

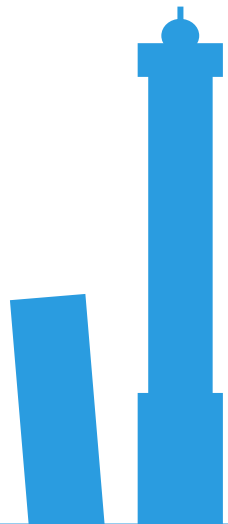


# Multi-Scale Analysis of the Radio-Thermal Aging of XLPE Cable Insulation in Nuclear Environment

## Part 1: Stabilization and Oxidation Mechanisms

15 November 2021

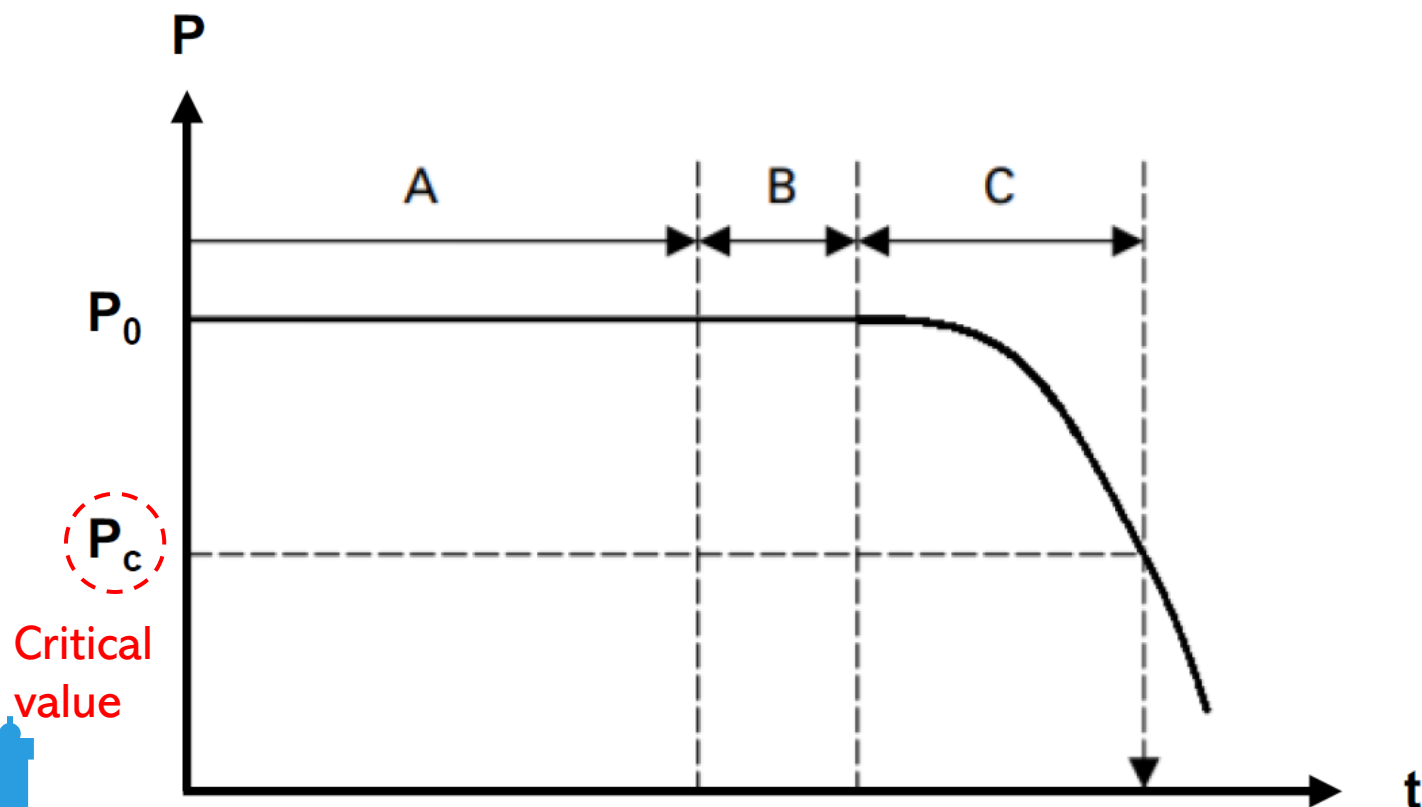
Presenter: Xavier Colin



# Outlines

- Main stages in polymer degradation by oxidation
- Polymer oxidation in nuclear environment
  - Initiation
  - Propagation
  - Termination
  - Secondary reactions
- Polymer stabilization
  - Preventive antioxidants
  - Chain breaking antioxidants
- Physical loss of antioxidants
- Conclusions

# Main stages in polymer degradation by oxidation



## (A) Antioxidant depletion

Polymer matrix a priori protected against the external environmental attacks

## (B) Oxidation induction period of unstabilised polymer (?)

## (C) Polymer oxidation

Causing the catastrophic drop in its use properties

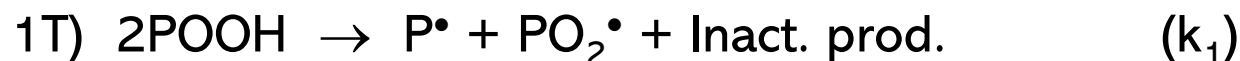
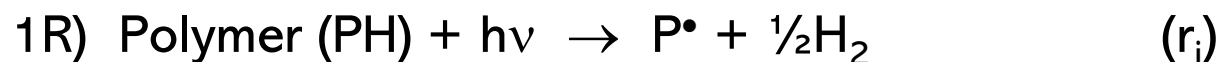
[1] Y.G. Hsuan, R.M. Koerner, J. Geotech. Geoenviron. Eng. 124 (1998) 532–541.

[2] R.K. Rowe, H.P. Sangam, Geotext. Geomembr. 20 (2002) 77–95.

# Polymer oxidation in nuclear environment

Radical chain oxidation both initiated by polymer radiolysis and POOH thermolysis

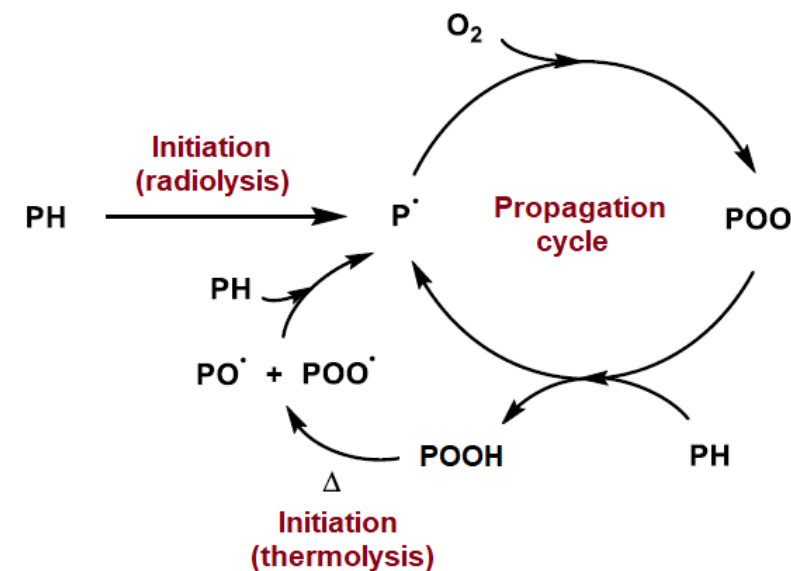
## Initiation



## Propagation



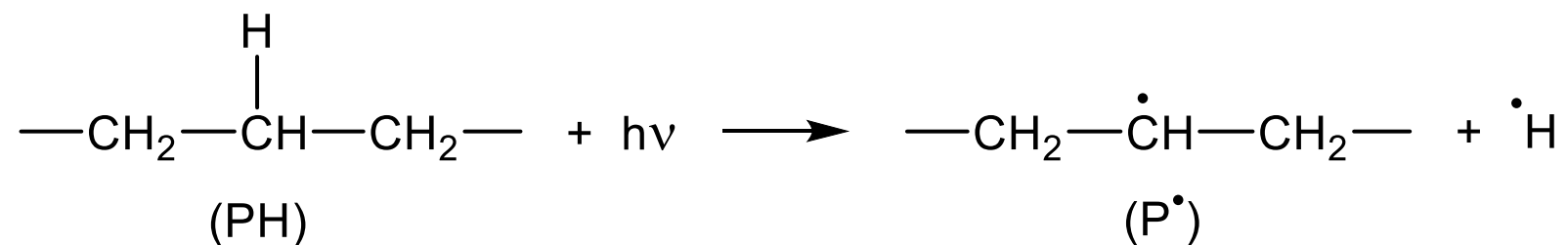
## Termination



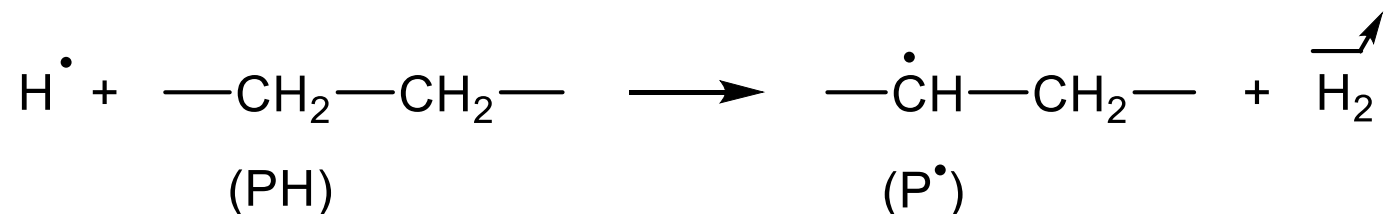
[3] X. Colin, C. Monchy-Leroy, L. Audouin, J. Verdu, Nucl. Instrum. Methods Phys. Res. B265 (2007) 251–255.

# Initiation 1R – Case of PE

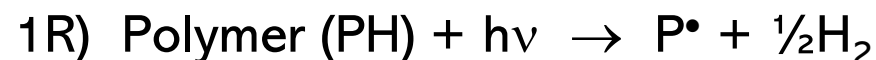
1<sup>st</sup> step – Radiolytic decomposition (with rate  $r_i$ )



2<sup>nd</sup> step – Hydrogen abstraction (much faster)

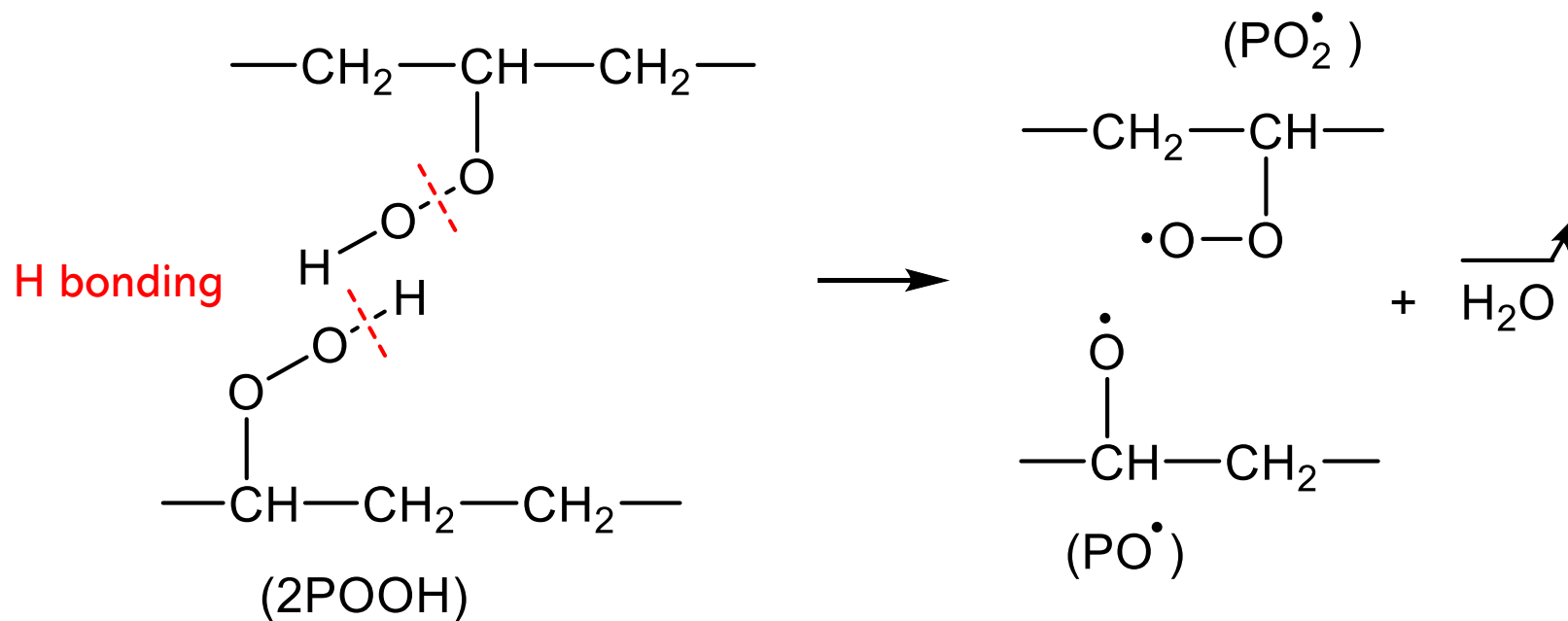


► Balance reaction (with rate  $r_i$ )



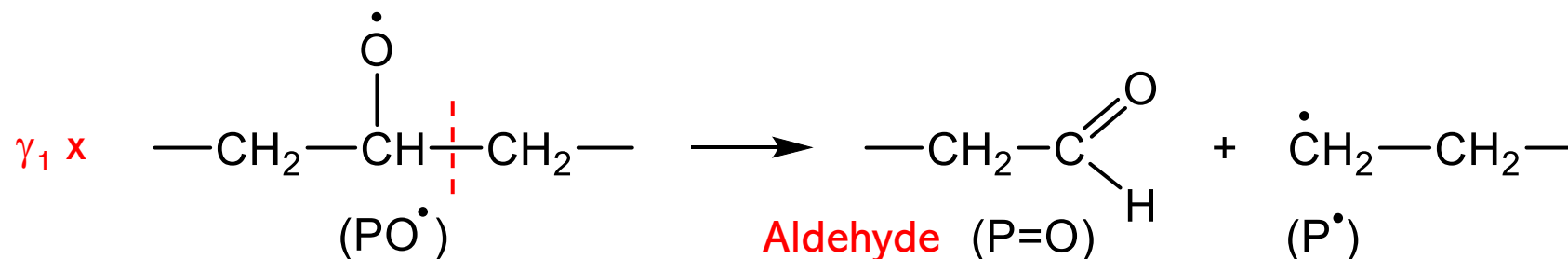
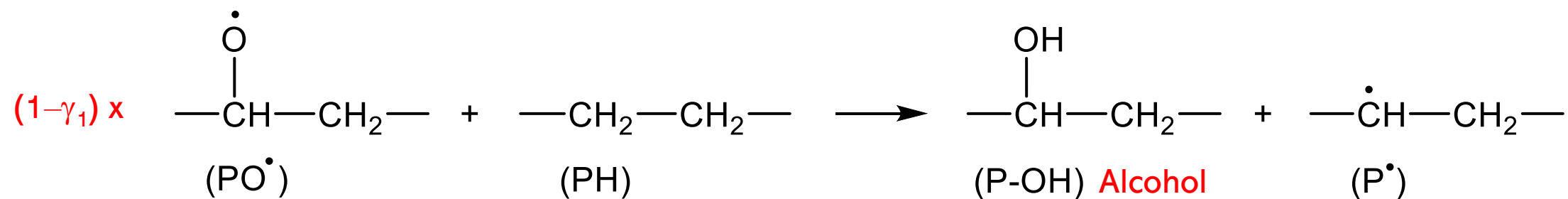
# Initiation 1T – Case of PE

1<sup>st</sup> step – Thermal decomposition (with rate constant  $k_1$ )



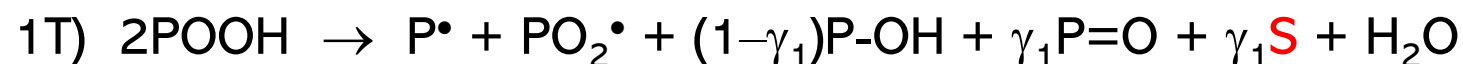
# Initiation 1T – Case of PE

2<sup>nd</sup> step – Hydrogen abstraction vs  $\beta$  scission (both much faster)



Main chain scission mechanism in polymer oxidation

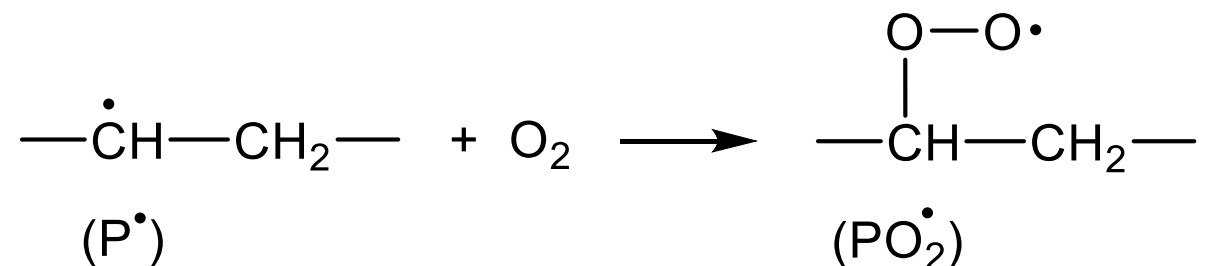
► Balance reaction (with rate constant  $k_1$ )



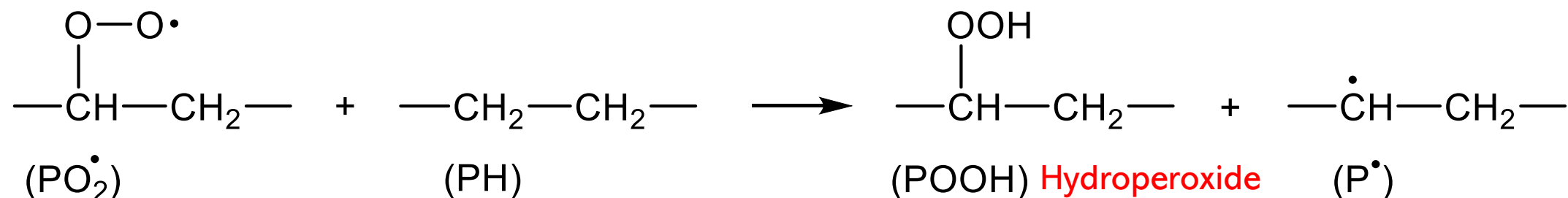
# Propagation – Case of PE

[4] Y. Kamiya, E. Niki, in *Aspect of Degradation and Stabilization of Polymers*, H.G. Jellinek ed., Chap. 3, p. 86, 1978.

1<sup>st</sup> step – Oxygen addition to radicals (very fast:  $k_2 \approx 10^8-10^9 \text{ L.mol}^{-1}.\text{s}^{-1}$ )



2<sup>nd</sup> step – Hydrogen abstraction (much slower)





# Order of magnitude for $k_3$

[5] S. Korcek, J.H.B. Chenier, J.A. Howard, K.U. Ingold, *Can. J. Chem.* 50 (1972) 2285–2297.

## Structure / $k_3$ relationship at 30°C

$$\text{Log}(k_3) = A - 4.8 \times 10^{-2} \times E_D$$

where A is a constant depending on the radical reactivity:

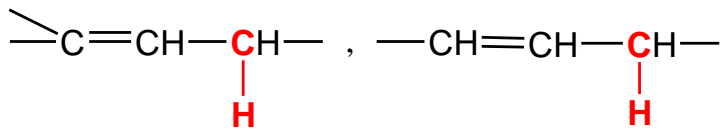
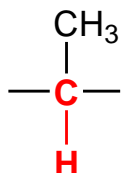
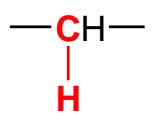
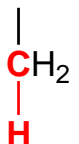
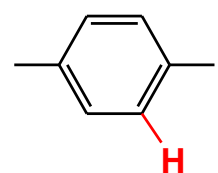
- $A = 15.4$  for tertiary radicals
- $A = 16.4$  for secondary radicals

Ex. for PE & PP at 25°C

$$k_3 = (2 \pm 1) \times 10^{-3} \text{mol. L}^{-1} \cdot \text{s}^{-1}$$

for IR & NR

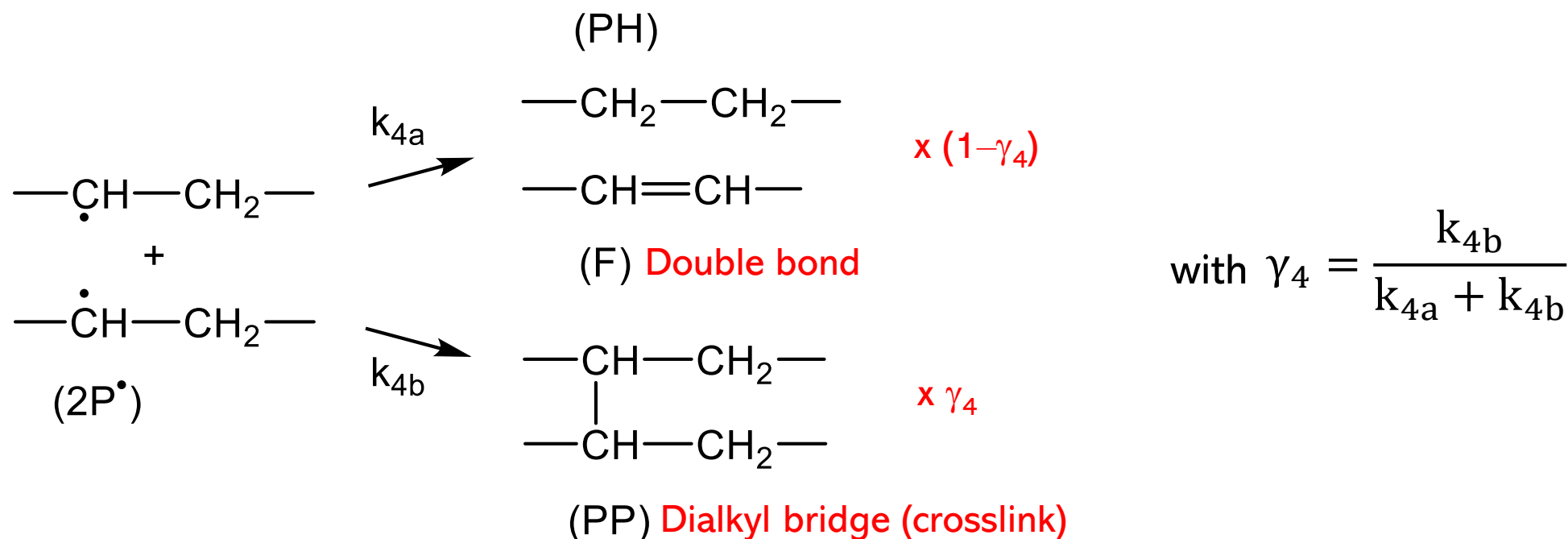
$$k_3 \approx 5 \times 10^{-2} \text{mol. L}^{-1} \cdot \text{s}^{-1}$$

Reactive sites	$E_D$ (kJ.mol <sup>-1</sup> )	Polymers
	326 – 343	IR, NR, PBD
	380	PP, BMI
	393	PE
	405 – 418	PC, PSU, PEI
	> 460	PEEK, PES

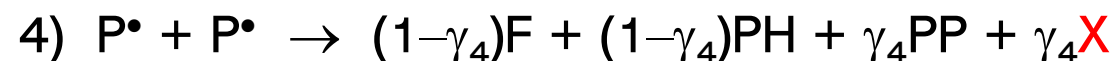
# Termination – Case of PE

[6] X. Colin, L. Audouin, J. Verdu, Polym. Degrad. Stab. 86 (2004) 309-321.

Bimolecular recombination of alkyl radicals (very fast:  $k_4 \approx 8 \times 10^{11} \text{ L.mol}^{-1}.\text{s}^{-1}$ )



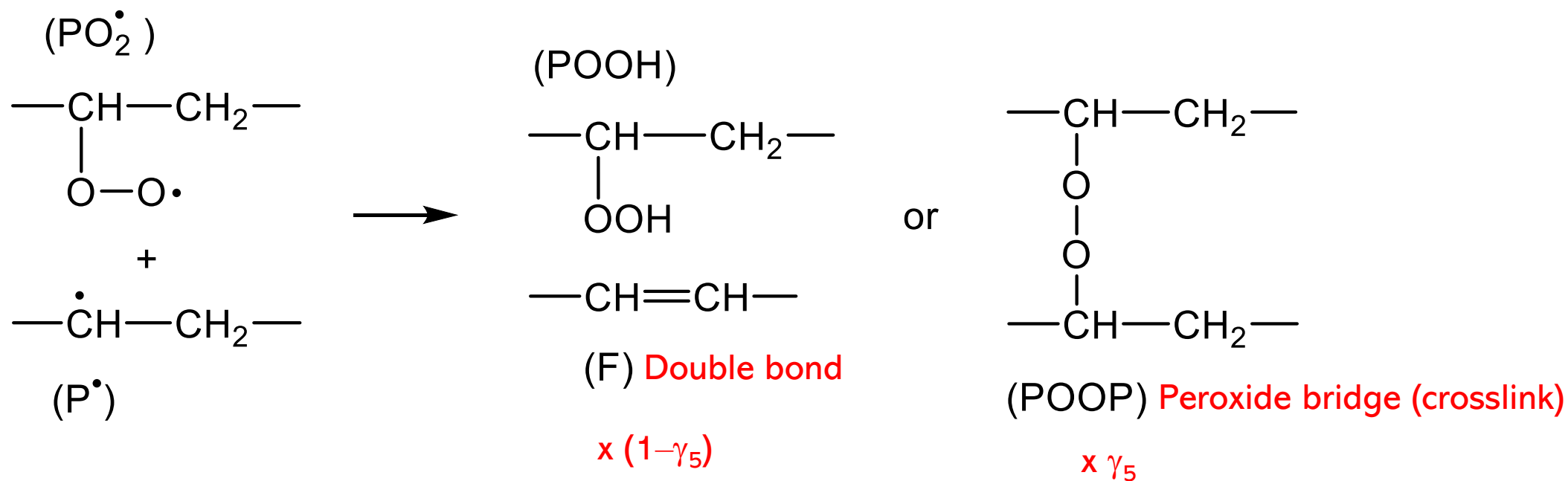
► Balance reaction



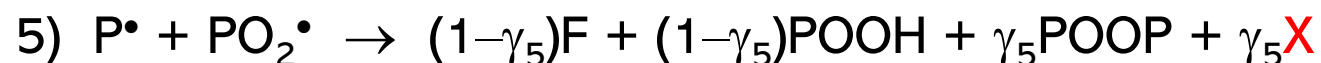
# Termination – Case of PE

[6] X. Colin, L. Audouin, J. Verdu,  
Polym. Degrad. Stab. 86 (2004) 309-321.

Recombination between alkyl and peroxy radicals (intermediary:  $k_6 \ll k_5 \leq k_4$ )

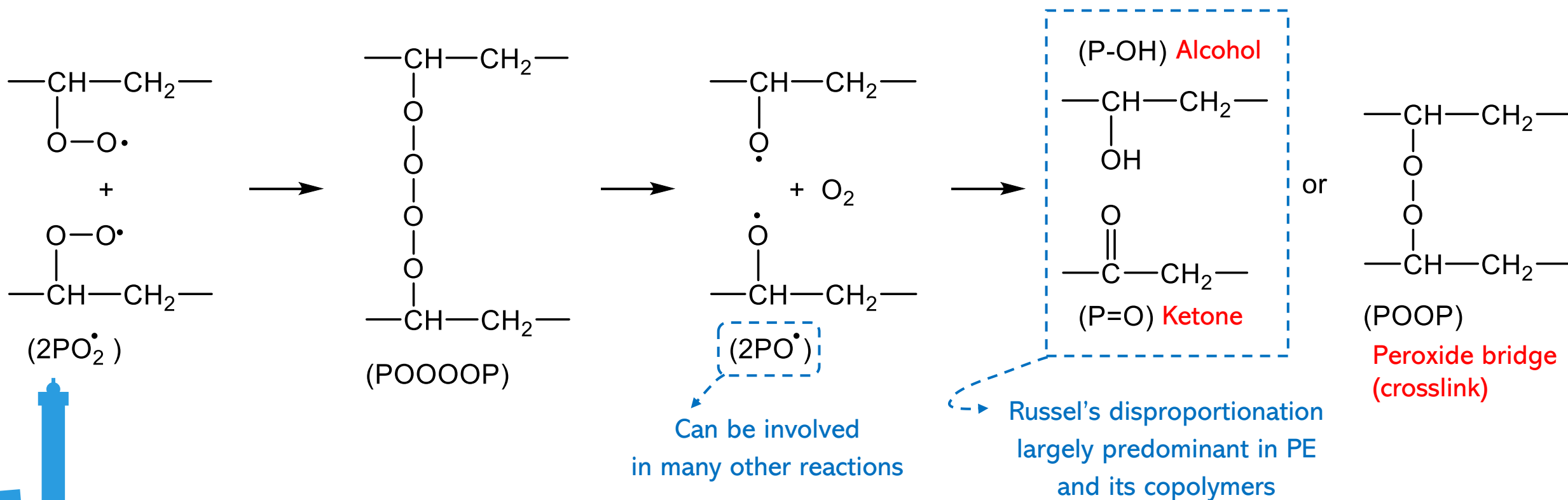


► Balance reaction



# Termination – Case of PE

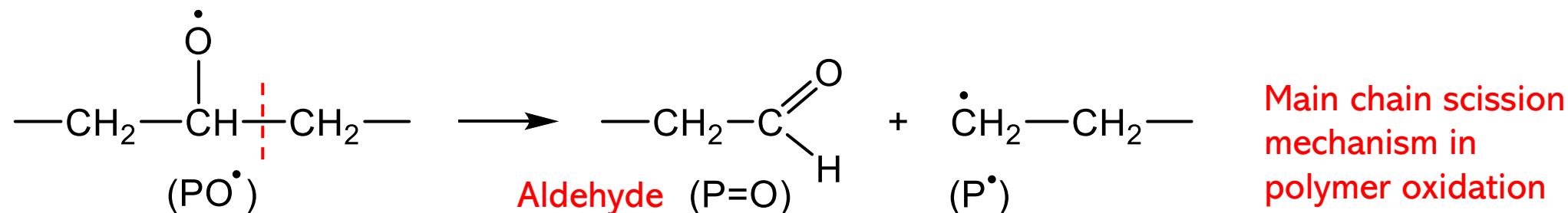
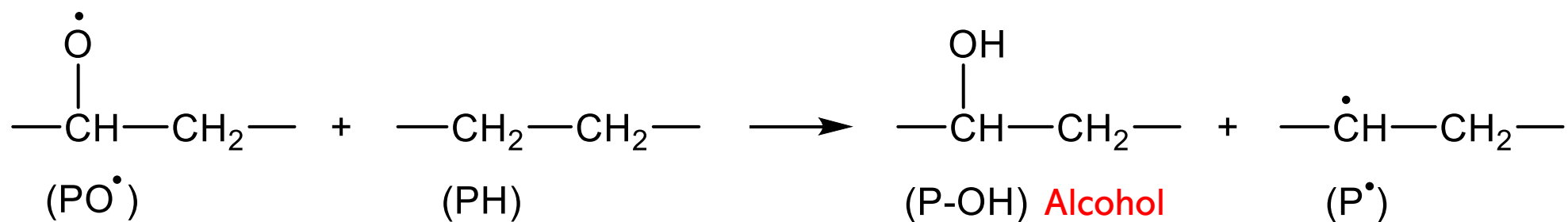
Bimolecular recombination of peroxy radicals (much slower)



[7] G.A. Russel, J. Amer. Chem. Soc. 57(14) (1957) 3871-3877.

# Termination – Case of PE

In competition with the fast rearrangement of alkoxy radicals



► Proposal of simplified balance reaction

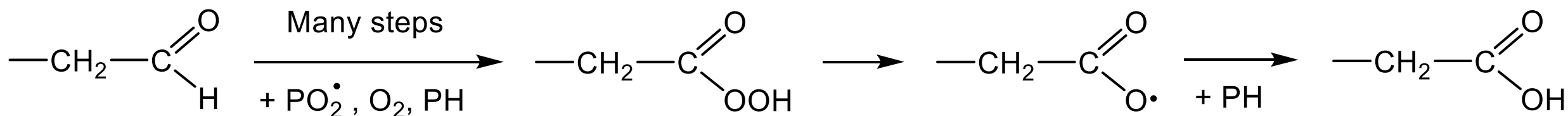


# Side reactions

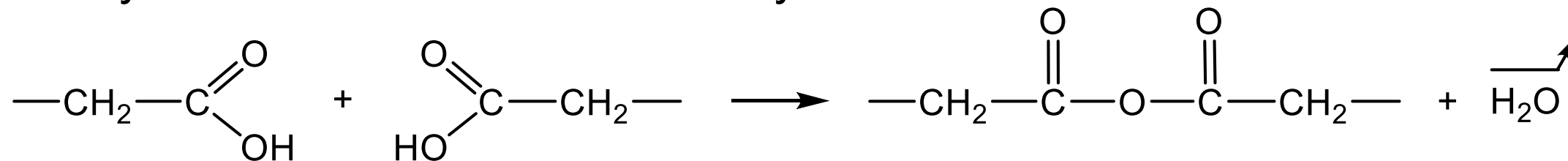
For instance

[8] L.K. Nait Ali, X. Colin, A. Bergeret,  
Polym. Degrad. Stab. 96 (2011) 236-246.

- Aldehydes can easily oxidize into carboxylic acids (for which  $E_D \approx 368 \text{ kJ.mol}^{-1}$ )

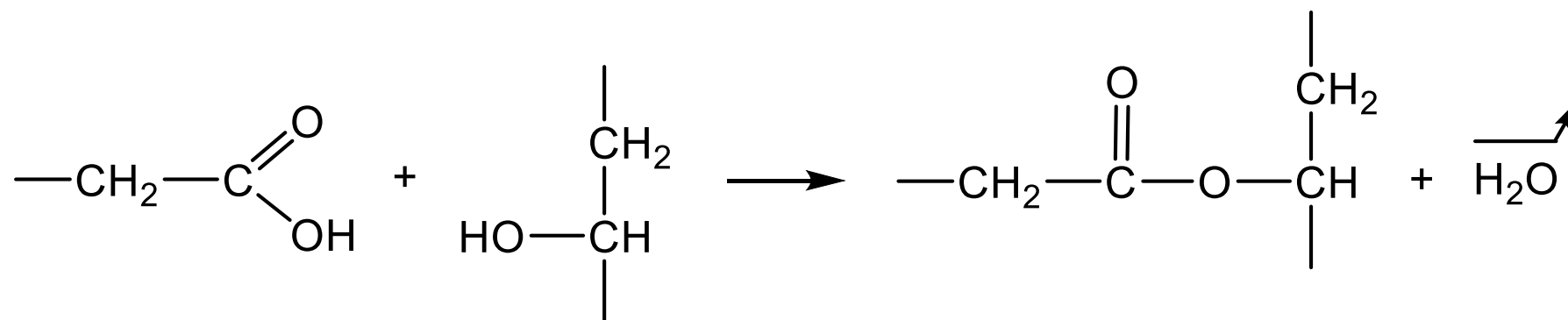


- Carboxylic acids can condensate into anhydrides



# Secondary reactions

- Carboxylic acids and alcohols can condensate into esters



- ▶ Wide variety of carbonyl products (P=O) detected by FTIR spectroscopy at different wavenumbers, e.g. in PE:
  - Unsaturated (1690 -1705 cm<sup>-1</sup>) and saturated ketones (1715 – 1725 cm<sup>-1</sup>)
  - Aldehydes (1730 - 1740 cm<sup>-1</sup>) and carboxylic acids (1710 – 1715 cm<sup>-1</sup>)
  - Linear (1735 -1750 cm<sup>-1</sup>) and cyclic esters (i.e.  $\gamma$ -lactones, 1770 – 1790 cm<sup>-1</sup>)
  - Anhydrides (1770 -1780 cm<sup>-1</sup>)

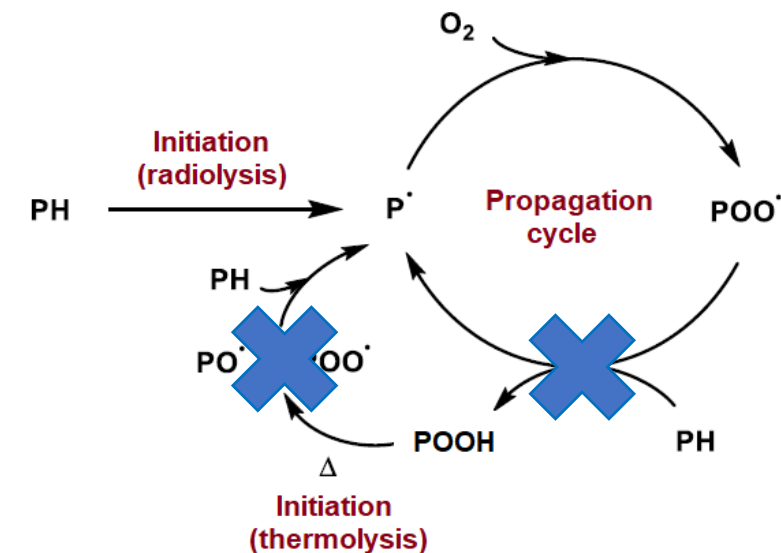
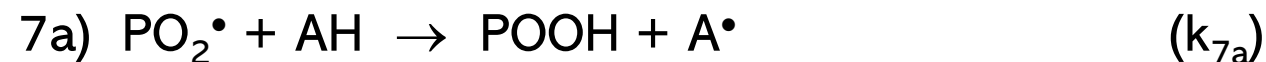
# Polymer stabilization

Two main types of current antioxidants to break the oxidation loop in two different places: initiation and propagation

- Preventive antioxidants (Dec)  
e.g. Organic phosphites and sulphides



- Chain breaking antioxidants (AH)  
e.g. Hindered phenols and secondary aromatic amines

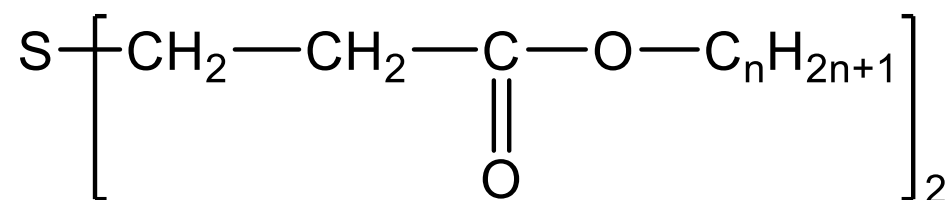


[9] H. Zweifel, R.D. Maier, M. Schiller, *Plastics additives handbook*, 6<sup>th</sup> Edition, Hanser Publishers, Munich, 2009.



# Preventive antioxidants – Case of thiodipropionates

General chemical formula

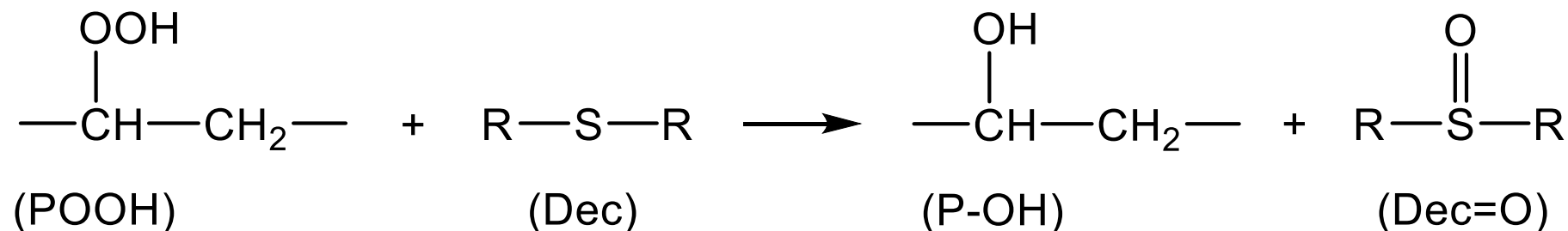


n = 12 Dilauryl (DLTDP)

n = 18 Distearyl (DSTDP)

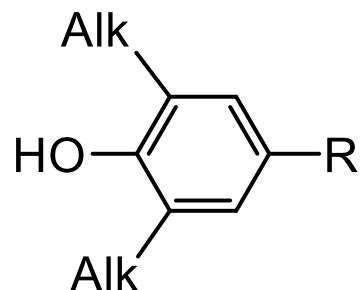
A higher value of n increases solubility in the polymer matrix and reduces physical loss

Main action mechanism



# Chain breaking antioxidants – Case of monophenols

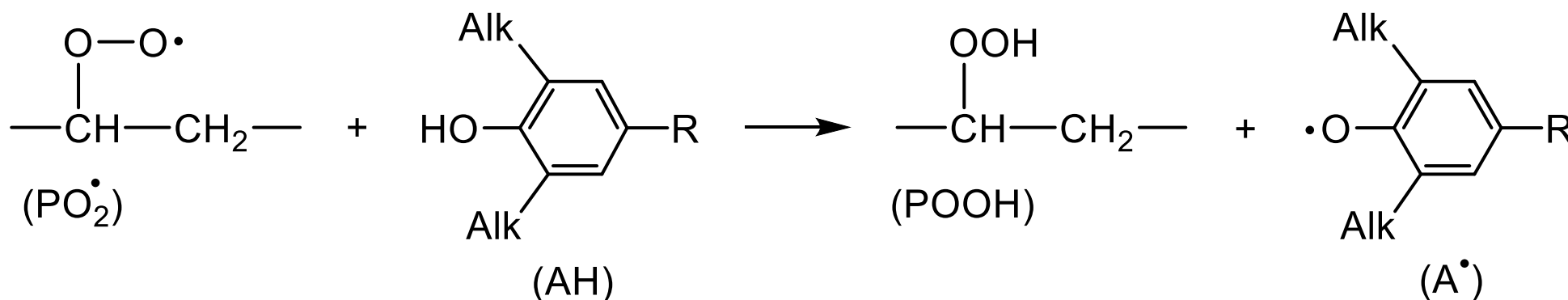
## General chemical formula



Alkyl = Often tertio-Butyl i.e.  $\text{—C(CH}_3\text{)}_3$

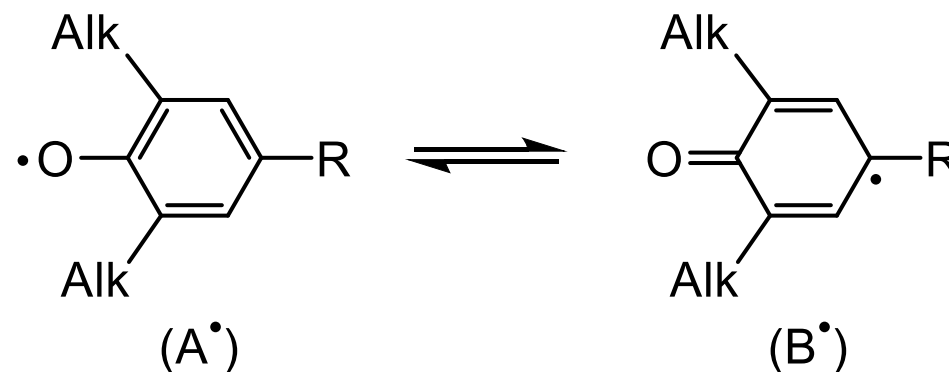
R = Long hydrocarbon chain in order to increase solubility in the polymer matrix and reduce physical loss

## Main action mechanism

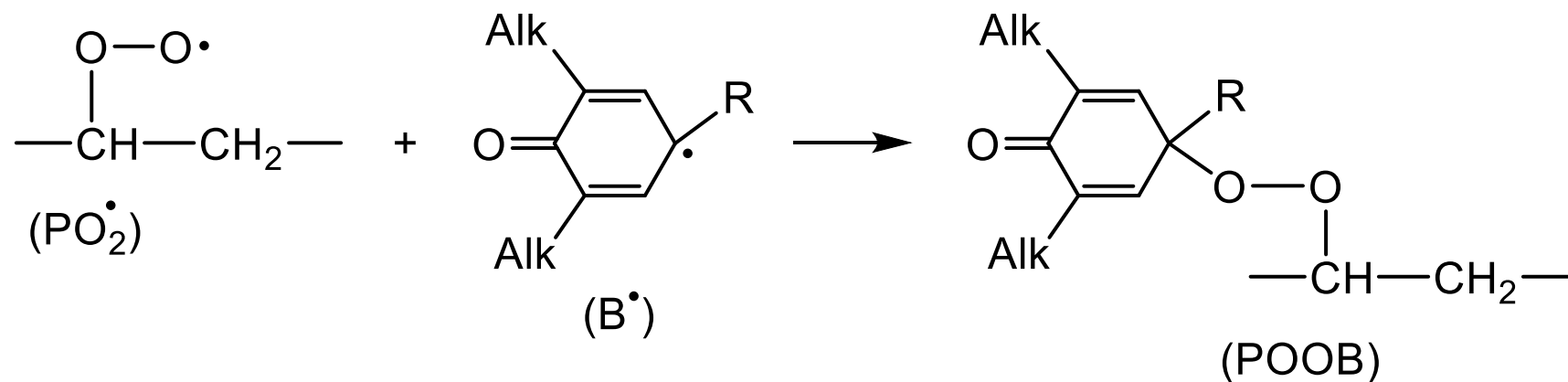


# Chain breaking antioxidants – Case of monophenols

Phenoxy radicals can isomerize rapidly



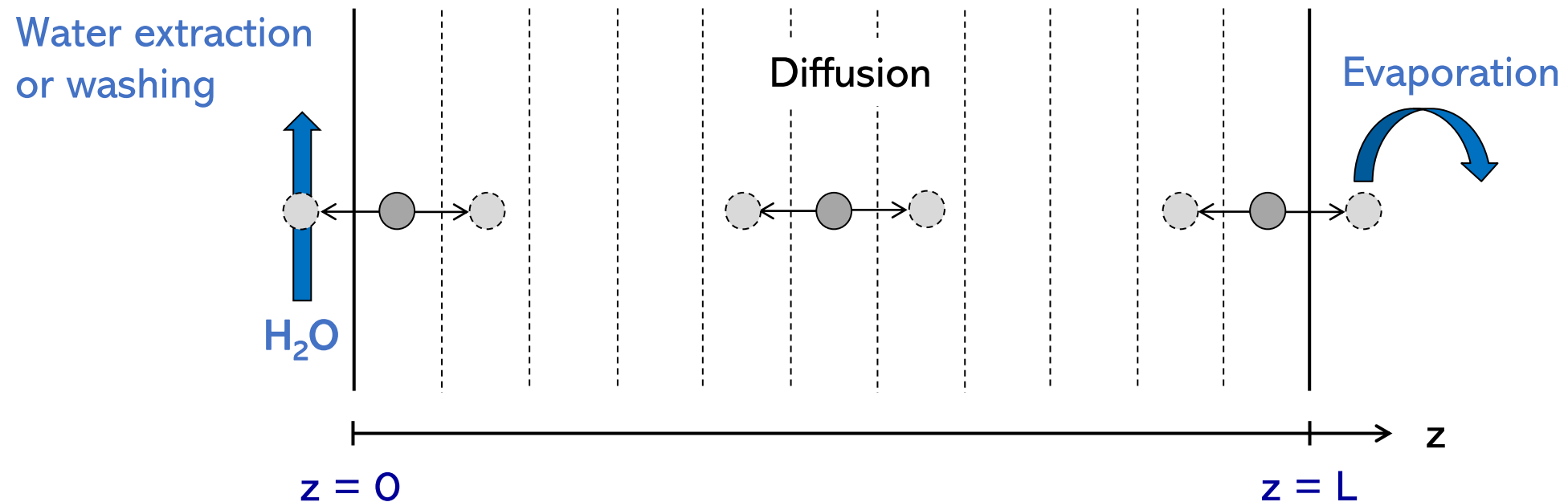
► 2<sup>nd</sup> possible stabilization step



# Physical loss of antioxidants

To be coupled with their chemical consumption

Two phenomena depending on the location in the sample depth: diffusion through the core and evaporation (or extraction by a liquid / solvent) from the surface



# Conclusions

Polymer oxidation preceded by the depletion of antioxidants (i.e. an induction period) due to their chemical consumption (through stabilization reactions) and their physical loss (through diffusion and evaporation or extraction)

Radical chain oxidation both initiated by polymer radiolysis and POOH thermolysis

- Wide variety of hydroxyl (alcohols and hydroperoxides) and carbonyl products (ketones, aldehydes, carboxylic acids, esters, anhydrides, etc.)
  - ▶ At high conversion ratios, impact on cohesive density and polarity, thus on density and electrical properties
- Changes in the macromolecular skeleton (chain scissions and crosslinks)
  - ▶ At low conversion ratios, impact on elastic and fracture properties