PO(OCH_3)_2$, $PO(OC_2H_5)_2$, $PO(OPhCl_2)_2$

R_2 = Br

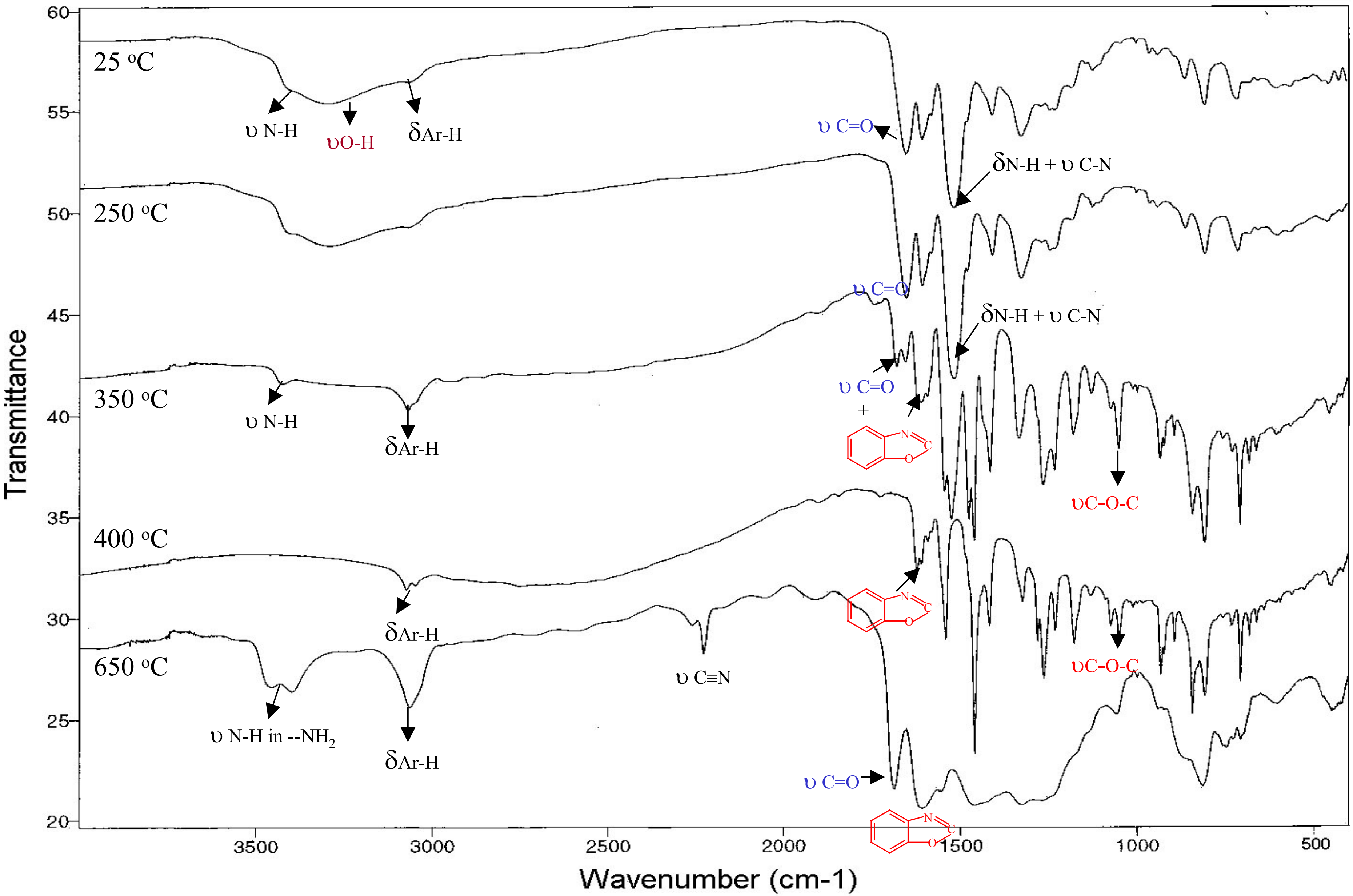
Elemental analysis of PHA-1



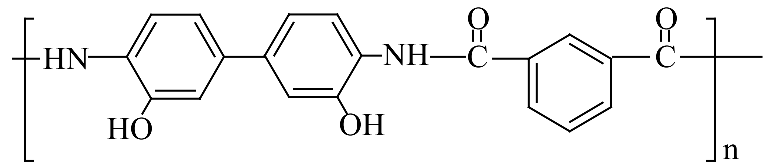
Temperature (^oC)	Measured (%) C	H	N	O	Calculated (%) C	H	N	O	Char (%)
250 (PHA)	67.26	3.78	7.56	21.4	69.4	4.1	8.1	18.4	100
400 (PBO)	75.96	3.26	8.62	12.16	77.4	3.2	9	10.4	90
650	79.97	2.93	7.84	9.26					75
1000	87.07	0.44	3.78	8.71					50

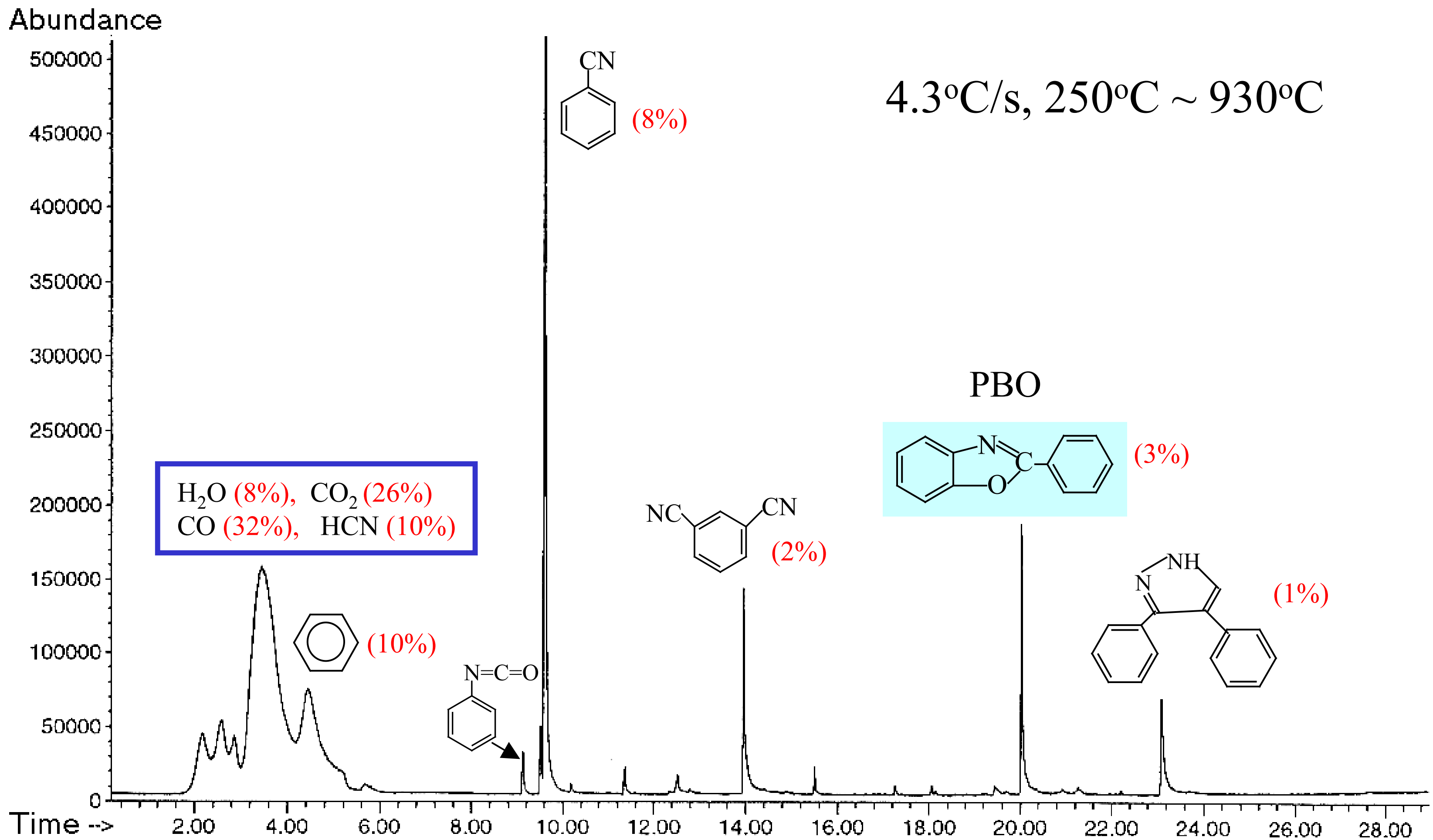
Nominal formula of char at 1000^{o}C : $C_{7.3}\ H_{0.44}\ N_{0.27}\ O_{0.5}$

IR spectra of PHA-1 at different temperatures



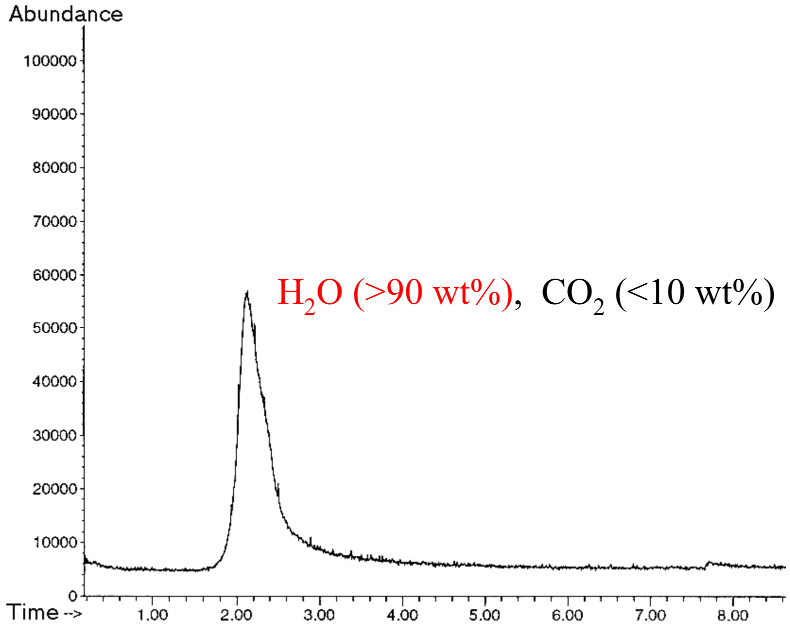
Pyrolysis GC/MS (PHA-1)





** The numbers in the parentheses are the weight percents of each volatile*

PHA-1 (-OH)

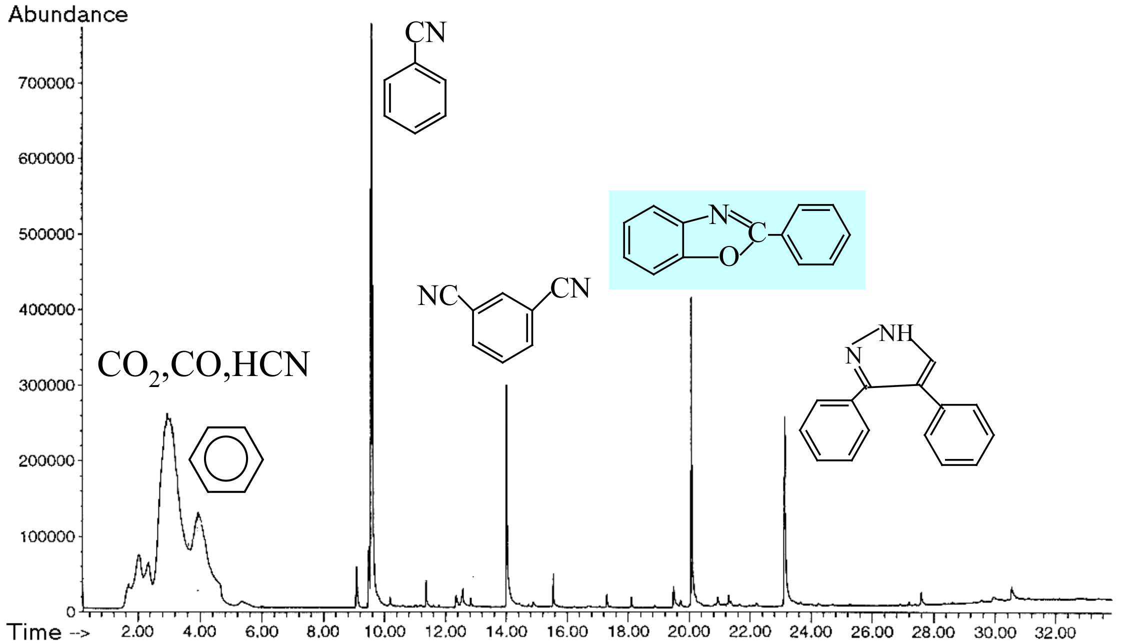


First stage: 250 ~ 380 ^oC

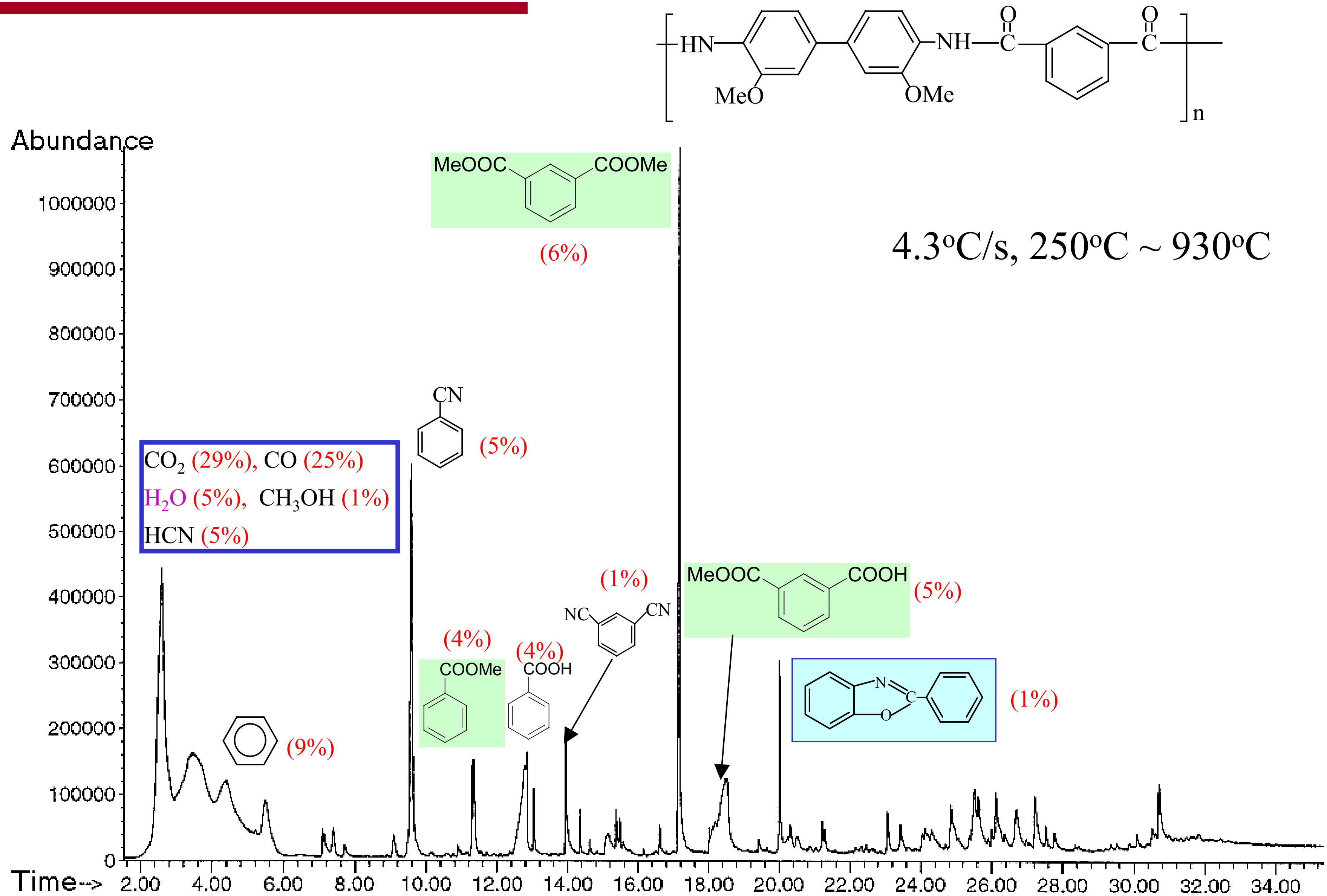
(Cyclization)

Second stage: 380 ~ 930 ^oC

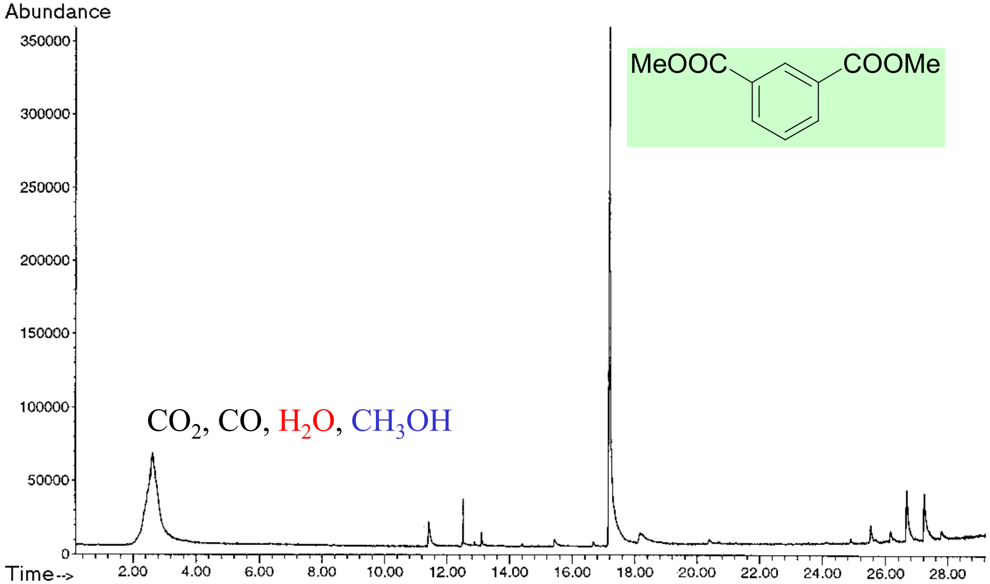
(Main chain scission)



Pyrolysis GC/MS (PHA-7)



PHA-7 (--OMe)

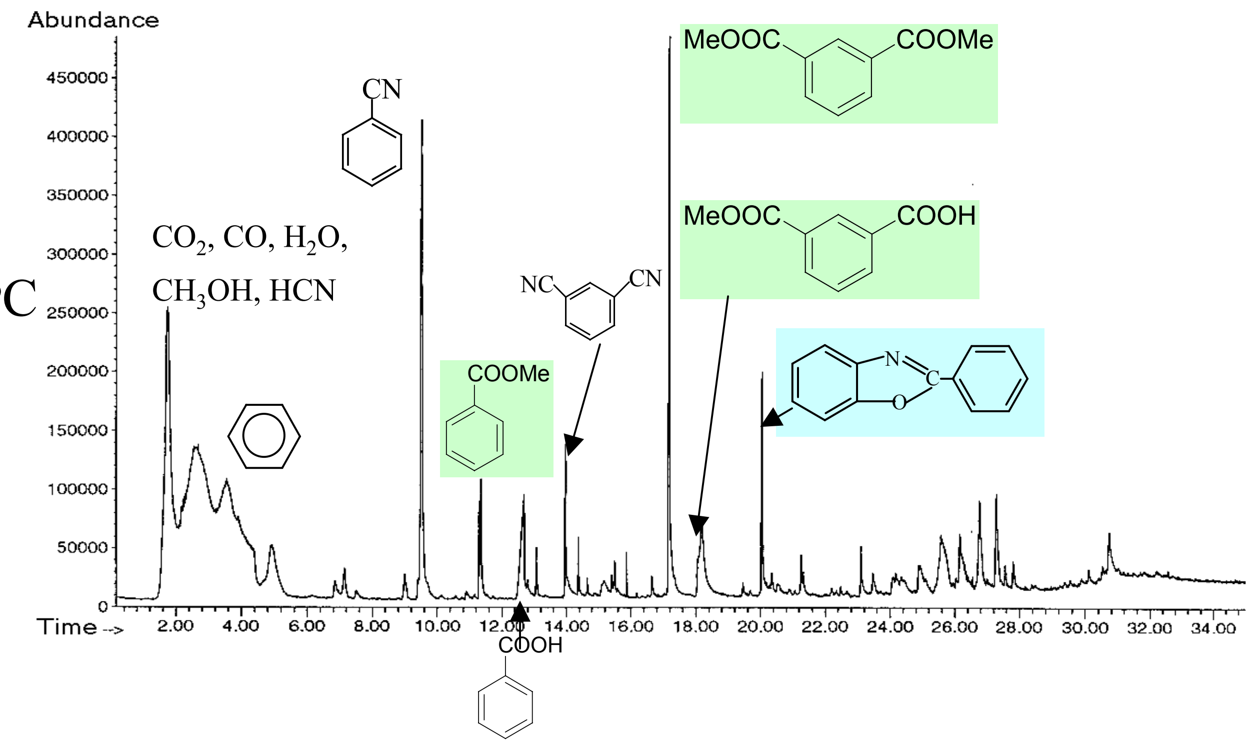


First stage: 350 ~ 465 ^oC

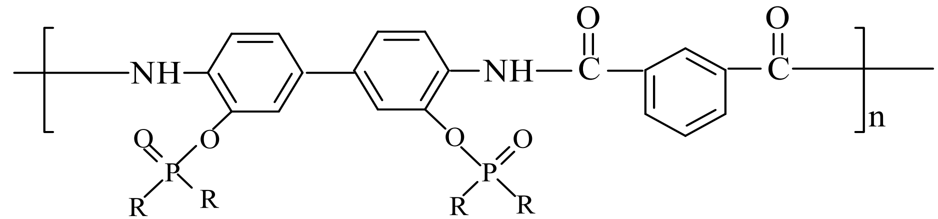
(Backbone scission and cyclization)

Second stage: 465 ~ 930 ^oC

(Random scission)

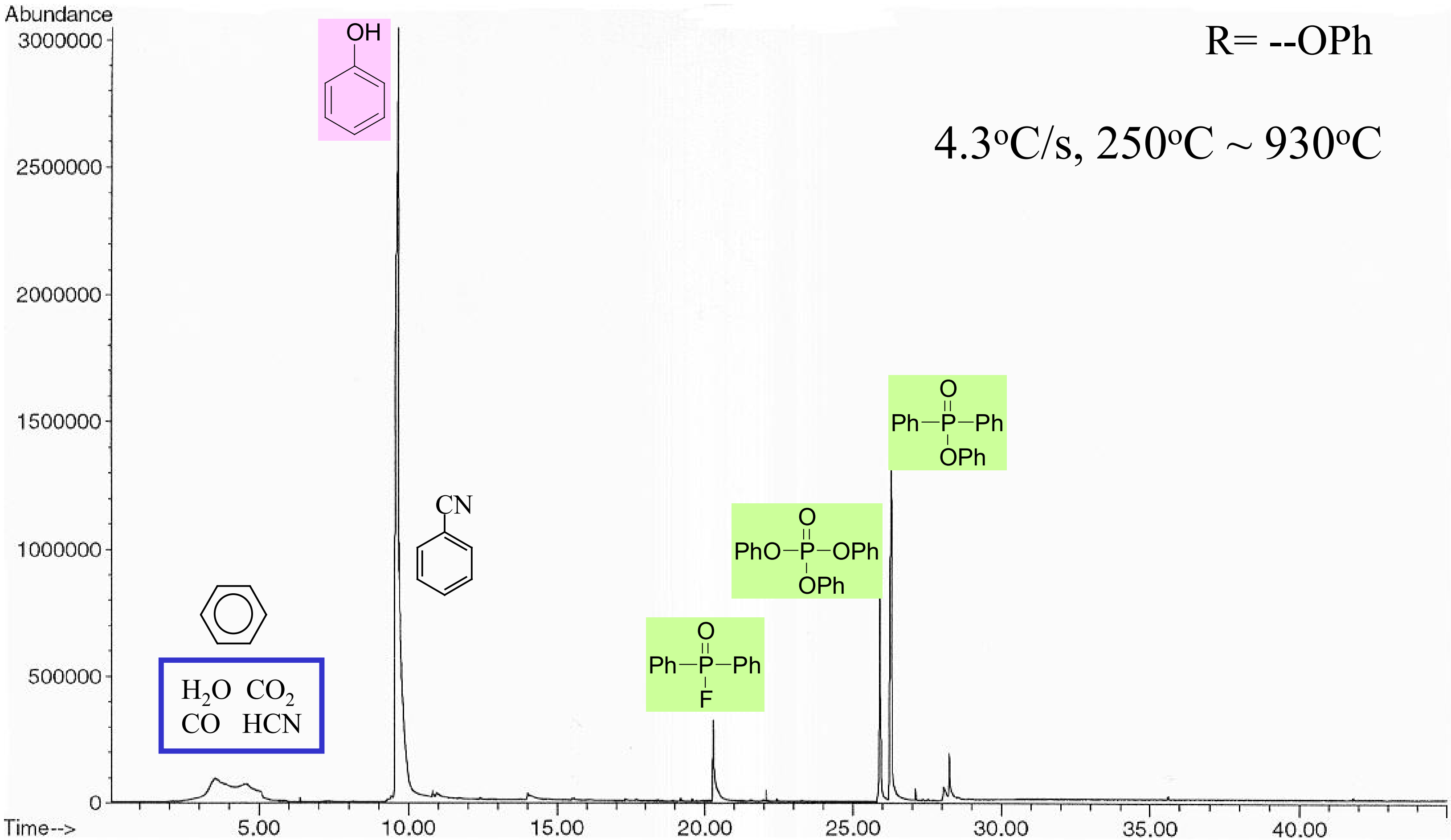


Pyrolysis GC/MS (PHA-10)



R= --OPh

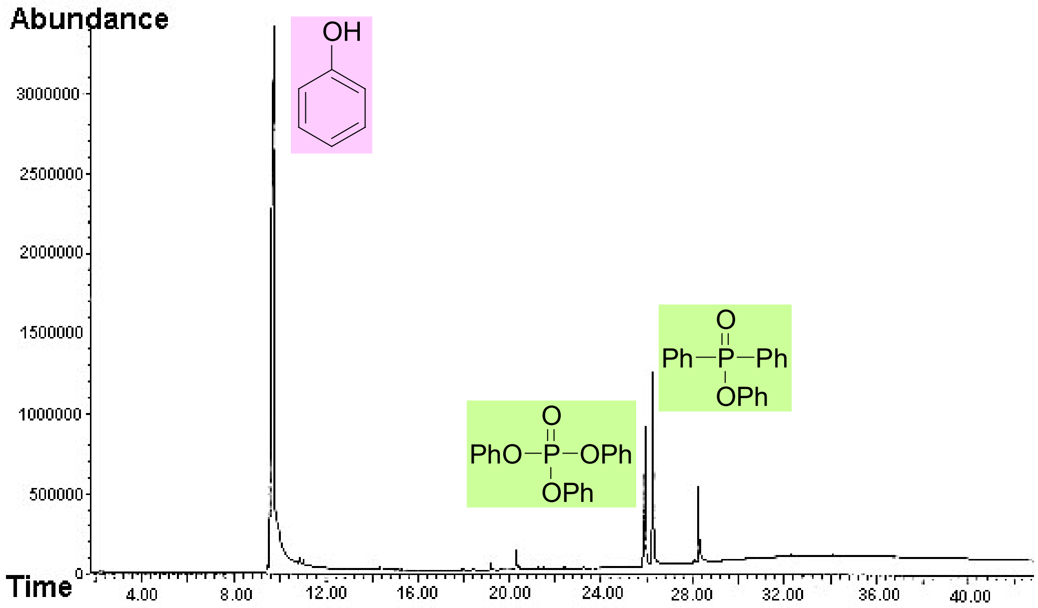
4.3^{o}C/s, 250^{o}C ~ 930^{o}C



PHA-10 (-OPh)

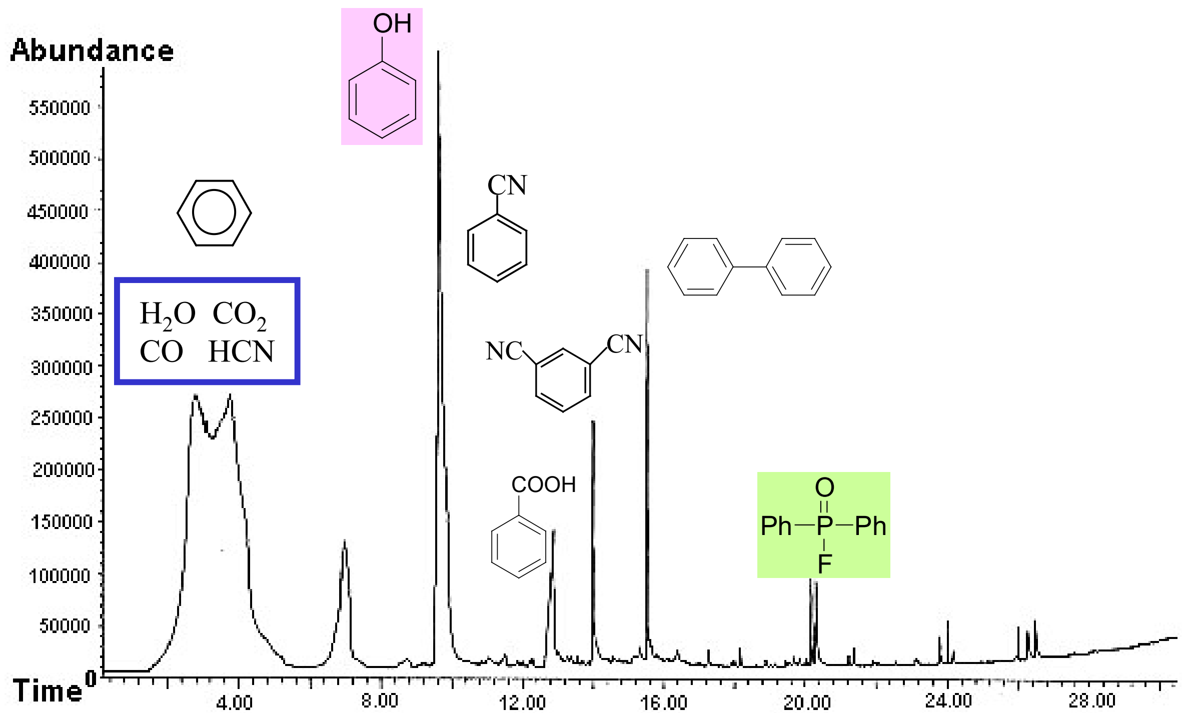
250 ~ 500°C

(Side group cleavage)

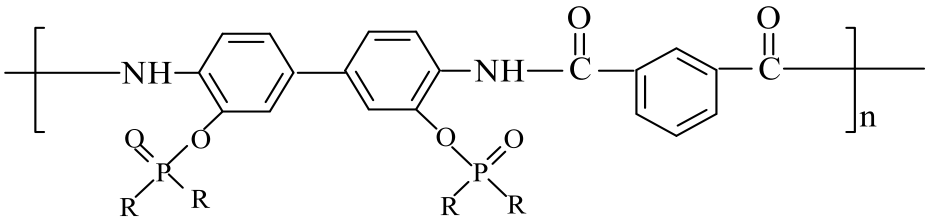


500 ~ 930°C

(Main chain scission)

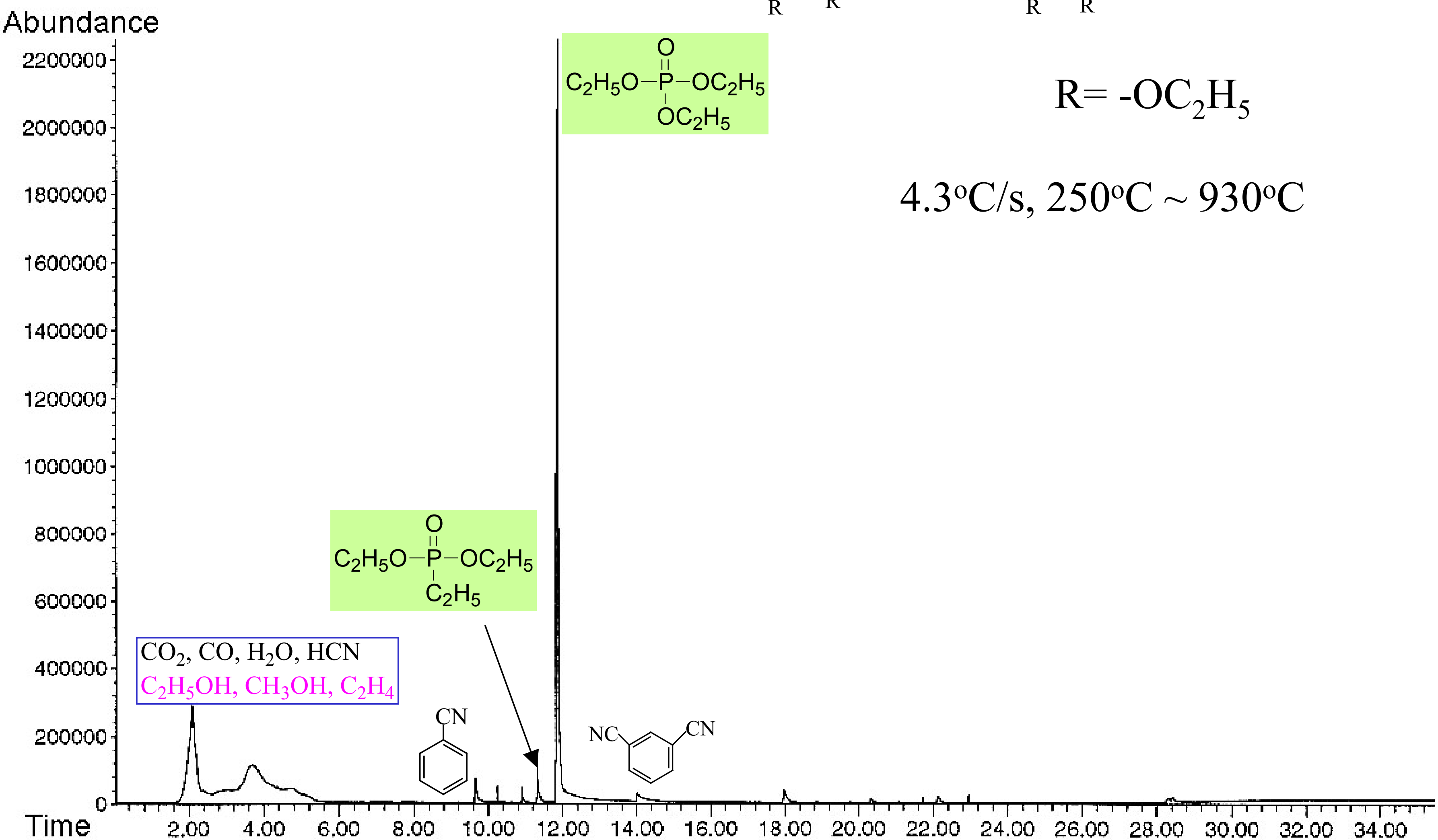


Pyrolysis GC/MS (PHA-12)

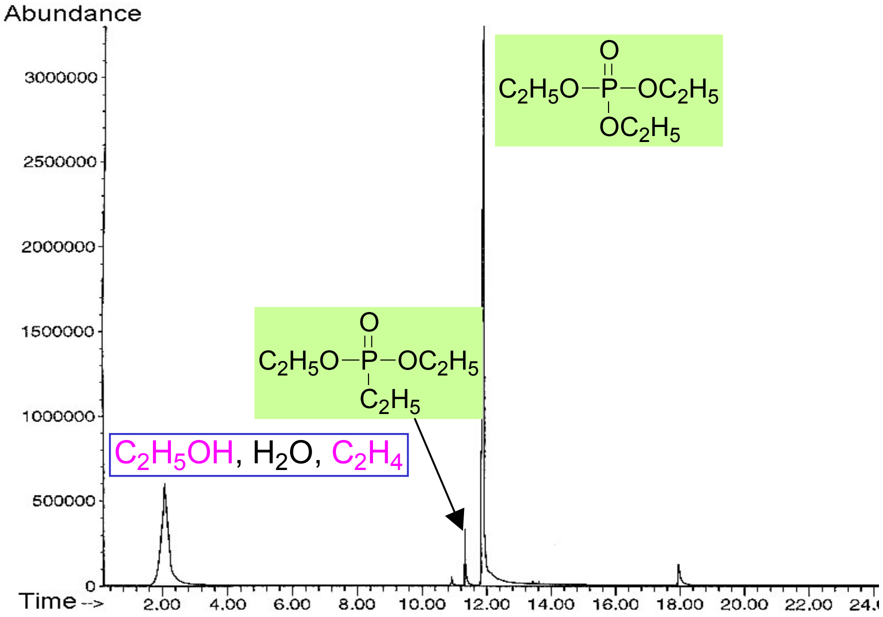


R= $-OC_2H_5$

4.3^{o}C/s, 250^{o}C ~ 930^{o}C



PHA-12 ($-OC_2H_5$)

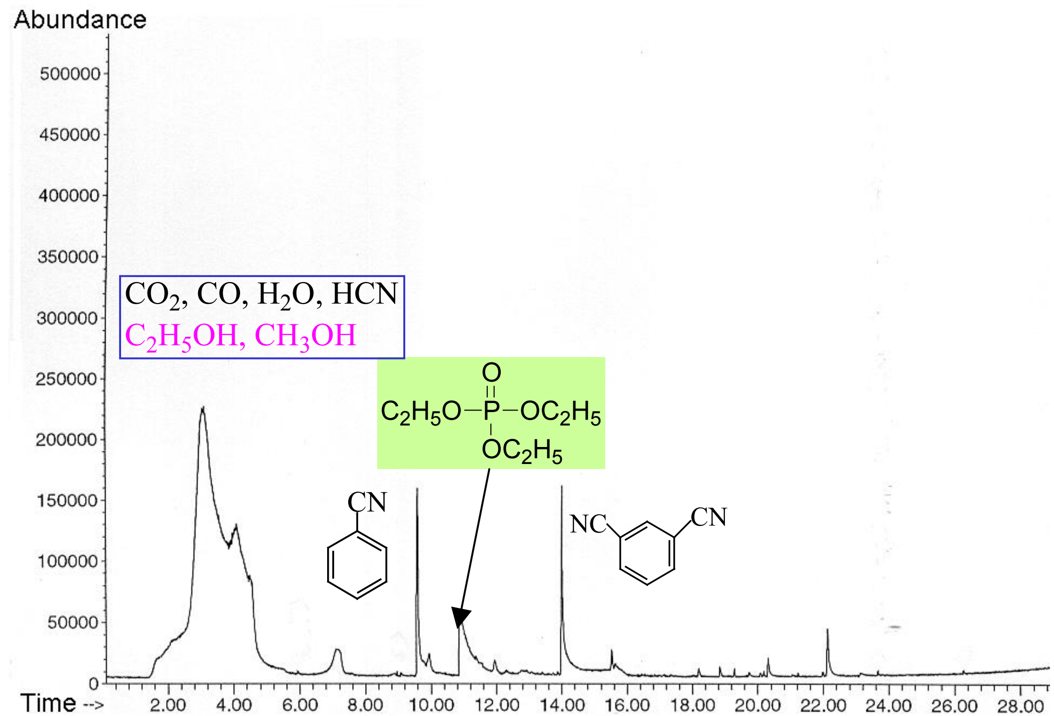


200 ~ 400^{o}C

(Side group cleavage)

400 ~ 930^{o}C

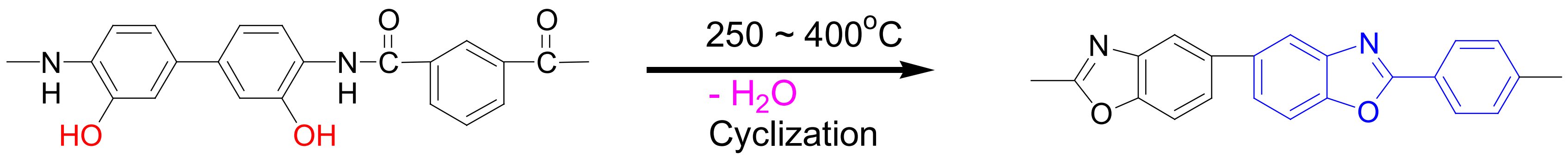
(Main chain scission)



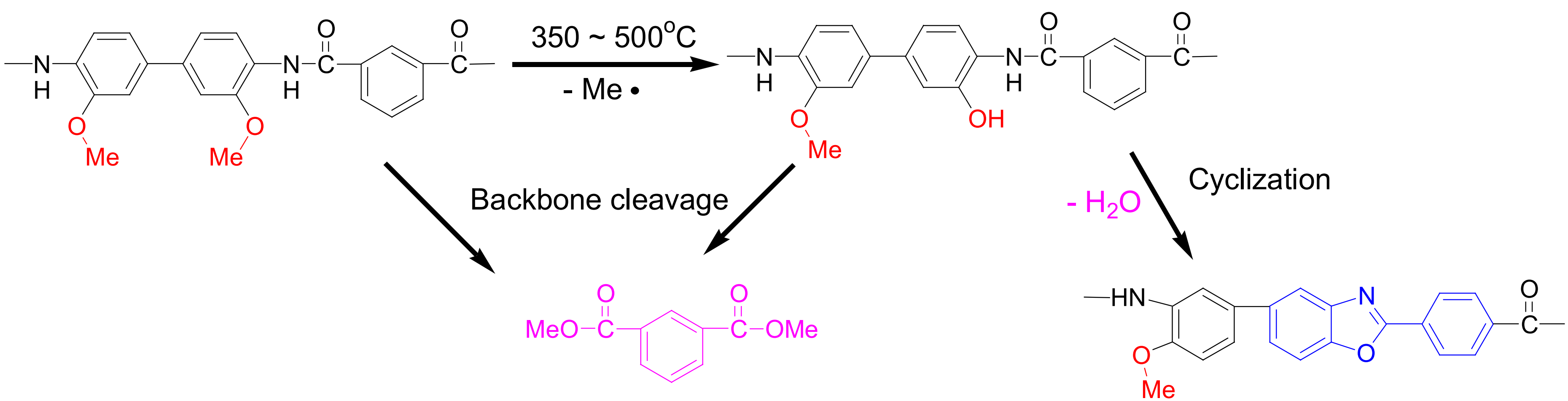
Decomposition mechanisms of PHA and its derivatives

(a) Low temperature (< 500°C)

I: PHA and halogenated PHAs

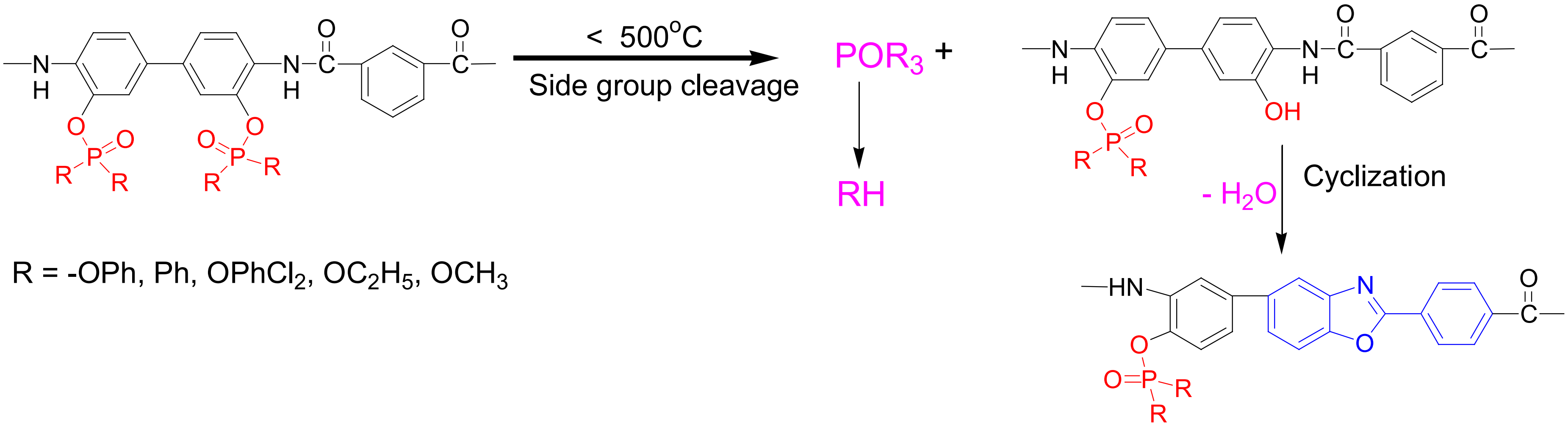


II: PHAs with methoxy groups

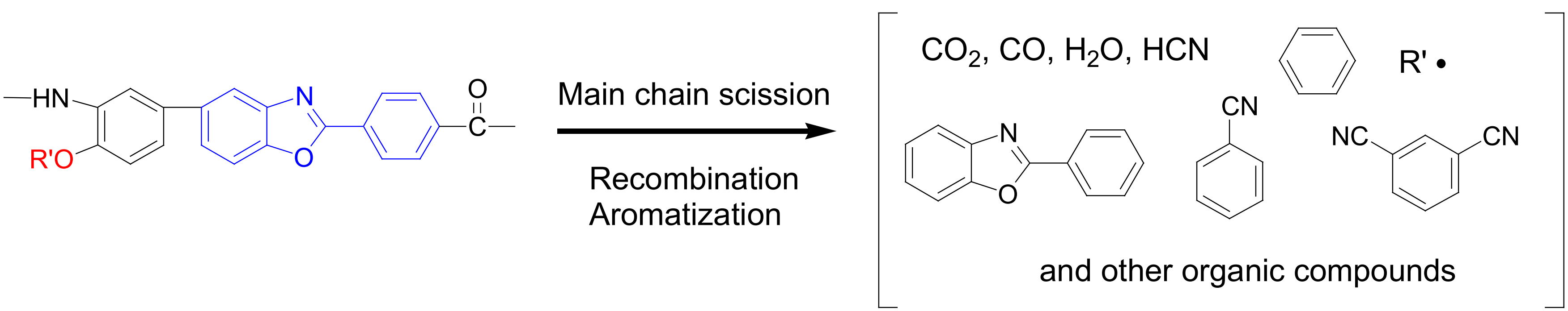


Decomposition mechanisms of PHA and its derivatives

(III) PHAs with phosphate groups



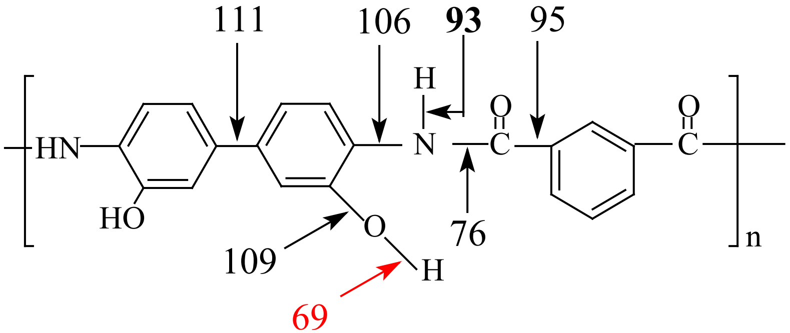
(b) High temperature (>500°C)



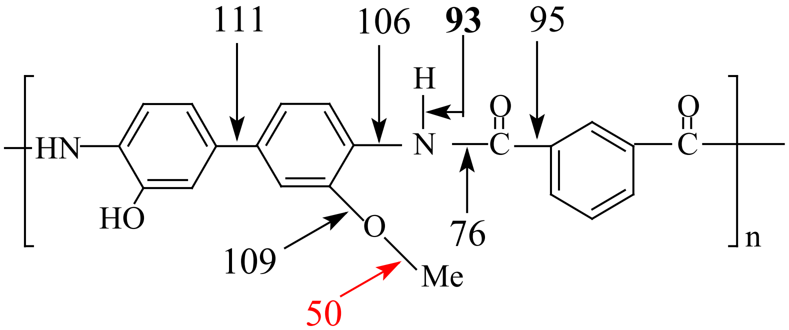
Calculated bond energies (kcal/mol)

Method: B3LYP/6-31G(d), Mean Error = 8kcal/mol

PHA-1



PHA-7



Weakest bonds: O-H (PHA-1), O-Me (PHA-7)

Conclusions

- PHA and its derivatives (except for some phosphate PHAs) are a series of new fire-safe polymers that have extremely low heat-release rates and very high char yields.
- PHA and halogenated PHAs decompose in two stages.
  - First stage, water release to form PBO structure (endothermic).
  - Second stage, random scission of PBO backbone (exothermic).
- Elemental analysis and IR prove that the first stage of decomposition of PHA-1 corresponds to cyclization into PBO.
- The major decomposition products of PHAs, except for PHA-7 and phosphate PHAs, are CO_2, CO, H_2O and HCN, which result in their low flammability.
- Substitution of hydroxyl groups with some other bigger groups such as methoxy or phosphate groups will lead to increase of the flammability due to the introduction of weak linkages between side groups and polymer main chain.
- PCFC is a very rapid and quantitative screening tool for newly-synthesized fire-resistant materials.

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