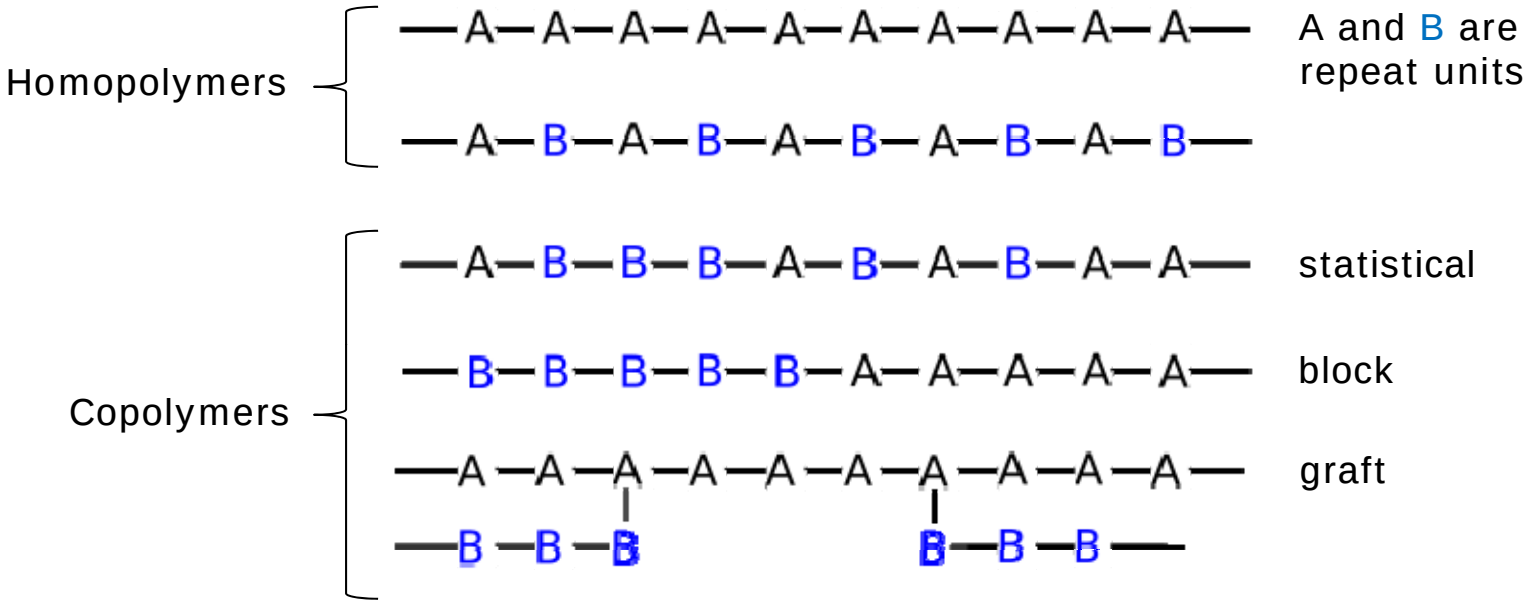
Reaction to Fire of Solids

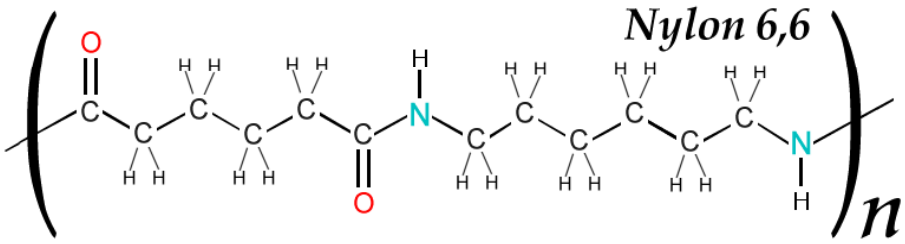
(Polymers and Composites)

Stanislav I. Stoliarov

Fire Protection Engineering

Chemical Classification of Polymers



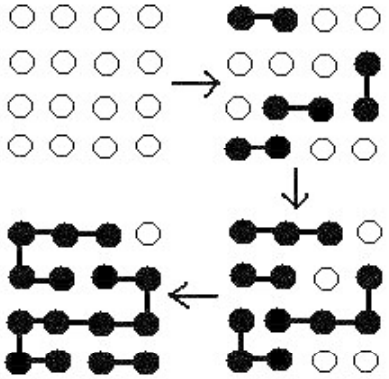


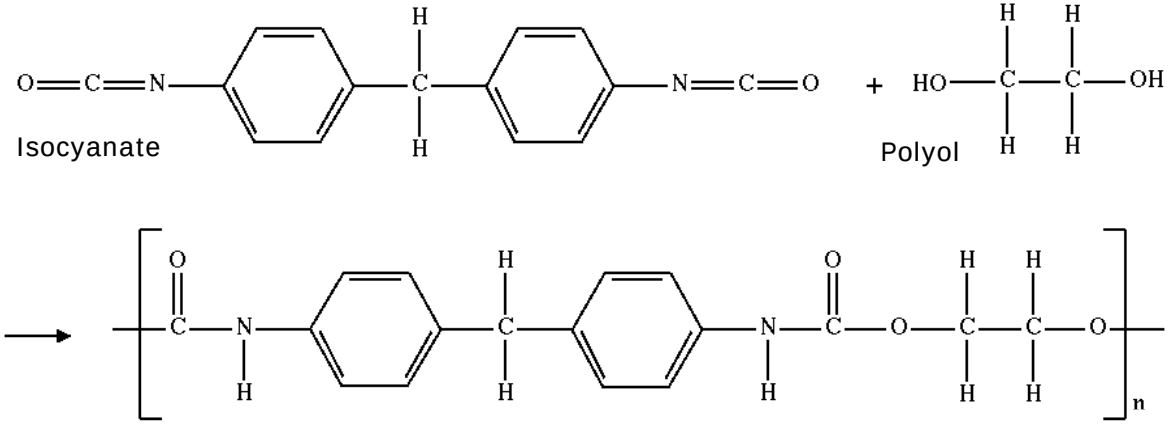
Poly[imino(1,6-dioxohexamethylene) imnohexamethylene] has high mechanical strength; it is used for bearing cages, electro-insulating elements, pipes, carpet fibers, ropes and conveyor belts.

Homo- or copolymer?

Polymerization Mechanisms

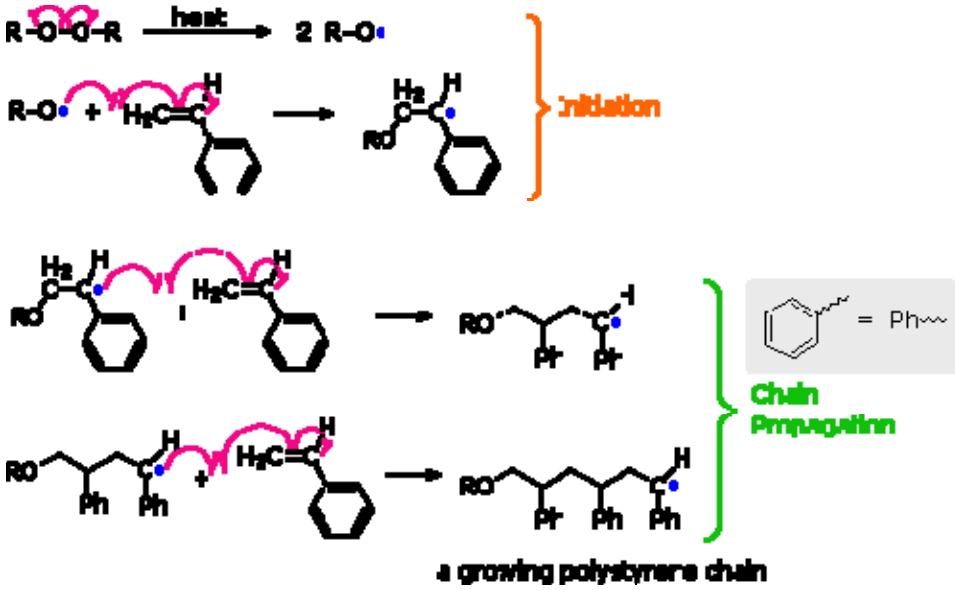
Step Polymerization:





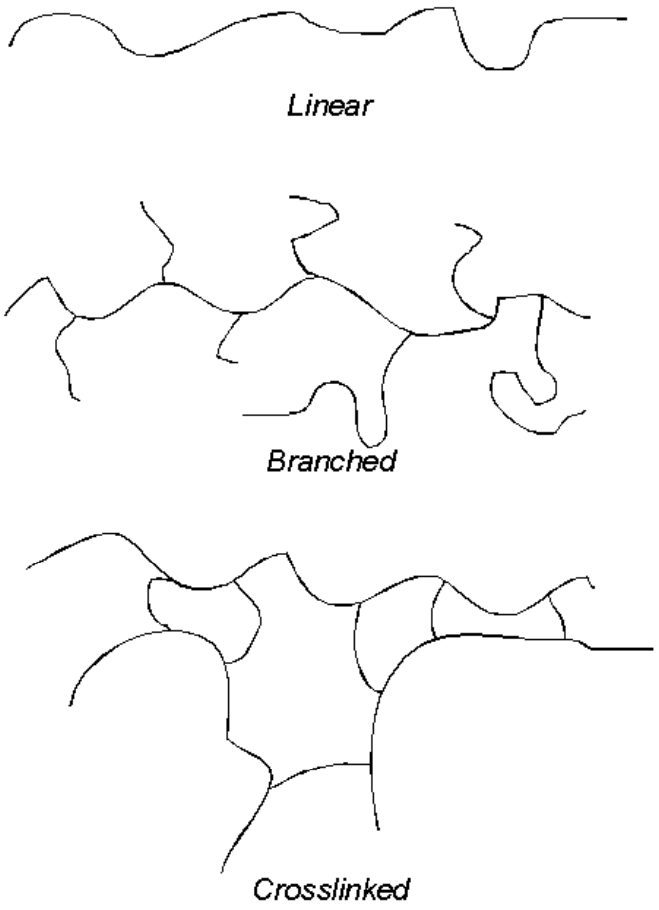
Polyurethanes are used in the manufacture of flexible foam, rigid foam insulation, automotive suspension bushings, high performance adhesives, surface coatings and surface sealants and hard-plastic parts for electronic instruments.

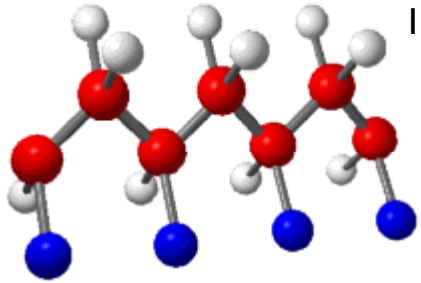
Chain Polymerization:



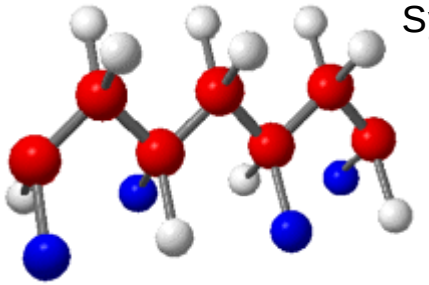
Polystyrene is one of the most widely used polymers; its uses include protective packaging (such as packing peanuts and DVD cases), building insulation, containers, lids, bottles, trays and disposable cutlery.

Skeletal Structure of Polymers



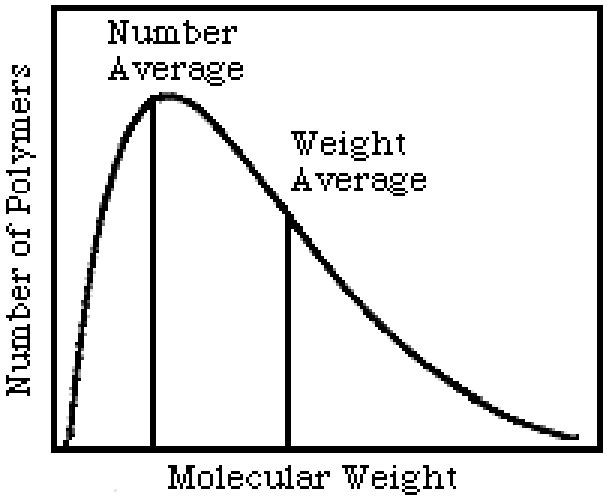


Isotactic



Syndiotactic

Molar Mass and Degree of Polymerization



$$\overline{M}_N = \sum \underbrace{\left(\frac{N_i}{\sum N_i} \right)}_{\text{mol fraction}} M_i = \frac{\sum N_i M_i}{\sum N_i}$$ - Number-average molar mass, kg mol^{-1}

$$\overline{M}_W = \sum \underbrace{\left(\frac{N_i M_i}{\sum N_i M_i} \right)}_{\text{mass fraction}} M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$ - Weight-average molar mass

$$PDI = \frac{\overline{M}_W}{\overline{M}_N}$$ - Polydispersity or heterogeneity index

$$\overline{x}_N = \frac{\overline{M}_N}{M_{\text{repeat unit}}}$$ - Number-average degree of polymerization

$$\overline{x}_W = \frac{\overline{M}_W}{M_{\text{repeat unit}}}$$ - Weight-average degree of polymerization

Composite Materials

Composites

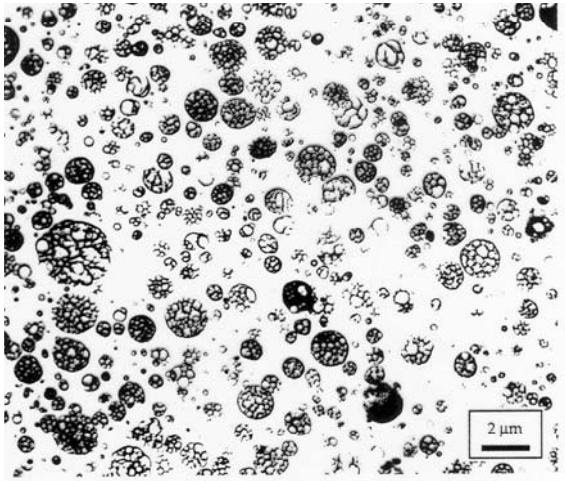
Macro: 10^{-3} to 10^{-6} m inclusions

Nano: 10^{-7} to 10^{-9} m inclusions

Particle

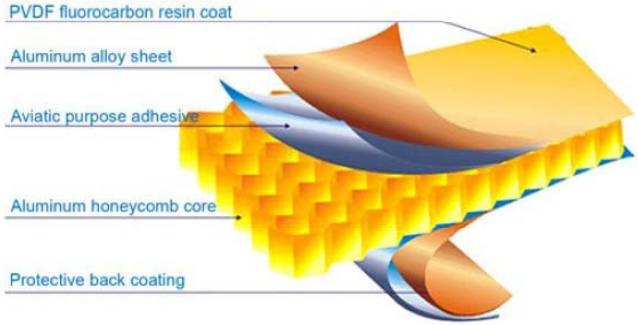
Sandwich

Fiber

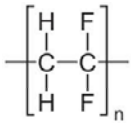


High-impact polystyrene (HIPS)

A transmission electron micrograph of a 50 nm section in a HIPS material, showing the multiple inclusion particle structure which results from the bulk polymerization technique.



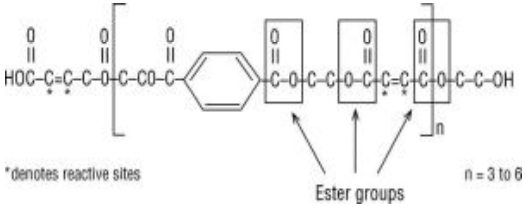
Poly(vinylidene fluoride) (PVDF) -> with aluminum honeycomb



Glass Carbon

+

Unsaturated polyester



dissolved in styrene

+

heat = Fiberglass

Applications include swimming pools, doors, sporting equipment and boat hulls.

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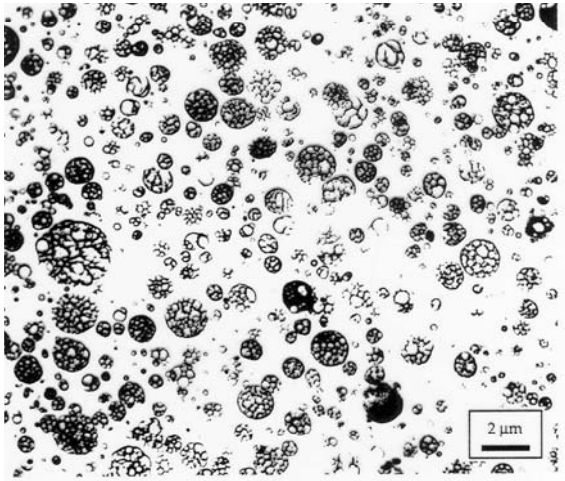
Particle

Sandwich

Fiber



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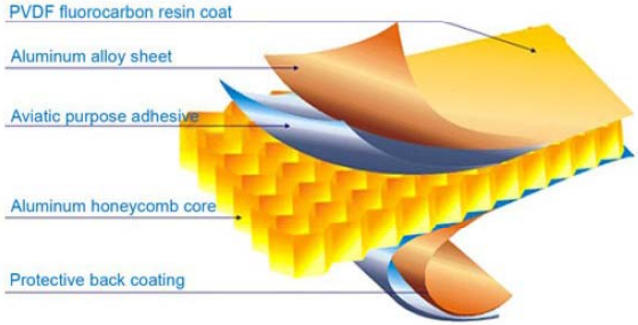

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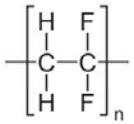
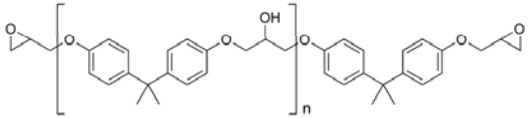


Glass

Carbon

+

Bisphenol A epoxy



+

hardener & heat = Carbon Fiber

Applications include aerospace, automotive and sporting equipment.

Composite Materials

Composites

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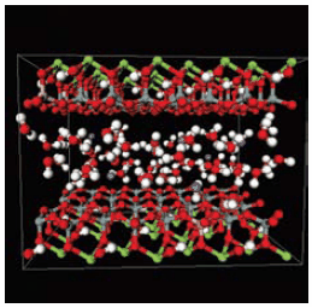
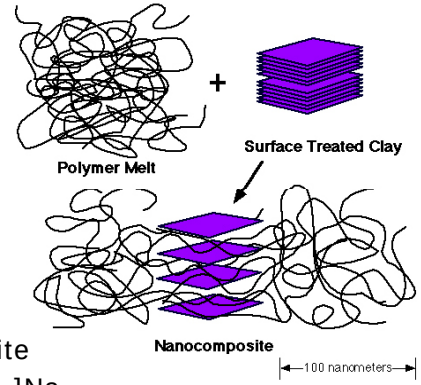
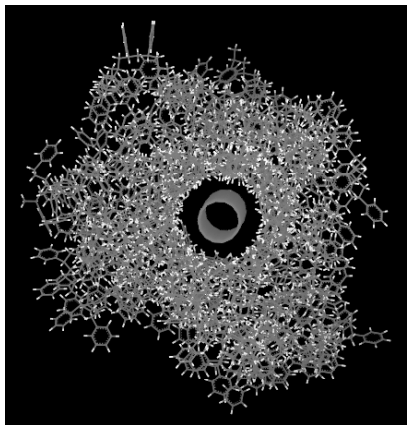
Clay platelet based



Hydrated montmorillonite
$(Mg_{0.33}Al_{1.67})Si_4O_{10}(OH)_2]Na_{0.33}$



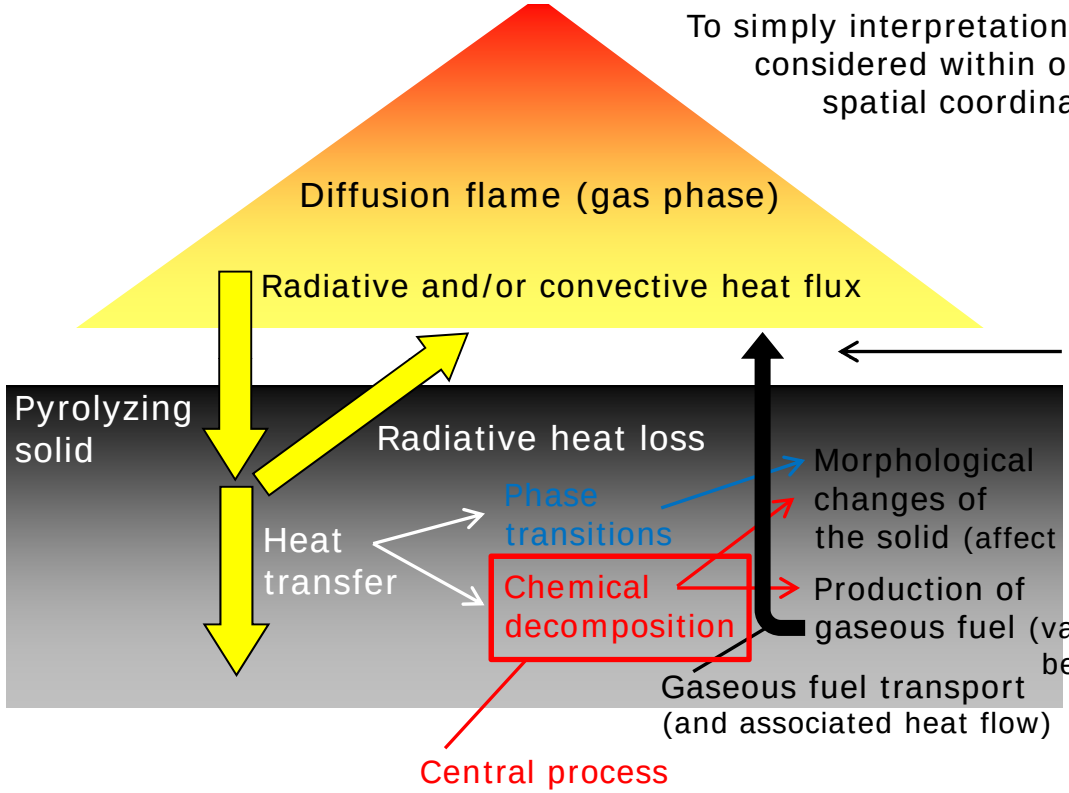
Carbon nanotube or platelet based



Single-wall carbon nanotube in polystyrene

- Nanoadditives may produce higher stiffness, strength and improved wear resistance at small (0.5-3 wt.%) loadings.
- Good dispersion in polymer is required and usually hard to achieve.

Mechanism of Polymer Combustion



To simply interpretation of key processes, the mechanism is considered within one-dimensional framework (only one spatial coordinate)

Flame consumes all oxygen (no oxygen at the surface)

Flame can be treated as a boundary condition turned on when a critical value of some a solid-phase descriptor is reached.

Morphological changes of the solid (affect heat transport)

Morphological changes may include
- formation of residue layer (char)
- bubbles and fissures
- melt flow

Production of gaseous fuel (vaporization is assumed to be a part of decomposition)

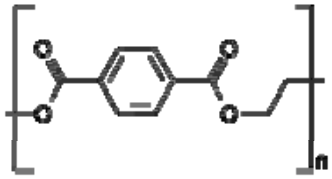
Gaseous fuel transport (and associated heat flow)

Typical Study of Decomposition Chemistry

Applied Polymer SCIENCE

Temperature-Dependent Pyrolytic Product Evolution Profile for Polyethylene Terephthalate (PET)

Ujwala Hujuri, Aloke K. Ghoshal, Sasidhar Gumma DOI: 10.1002/APP.39681

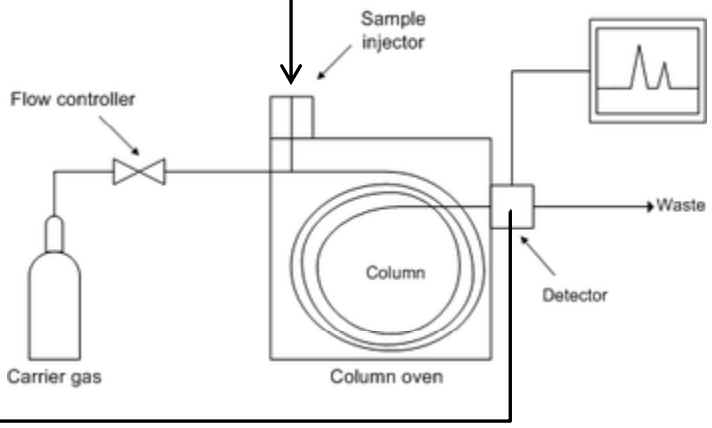


Widely utilized for production of beverage and food containers.

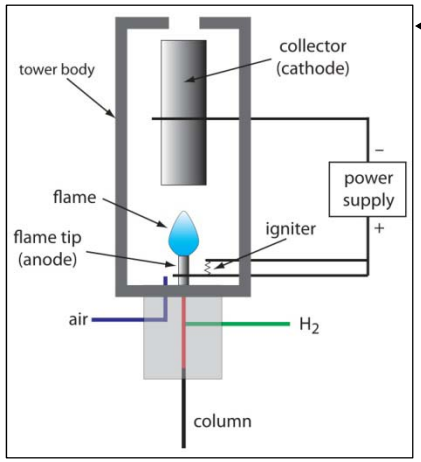
Experimental setup:

Temperature controlled pyrolyzer (< 1 mm thick sample, inert atmosphere)

Gas chromatograph



Flame ionization detector (FID)



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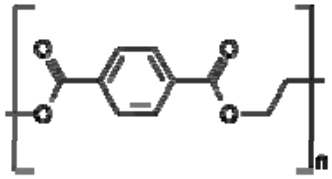

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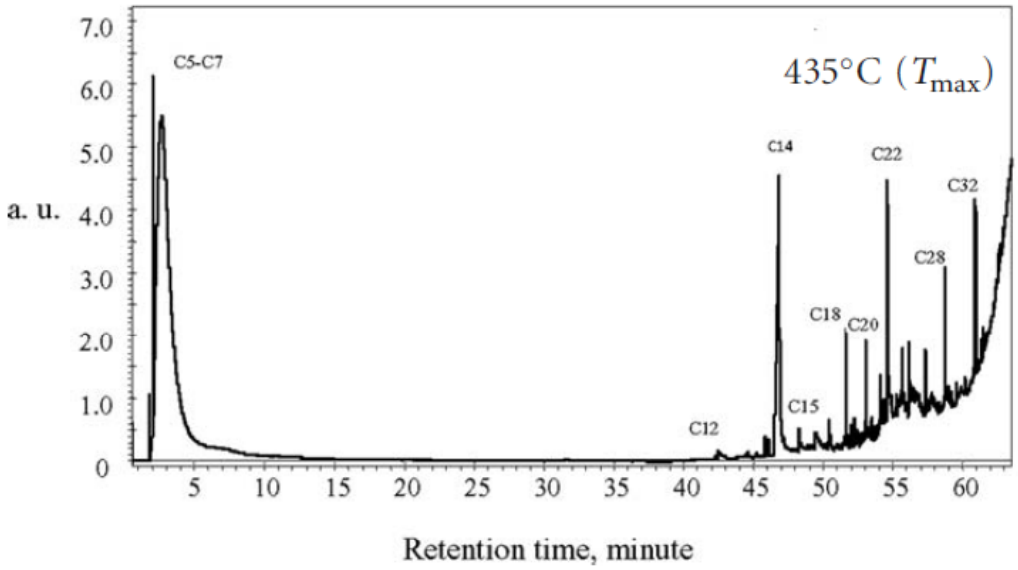

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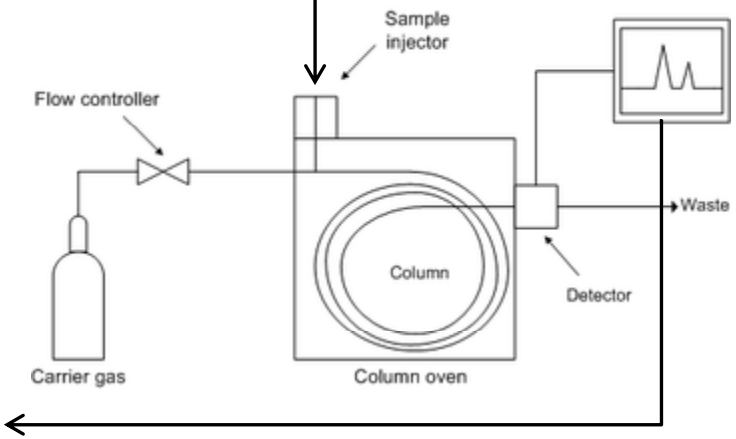

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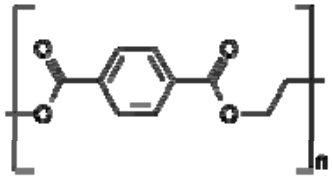

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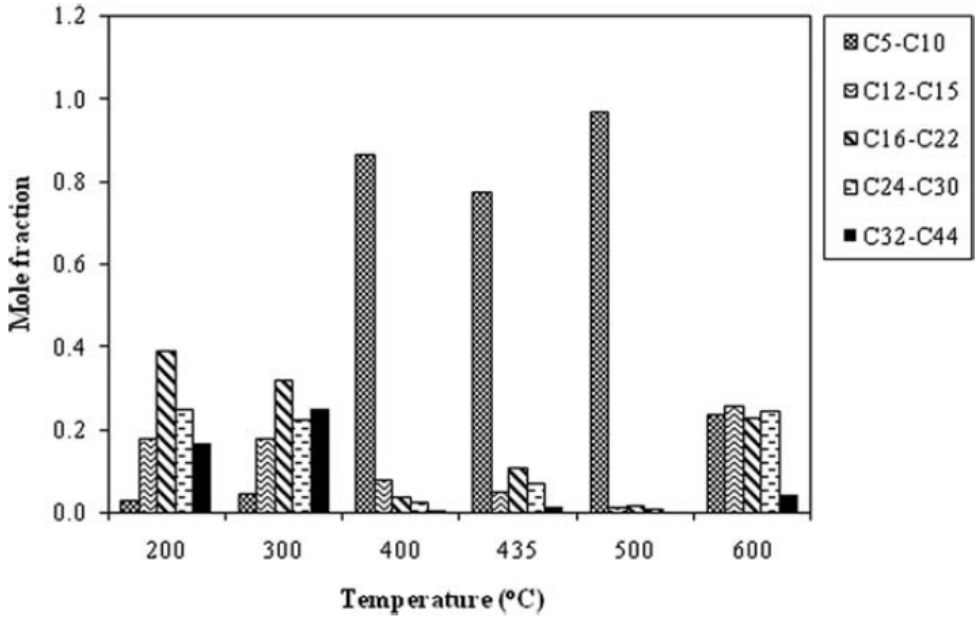

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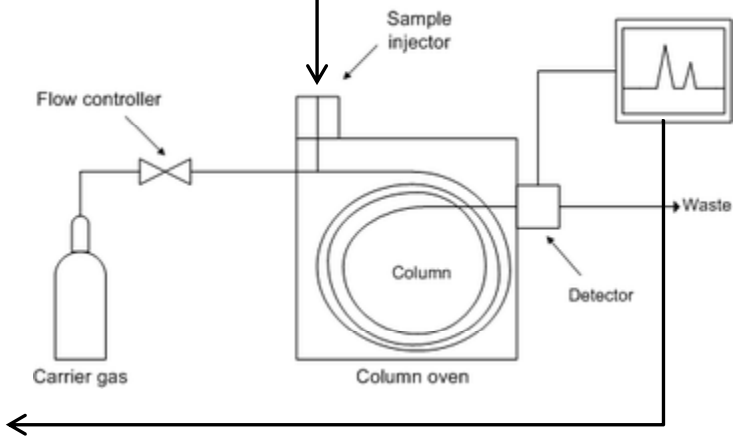

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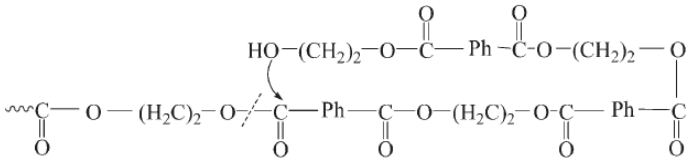
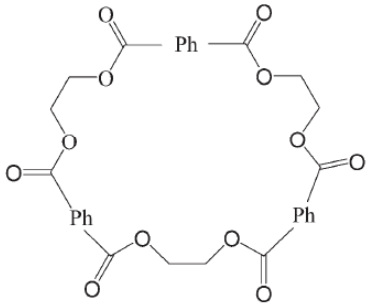
Possible decomposition mechanism:

The polymer has been reported to produce cyclic oligomers.
The oligomers **might** form this way:





Cyclic Trimer

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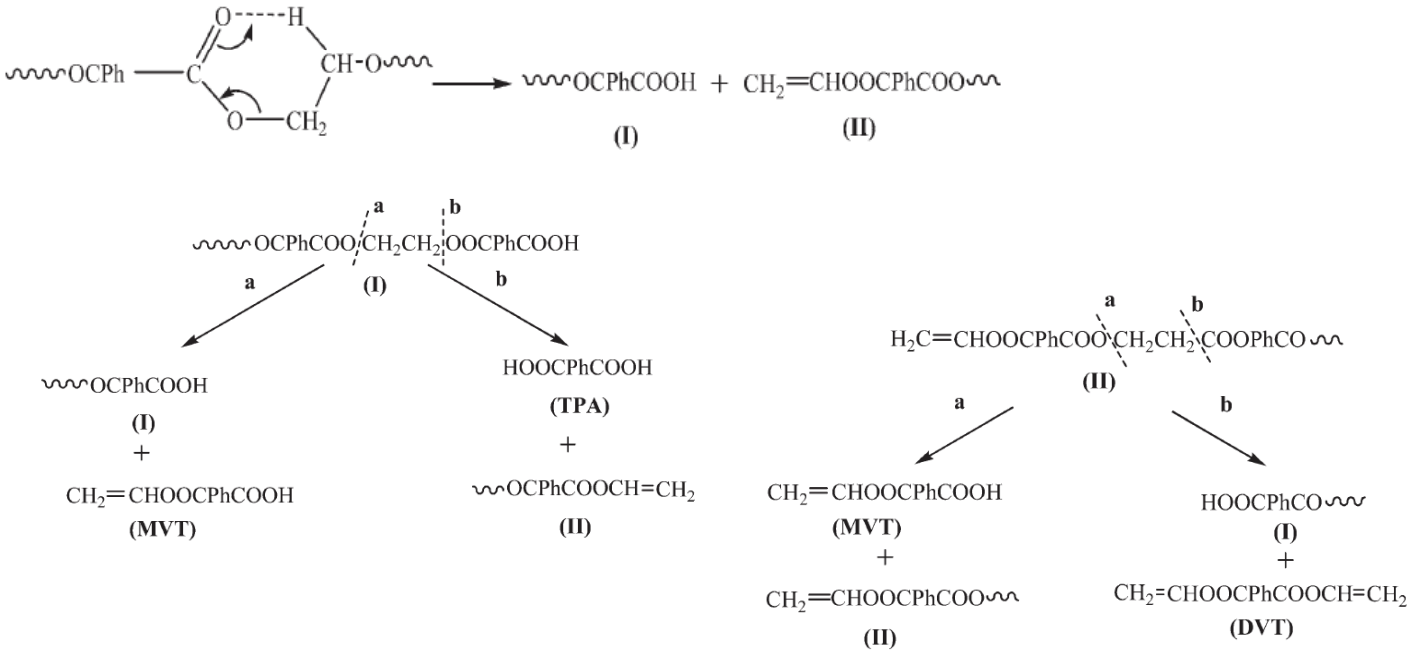
Possible decomposition mechanism (continued):



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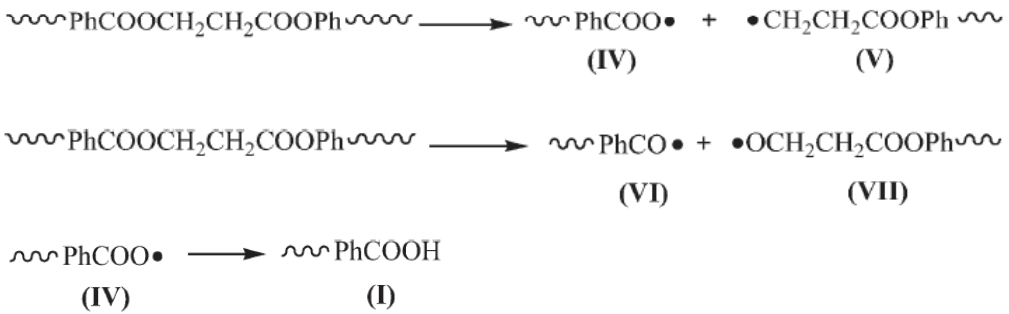

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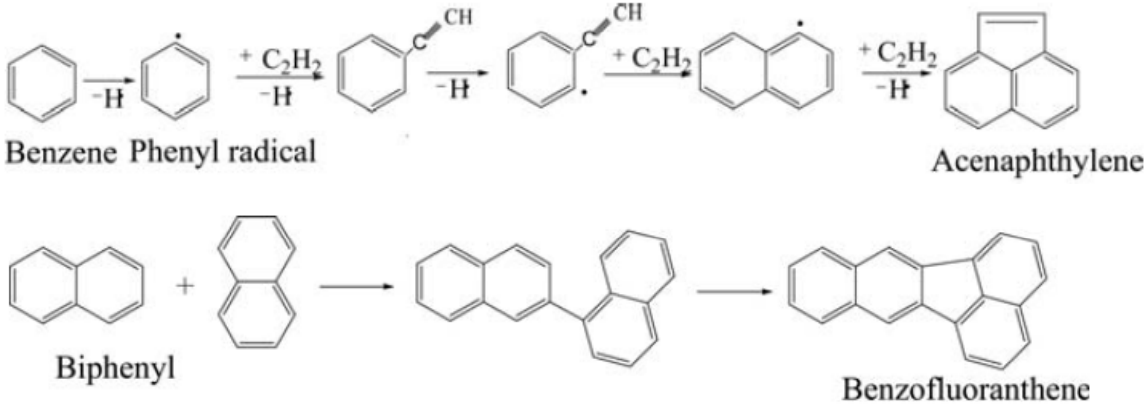
Possible mechanisms for formation of char:



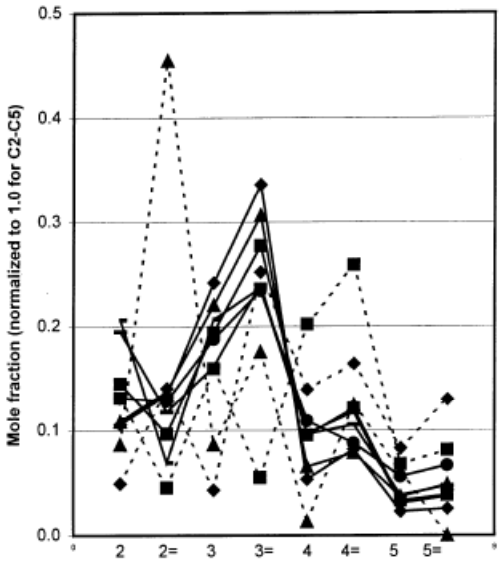
Decomposition of Polyethylene

Reexamination of the Pyrolysis of Polyethylene: Data Needs, Free-Radical Mechanistic Considerations, and Thermochemical Kinetic Simulation of Initial Product-Forming Pathways

Marvin L. Poutsma†

Macromolecules **2003**, *36*, 8931−8957

- A review of over 200 publications.
- A decrease in polymer molar mass occurs prior to mass loss.
- Alkenes and alkanes with $C_{up\ to\ 140}$ are observed among gaseous products.
- Quantification of product yields especially of those of high molecular mass is difficult. Measurement results lack consistency of the atomic (C and H) ratio.



Distributions of individual C_{2-5} hydrocarbons from low-T pyrolyses of PE: solid line ■, HDPE, 415 °C, 10 min, GC, ref 56; solid line ♦, HDPE, 375 °C, 20 min, GC, ref 63a; solid line ▲, HDPE, 425 °C, 20 min, GC, ref 63a; solid line ●, PM, 437 °C, 20 min, GC, ref 63b; solid line −, HDPE, 420 °C, 150 min, GC, ref 64; solid line —, HDPE, 420 °C, 15 h, GC, ref 65; broken line ■, PE, 405−475 °C, 30 min, MS, ref 62; broken line ♦, PM, 405−475 °C, 30 min, MS, ref 43; broken line ▲, PE, 500 °C, 20 s, GC, ref 20.

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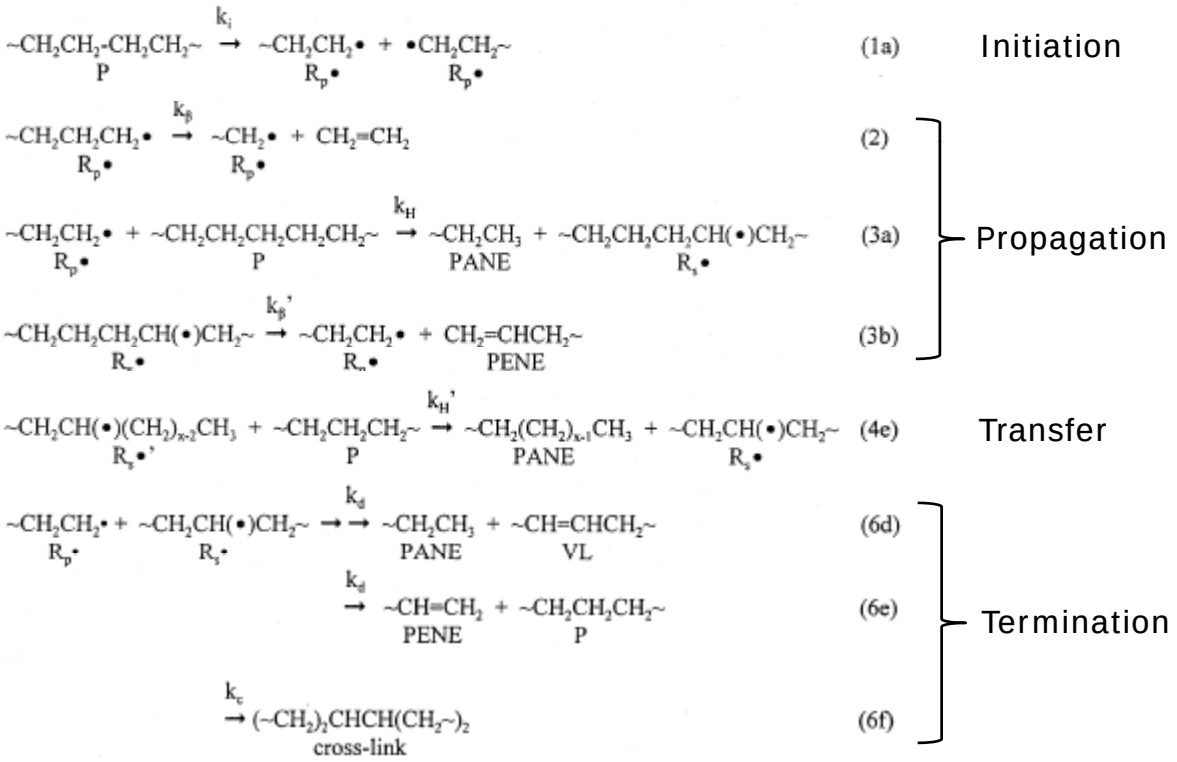

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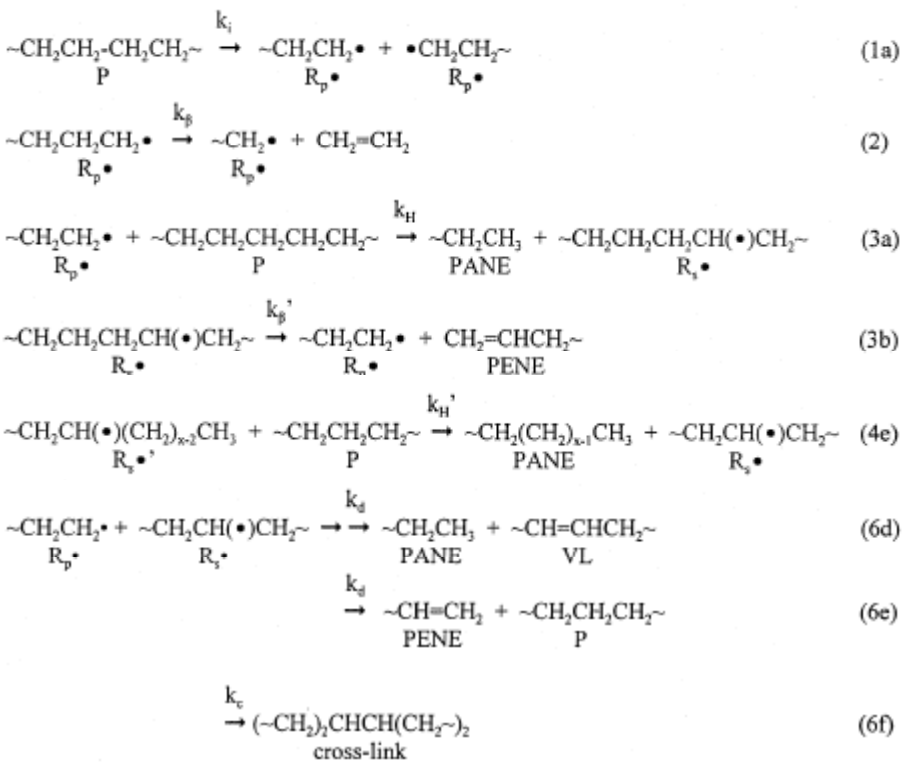

The proposed kinetics is based on the assumption that reaction rates are the same as those of similar compounds in the gas phase. I.e., the reaction rates are assumed to be not affected by the size of the molecule or condensed phase environment.

Rate Constants Used for Modeling Initial Product Distributions

	base set[a]			F−R set[a,b]		
process	log A	E	log k_{773}	log A	E	log k_{773}
k_H(p,s)[c]	8.28	12.8	4.66	8.00	11.2	4.83
k_H(s,s)[c]	8.11	14.2	4.10	8.00	12.2	4.55
k_β(p,Me)	12.76	30.1	4.26	14.00	32.0	4.95
k_β(p,p)	13.03	27.8	5.16	14.00	30.0	5.52
k_β(s,Me)	14.04	32.8	4.78	14.00	33.0	4.67
k_β(s,p)	14.48	31.7	5.51	14.00	31.0	5.23
k_{14}(p,p)[c]	11.00	22.0	4.78	11.00	20.6	5.18
k_{14}(p,s)[c]	11.20	20.8	5.31	11.00	18.3	5.83
k_{14}(s,p)[c]	10.91	23.7	4.21	11.00	21.6	4.89
k_{14}(s,s)[c]	11.00	22.2	4.73	11.00	19.3	5.54
k_{15}(p,p)[c]	10.10	15.0	5.85	10.20	14.5	6.10
k_{15}(p,s)[c]	10.26	13.7	6.38	10.20	12.2	6.75
k_{15}(s,p)[c]	9.97	16.6	5.28	10.20	15.5	5.82
k_{15}(s,s)[c]	10.10	15.2	5.81	10.20	13.2	6.47
k_{16}(p,p)[c]	9.86	15.6	5.45	9.70	14.5	5.60
k_{16}(p,s)[c]	10.02	14.3	5.98	9.70	12.2	6.25
k_{16}(s,p)[c]	9.73	17.2	4.88	9.70	15.5	5.32
k_{16}(s,s)[c]	9.86	15.8	5.40	9.70	13.2	5.97

[a] Units are M, s, and kcal mol^{-1} as appropriate

The main source of rate constants is the NIST Kinetic Database.

Decomposition of Polystyrene

Mechanistic Modeling of Polymer Degradation: A Comprehensive Study of Polystyrene

Todd M. Kruse, Oh Sang Woo, Hsi-Wu Wong, Shumaila S. Khan, and Linda J. Broadbelt*

Macromolecules **2002**, *35*, 7830−7844

- The study consists of experiments and modeling.

- The experiments include controlled temperature pyrolysis (in sealed glass ampules)
  accompanied by gel-permeation chromatography (polymer molecular mass analysis)
  gas chromatography with FID (product yields)
  gas chromatography - mass spectroscopy (product structure analysis)

- The modeling is based on the method of moments.

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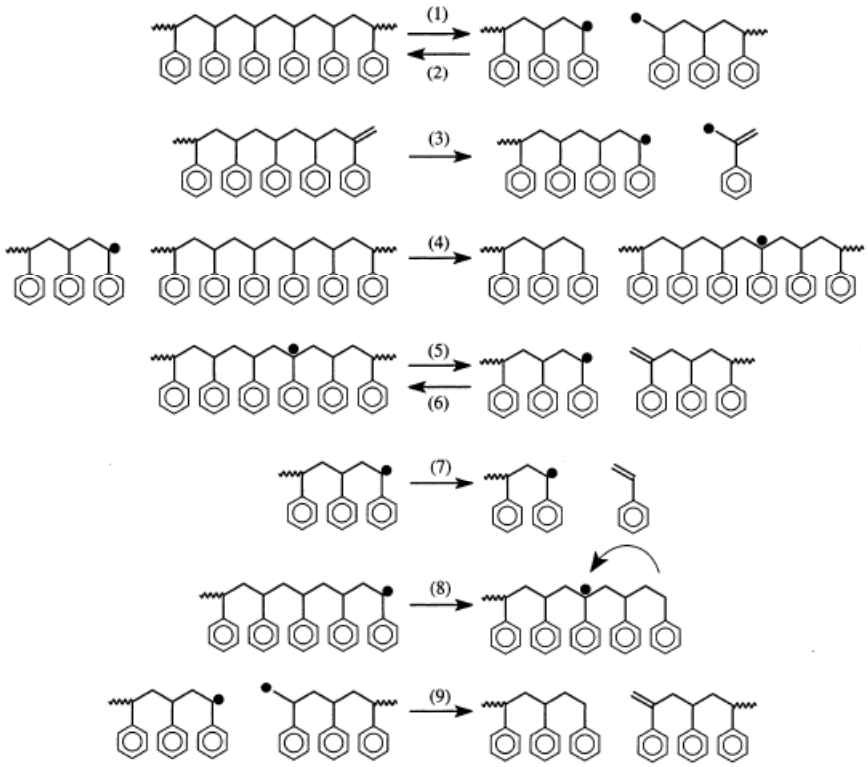
The proposed reaction mechanism:



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The proposed kinetics (also based on analogy with the gas phase reactions):

Representative Values of Kinetic and Thermodynamic Parameters for Reaction Types Incorporated into a Mechanistic Model of Polystyrene Degradation

reaction type	frequency factor, A (s^{-1} or l mol^{-1} s^{-1})	intrinsic barrier, E_0 (kcal mol^{-1})	α, transfer coeff	representative heat of reaction (kcal mol^{-1})	activation energy (kcal mol^{-1})
chain fission	1.0×10^{16}	2.3[c]	1.0	65.0[i]	67.3
chain fission allyl	5.5×10^{13} [a]	2.3[c]	1.0	55.0	57.3
radical recombination	1.1×10^{11} [b]	2.3[c]	0.0	−65.0[i]	2.3
disproportionation	5.5×10^{9} [d]	2.3[c]	0.0		2.3
end-chain β-scission	4.1×10^{12} [f]	11.4[e]	0.76	17.5[f]	24.7
midchain β-scission	4.1×10^{12} [f]	11.4[e]	0.76	22.0	28.1
radical addition	1.5×10^{7} [e]	11.4[e]	0.24	−22.0	6.1
hydrogen abstraction	2.1×10^{6} [g]	12.0[g]	0.30−0.70[j]	−3.1	10.5
1,5-hydrogen transfer	5.0×10^{6} [h]	12.0	0.30−0.70[j]	−3.1	10.5
1,3-hydrogen transfer	4.5×10^{11} [h]	25.0	0.30−0.70[j]	−3.1	23.5

[a] Frequency factor calculated from transition state theory.[42] [b] Frequency factor from data on the termination of 1-ethyl-2-phenyl radicals.[43] [c] Intrinsic barrier determined from polystyrene termination rate constants.[44] [d] Disproportionation estimated to be 5% of recombination rate from Schreck et al., 1989.[45] [e] Frequency factor and intrinsic barrier from Deady et al., 1993.[46] [f] Frequency factor backed out from equilibrium data.[47] [g] Parameters obtained from Gregg and Mayo, 1947.[48] [h] Estimated from data obtained by Kim et al., 1999.[49] [i] Bond strength for polystyrene from Aguado and Serrano, 1999.[10] [j] Calculated using the Blowers and Masel equation.[50]

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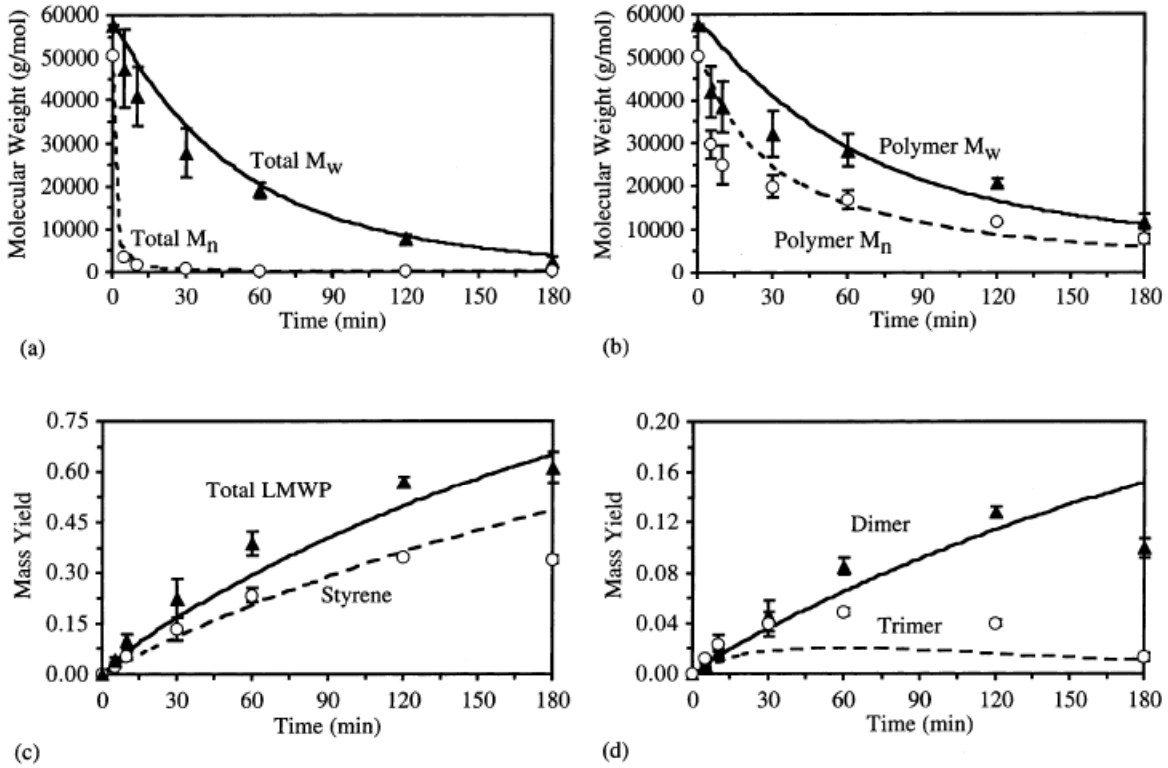
Comparison of modeling predictions with experiments:



Comparison of results of model with experimental data for 50 550 molecular weight polystyrene at 350 °C for (a) total M_n and M_w, (b) polymer M_n and M_w, (c) styrene yield and total low molecular weight product (LMWP) yield, and (d) dimer and trimer yields.

Lessons from the Decomposition Case Studies

- A detailed, quantitative understanding of the polymer decomposition chemistry has not been achieved and unlikely to be achieved in the near future.

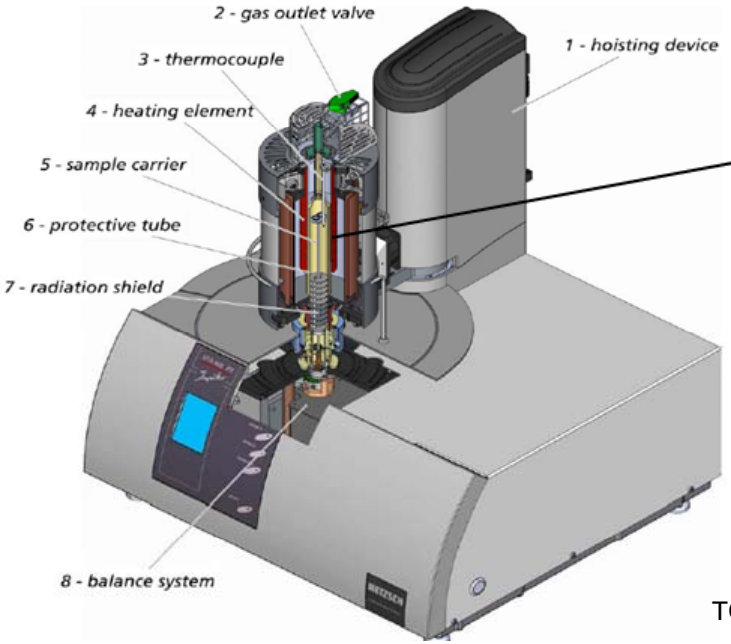
- The main obstacle is an inability of the state of the art analytical methods to provide quantitative information on elementary chemical processes operating in the condensed phase.

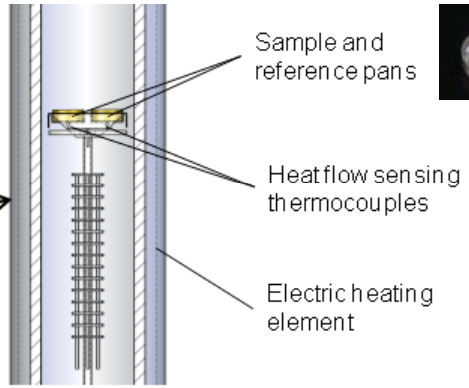
- Existing detailed kinetic models of polymer decomposition are few. These models rely heavily on the analogy with the gas phase and their validation is incomplete.

- Chemical mechanism of char formation in polymers is unknown (even at a qualitative level).

- Perhaps, a more rational approach to incorporating chemistry of decomposition into a material burning model is to focus on the overall rate of production of gases (mass loss rate) and solid residue or char.

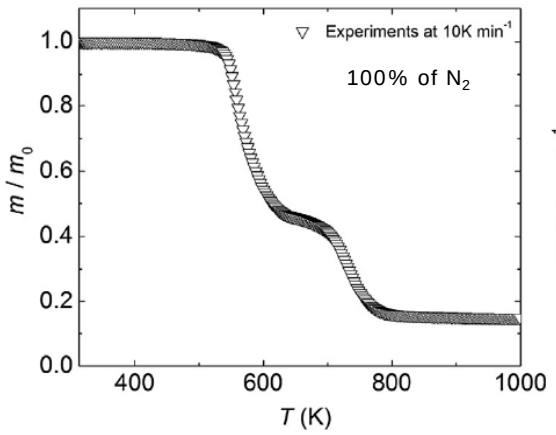
Thermogravimetric Analysis (TGA)

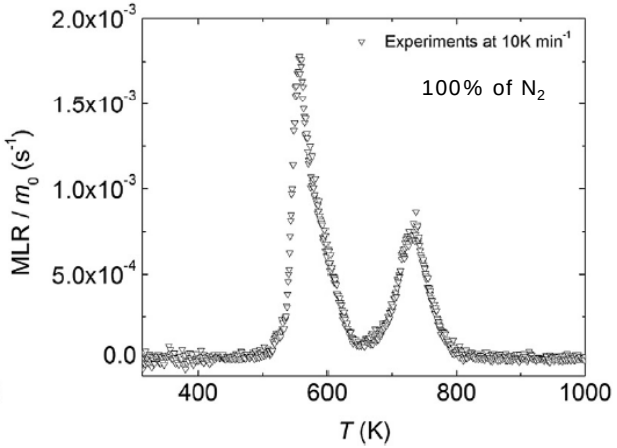




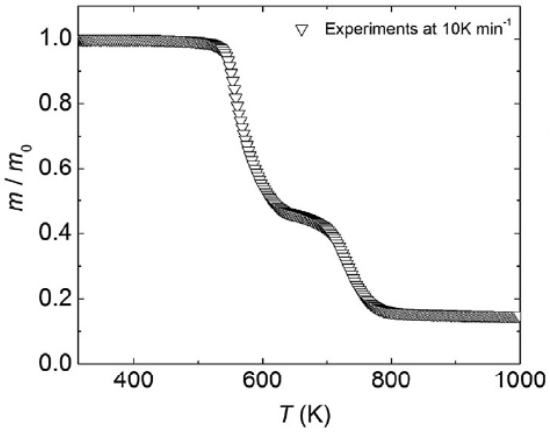
- Solid sample of 2-10 mg
- Heating rate of 3-50 K min^{-1}
- Customizable gaseous atmosphere

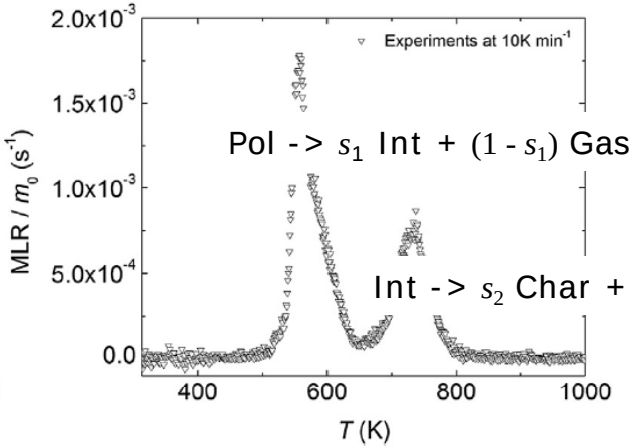
TGA of Kydex (alloy of poly(methyl methacrylate) and poly(vinyl chloride))





TGA Data Interpretation





Pol -> s_1 Int + $(1 - s_1)$ Gas1

Int -> s_2 Char + $(1 - s_2)$ Gas2

$$\frac{d[\text{Pol}]}{dt} = -k_1[\text{Pol}] \quad \text{or} \quad \frac{dm_{\text{Pol}}}{dt} = -k_1 m_{\text{Pol}}$$ (TGA sample composition is assumed to be spatially inform)

$$\frac{dm_{\text{Gas1}}}{dt} = -(1-s_1)\frac{dm_{\text{Pol}}}{dt}$$

$$\frac{dm_{\text{Int}}}{dt} = s_1 k_1 m_{\text{Pol}} - k_2 m_{\text{Int}}$$

$$\frac{dm_{\text{Char}}}{dt} = s_2 k_2 m_{\text{Int}}; \quad \frac{dm_{\text{Gas2}}}{dt} = (1-s_2)k_2 m_{\text{Int}}$$

$$k_1 = A_1 \exp(-E_1 / RT); \quad k_2 = A_2 \exp(-E_2 / RT)$$

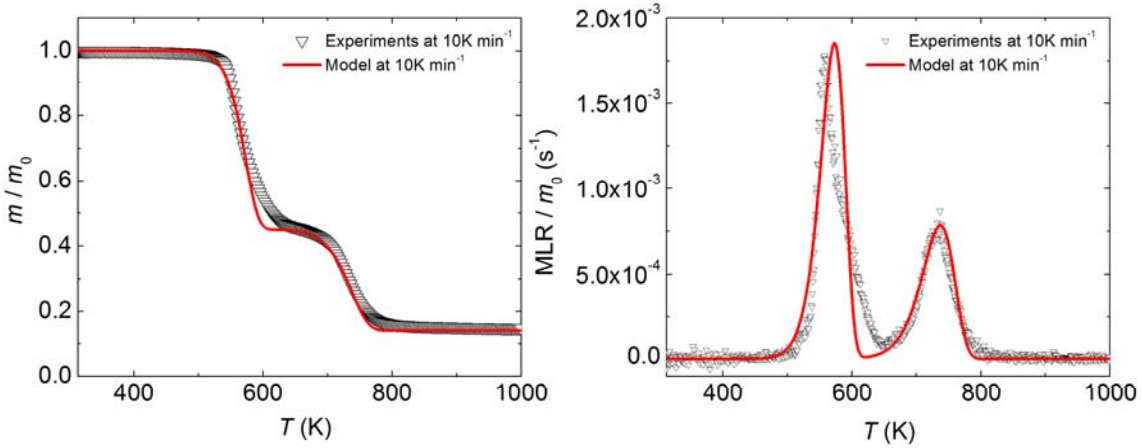
$$T = T_0 + \beta t$$

At $t = 0$: $m_{\text{Pol}} = m; \; m_{\text{Int}} = m_{\text{Gas1}} = m_{\text{Char}} = m_{\text{Gas2}} = 0$

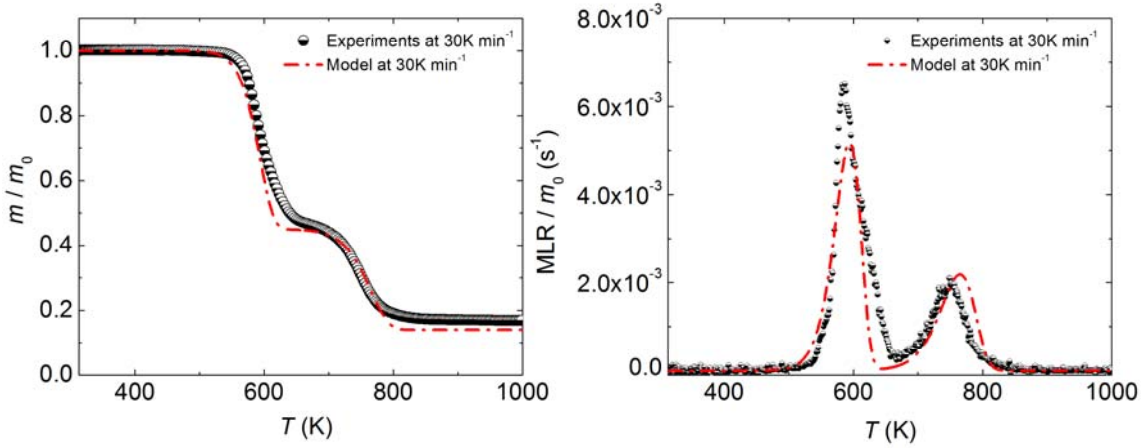
boundary conditions

s_1, A_1, E_1, s_2, A_2, and E_2 are fit to the TGA data. The model curve is computed by solving the kinetic equations numerically using a simple explicit finite difference approach.

TGA Data Interpretation



Predicting mass loss at different heating rates (β) is used for model validation:



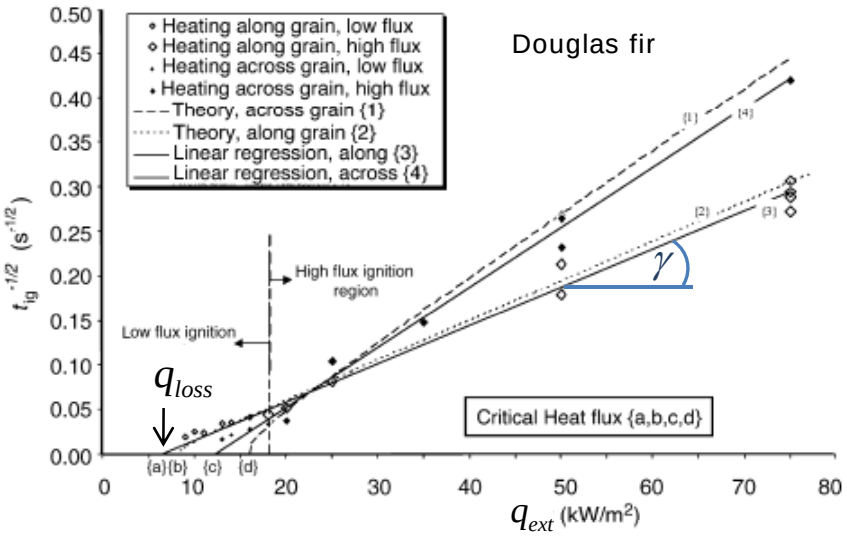
The Simplest Model of Burning Process

- Let us assume a thermally thick solid that decomposes at T_p:

$$t_{ign} = \frac{\pi}{4} k\rho c \frac{\left(T_p - T_{env}\right)^2}{\left(\varepsilon q_{ext} \underbrace{- \varepsilon\sigma T_s^4 - h\left(T_s - T_{env}\right)}\right)^2}$$

$-q_{loss}$ (assumed to be approximately constant)

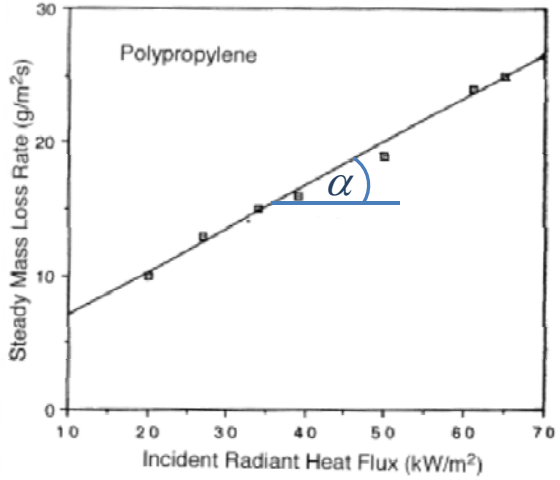
$$\frac{1}{\sqrt{t_{ign}}} = \underbrace{\sqrt{\frac{4}{\pi}} \frac{1}{\sqrt{k\rho c}\left(T_p - T_{env}\right)}}_{\tan\gamma} \left(q_{ext} - q_{loss}\right)$$



- The burning rate is steady and expressed as:

$$mF = \frac{q_{ext} + q_{flame} - \sigma T_p^4}{\underbrace{\int_{T_{env}}^{T_p} c dT - \sum_{\substack{reactions\ \&\\ transitions}} \Delta H}_{\text{heat of gasification, } L}} = \frac{q_{flame} - \sigma T_p^4}{L} + \underbrace{\frac{1}{L}}_{\tan\alpha} q_{ext}$$

$$HRR = mF \times \Delta H_{comb}^{eff}$$



Detailed, Numerical Pyrolysis Models

	Gpyro	ThermaKin	FDS, sold phase
Chemical reactions	multiple reactions; Arrhenius, nth order; 1 or 2 reactants	multiple reactions; Arrhenius, 1st or 2nd order; 1 or 2 reactants	multiple reactions; Arrhenius, nth order; 1 reactant
Phase transitions	--	through constant rate reactions turned on at threshold temperature	--
Heat transport	transient conduction; temperature dependent properties; in-depth absorption with surface re-radiation	transient conduction; temperature dependent properties; in-depth absorption with in-depth re-radiation	transient conduction; temperature dependent properties; in-depth absorption with in-depth re-radiation
Mass transport	Darcy's law	Darcy's law and diffusion (hybrid)	No mass transport
Problem dimensionality	1-3 D	1-2 D	1 D
Boundary conditions	somewhat flexible; can be coupled to FDS	highly flexible; include empirical pool and wall fire models	highly flexible; coupled to CFD
Implementation	MatLab	C++	Fortran

Material Is Represented by a Mixture of Components

Components are characterized by:

- mass density
- heat capacity
- thermal conductivity
- gas transfer coefficient
- radiation absorption coefficient
- surface emissivity

The properties depend on temperature: $property = p_0 + p_1 T + p_n T^n$

Components are classified as:

- solid
- liquid or
- gaseous

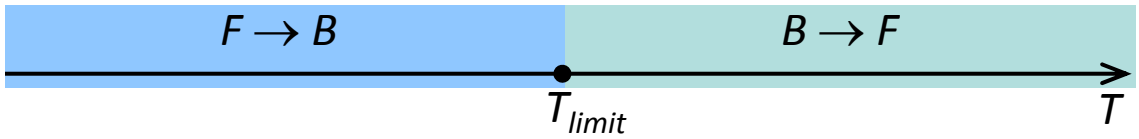
Components May Undergo Reactions

θ_B COMP B + θ_C COMP C $\rightarrow$ θ_D COMP D + θ_F COMP F + *heat*

$$rate = A\,exp\left(-\frac{E}{RT}\right)\left[\frac{m_B}{V}\right]\left[\frac{m_C}{V}\right]$$

$$heat = h_0 + h_1 T + h_n T^n$$

Reactions are used to simulate temperature transitions:



Material Volume and Swelling Factor (γ)

$$V = \sum^{solids} \frac{m_s}{\rho_s} + \sum^{liquids} \frac{m_l}{\rho_l} + \gamma \sum^{gases} \frac{m_g}{\rho_g}$$

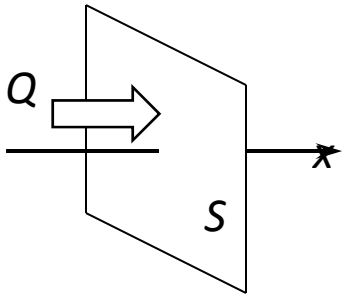
$\gamma = 0$: solids & liquids + gases = material

$\gamma = 1$: solids & liquids + gases = material

$$\gamma = \frac{\gamma_s \sum^{solids} \frac{m_s}{\rho_s} + \gamma_l \sum^{liquids} \frac{m_l}{\rho_l} + \tau \sum^{gases} \frac{m_g}{\rho_g}}{\sum^{solids} \frac{m_s}{\rho_s} + \sum^{liquids} \frac{m_l}{\rho_l} + \tau \sum^{gases} \frac{m_g}{\rho_g}}$$

Heat Transfer

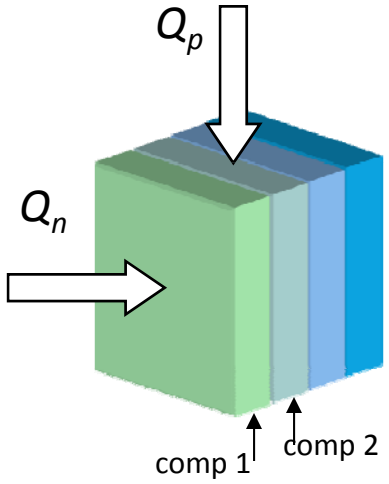
The rate of transfer $Q = -kS\frac{\partial T}{\partial x}$



Material conductivity $k = \beta k_p + (1-\beta)k_n$

$$k_p = \frac{1}{V}\sum^{comps} k_c V_c$$

$$k_n = \frac{V}{\sum^{comps} \frac{V_c}{k_c}}$$



Gas Transfer

The rate of transfer of gas *g*,

$$J_g = -\lambda \rho_g S \frac{\partial\left(\frac{m_g/\rho_g}{V}\right)}{\partial x}$$

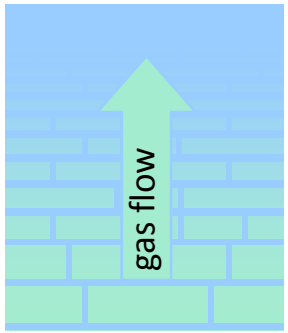
volume fraction of material occupied by gases

According to Boyle's law,

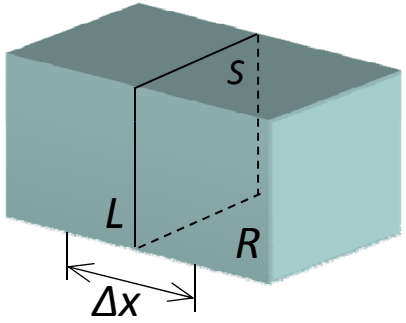
$$J_g = -\lambda \rho_g S \frac{\partial\left(\frac{\alpha(m_g/\rho_g)}{\alpha V}\right)}{\partial x} = -\frac{\lambda \rho_g S}{P^{def}} \frac{\partial(\alpha P_g)}{\partial x}$$

$\gamma = 0$: $\alpha = const$ $\Rightarrow$ $J_g = -\frac{\lambda \rho_g S \alpha}{P^{def}} \frac{\partial P_g}{\partial x}$

$\gamma > 0$: $P = const$ $\Rightarrow$ $J_g = -\lambda \rho_g S \frac{P}{P^{def}} \frac{\partial \alpha_g}{\partial x}$, $\frac{P}{P^{def}} = \frac{1}{\gamma}$



Conservation Equations Are Formulated using Finite Elements

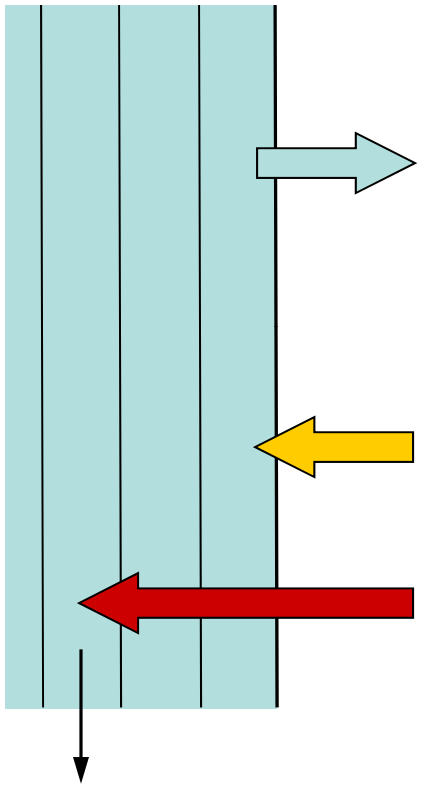


- Elements have rectangular shape.
- Elements are defined by component masses and temperature.

$$\frac{\Delta m_g^R}{\Delta t} = V^R \sum^{rxns} \theta_r^g rate_r^R + \lambda^{LR} \rho_g^{LR} S \frac{\frac{m_g^L}{\rho_g^L V^L} - \frac{m_g^R}{\rho_g^R V^R}}{\Delta x}$$

$$m^R c^R \frac{\Delta T^R}{\Delta t} = V^R \sum^{rxns} heat_r^R rate_r^R + k^{LR} S \frac{T^L - T^R}{\Delta x} + \frac{1}{2} \sum^{gases} c_g^{LR} (T^L - T^R) J_g^{LR}$$

Boundary Conditions for 1-Dimensional Model



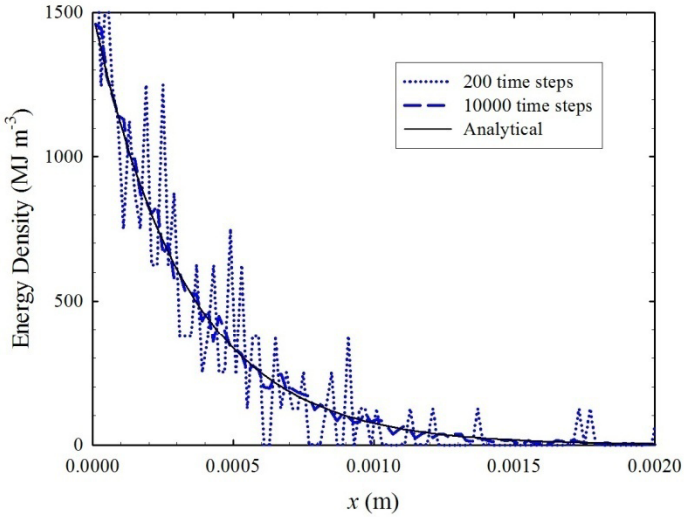
$$J_c^B = \begin{cases} j_0^c \left(\frac{m_c^B}{V^B} - j_1^c \rho_c^B \right) \\ j_0^c \exp\left(-\frac{j_1^c}{RT^B} \right) \end{cases}$$

$$Q_{cnv}^B = h_{env}\left[T_{env}(t) - T^B\right]$$

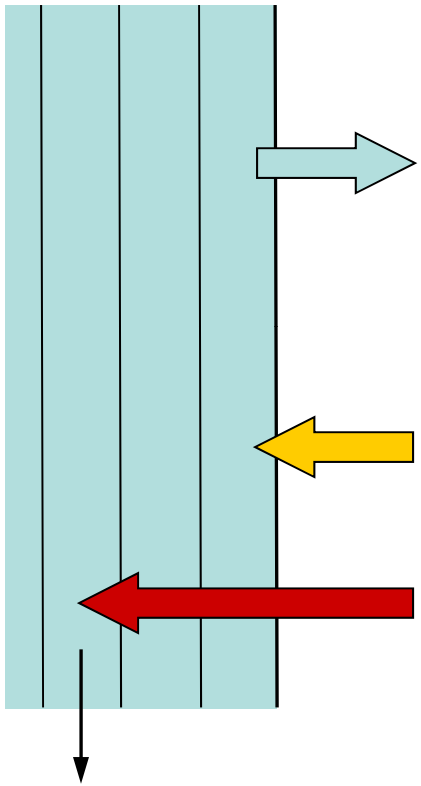
$$Q_{rad}^B = \varepsilon^{in}\left[q_{rad}(t) - \sigma\left(T^{in}\right)^4\right]$$

Element “in” is selected at random at each time step using Beer-Lambert law energy distribution as a probability density.

The random algorithm verification:



Boundary Conditions for 1-Dimensional Model



$$J_c^B = \begin{cases} j_0^c \left(\dfrac{m_c^B}{V^B} - j_1^c \rho_c^B \right) \\ j_0^c \exp\left(-\dfrac{j_1^c}{RT^B} \right) \end{cases}$$

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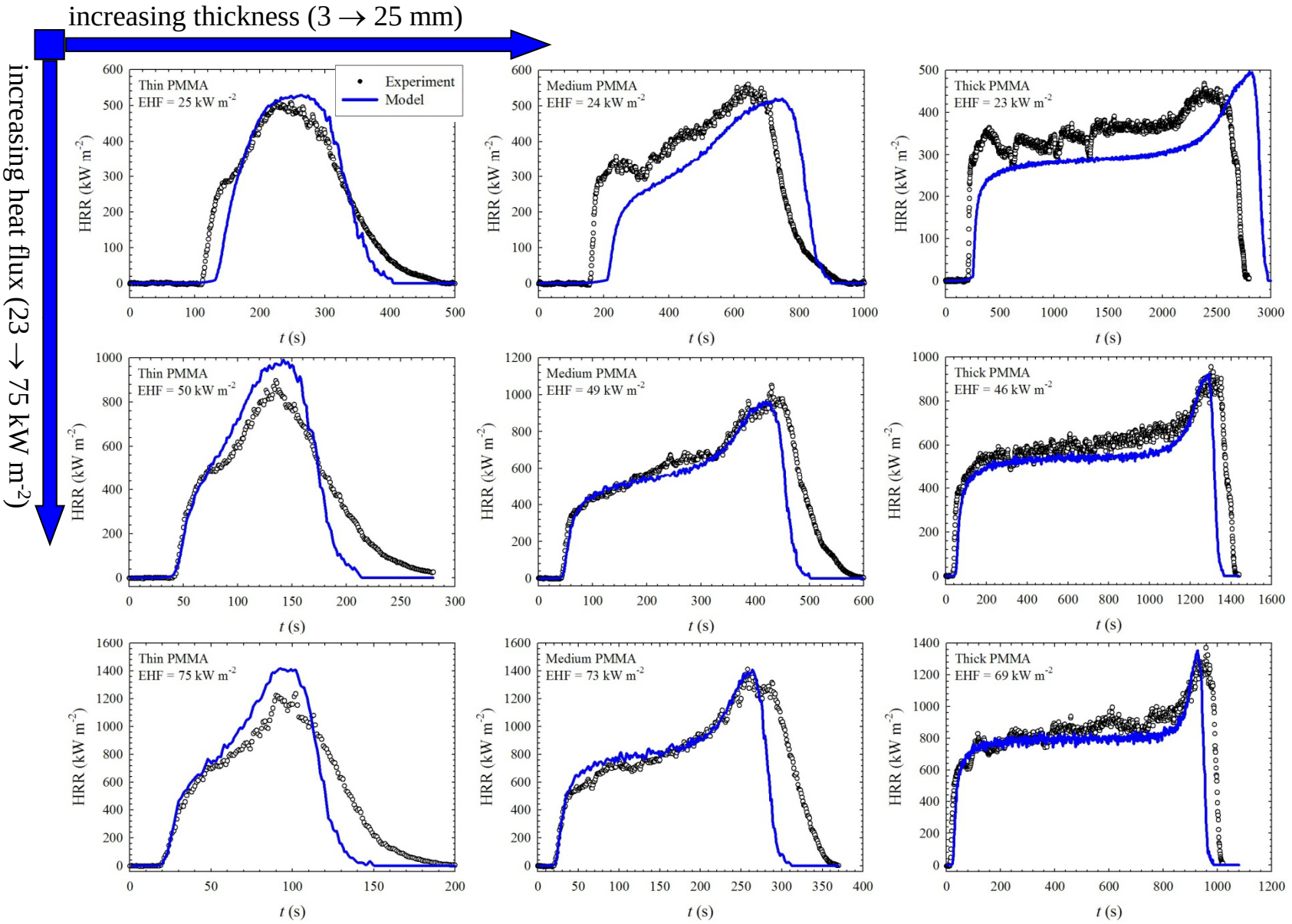
Element “in” is selected at random at each time step using Beer-Lambert law energy distribution as a probability density.

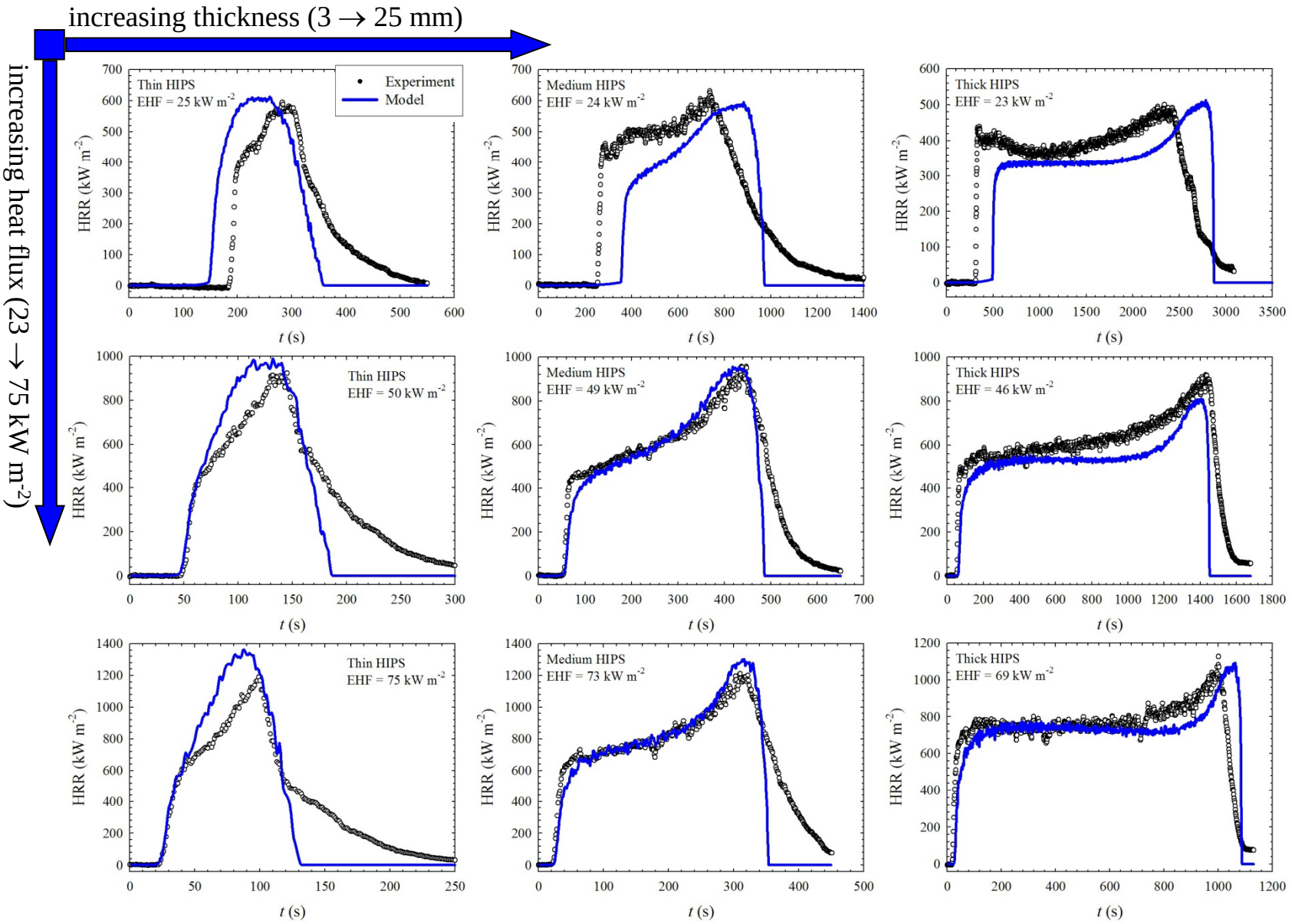
Surface flame:

$$\sum_{comps} \frac{J_c^B}{J_{flm}^c} > 1 \Rightarrow q_{rad}(t) = q_{rad}(t) + q_{flm},$$
$$h_{env} = h_{flm}, T_{env}(t) = T_{flm}$$

Modeling Cone Calorimetry of PMMA



Modeling Cone Calorimetry of HIPS



Modeling Cone Calorimetry of PC

5 mm PC sample after 160 s at 75 kW m^{-2}.

Flame heat flux = 15 kW m^{-2}.

The main mode of heat transfer inside char is radiation. The rate of transfer is defined by a single adjustable parameter.