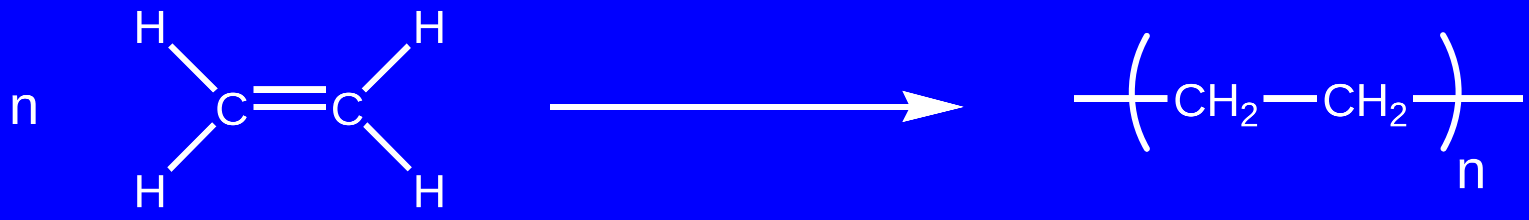
$$\left(CH_2 - CH_2 \right)_n$$

Oxidation and Stabilisation of Polyethylene

Norman Billingham

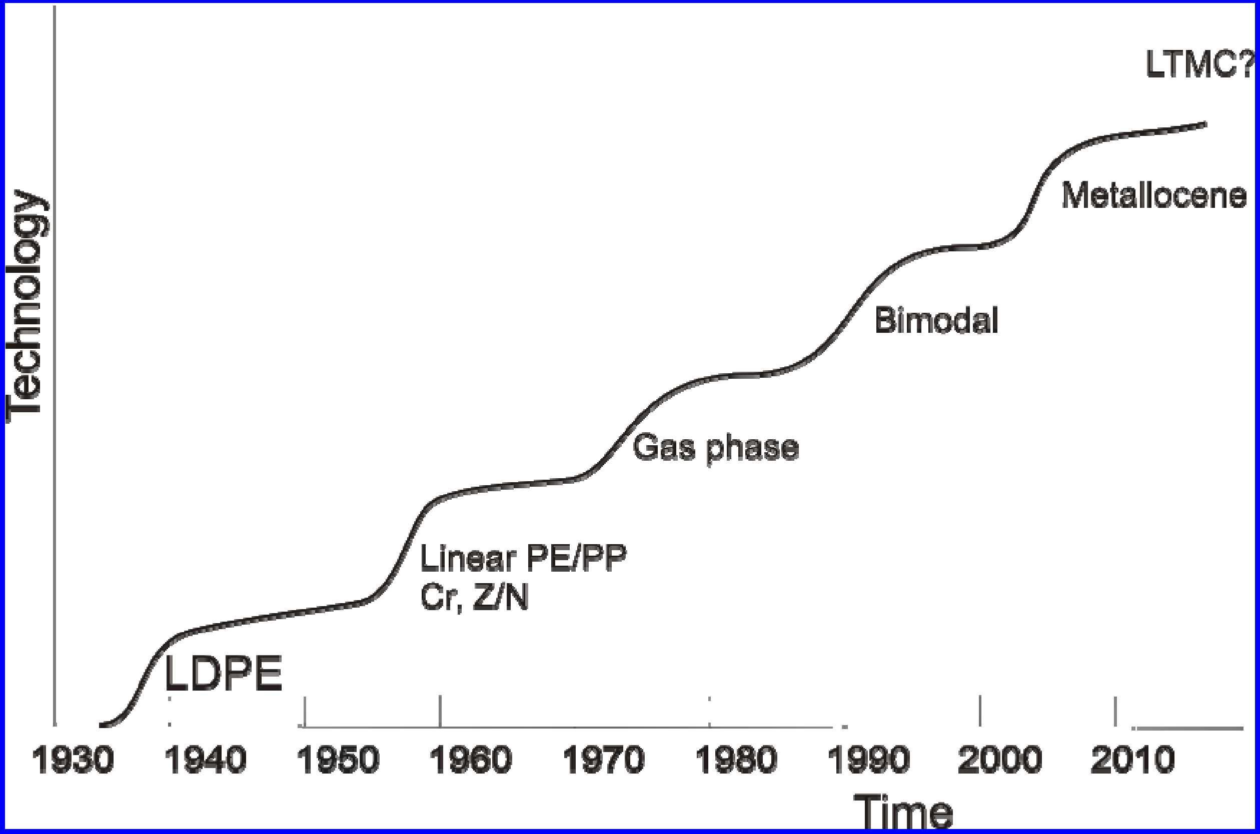
Department of Chemistry and Biochemistry,
University of Sussex, Brighton, UK

Polyethylene

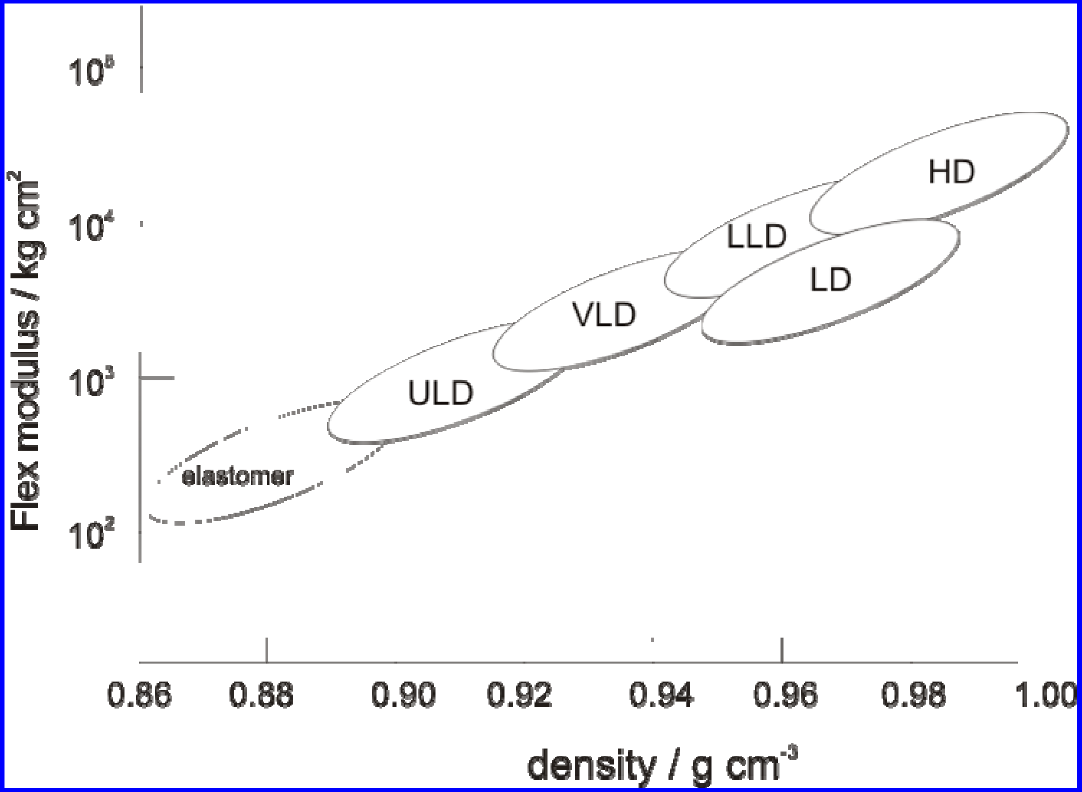


- The simplest polymer?
- Or the most complex?

Polyolefin technology



Polyethylene properties

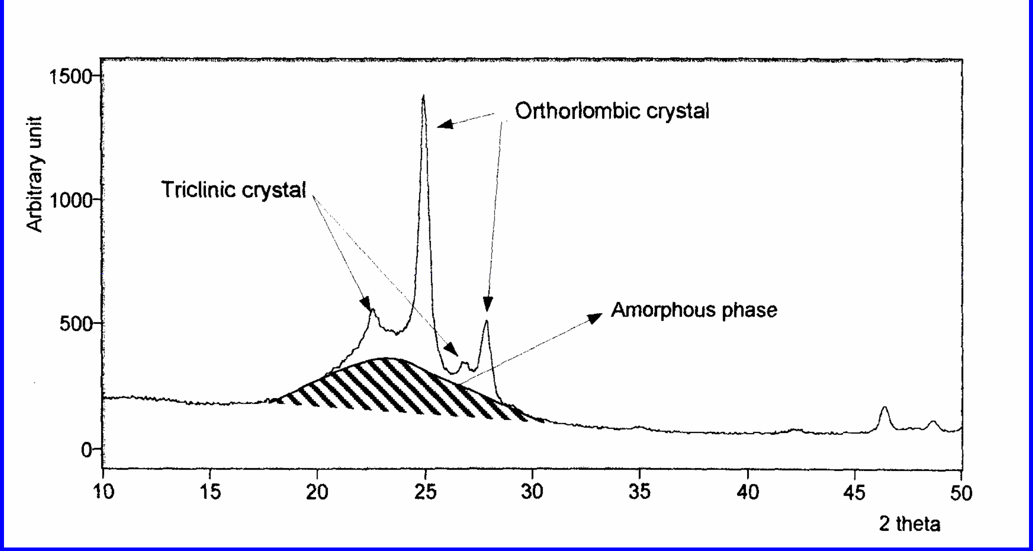


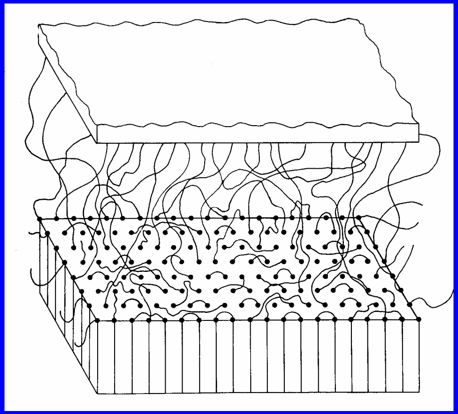
Properties of commercial PE's

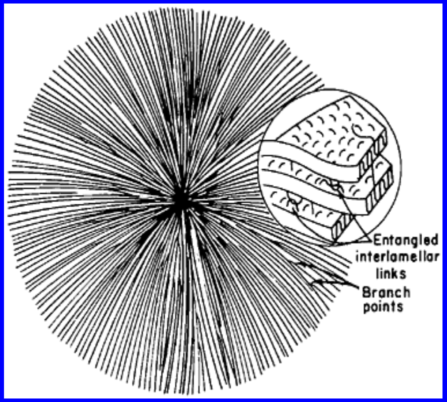
Property	LDPE	HDPE	UHMWPE
Molecular weight	50,000 – 200,000	50,000 – 200,000	>2,000,000
Crystallinity /%	40	60	50-60
Density /gcm^{-3}	0.91 – 0.93	0.94 – 0.97	0.93 – 0.95
Elastic modulus/MPa	100-500	400-1500	1000-2000
Elongation to break /%	50-800	40-1000	>300

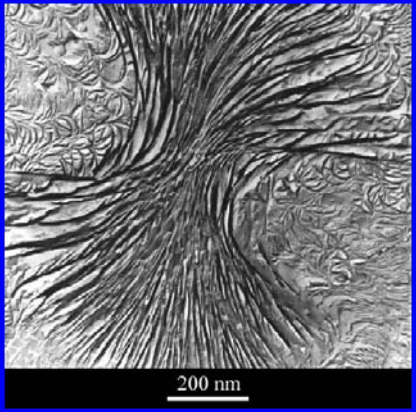
Crystallinity in polyethylene

- X-ray diffraction shows mixture of crystals and amorphous material

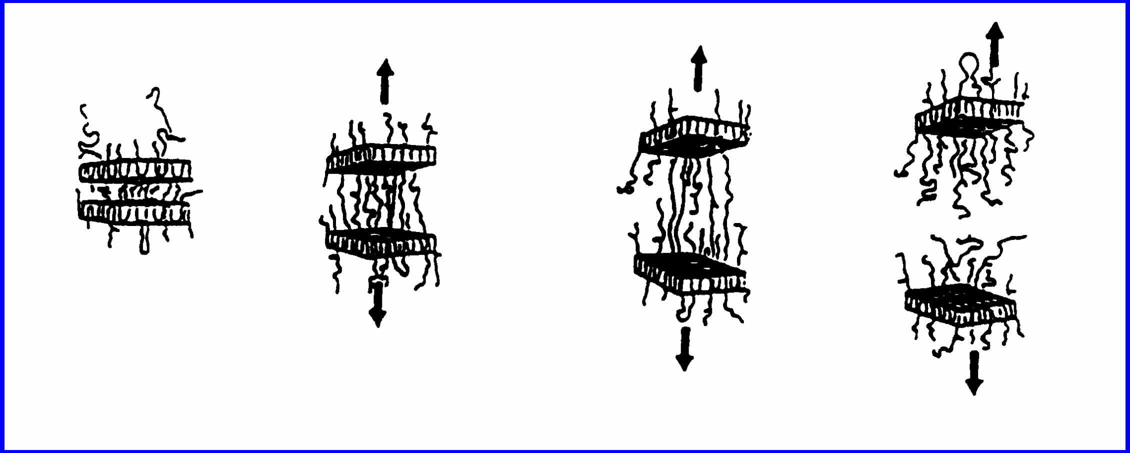








Toughness in semi-crystalline polymers

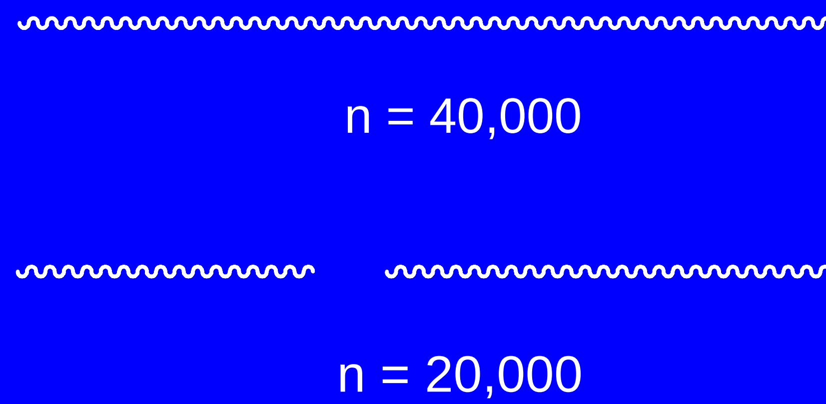


- Crystallites act as “cross-links” and “fillers”
- Increase stiffness and toughness
- Polymer responds to load by chains pulling through crystals
- Critically dependent on “tie molecules”

The perfect nanocomposites?

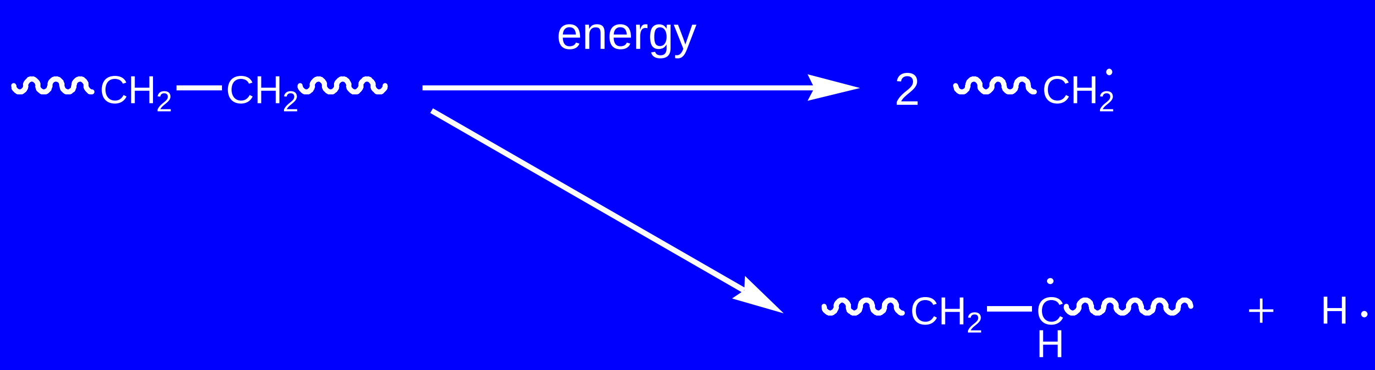
Sensitivity to degradation

- Since the properties of polymers, and of UHMWPE in particular derive from the long molecular chains, anything which breaks those chains can have a very profound effect on properties



Percentage of C atoms reacted = 0.003

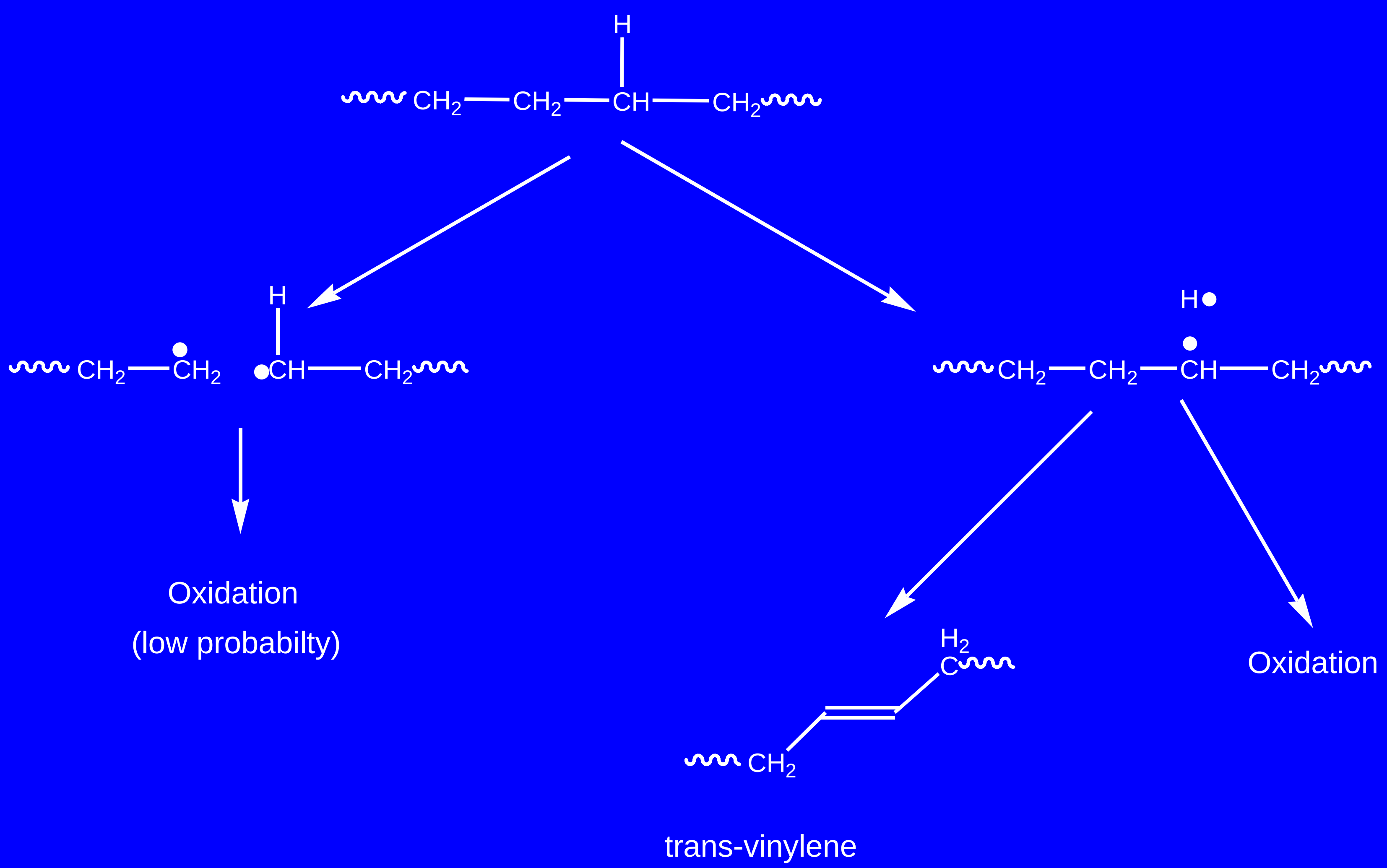
Formation of free-radicals



Energy from:

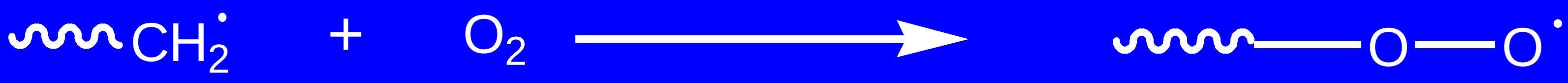
- Reaction of impurities in the polymer –peroxides
- Mechanical breaking of chains
- Irradiation –high-energy (γ, e-beam etc)

Radicals from irradiation



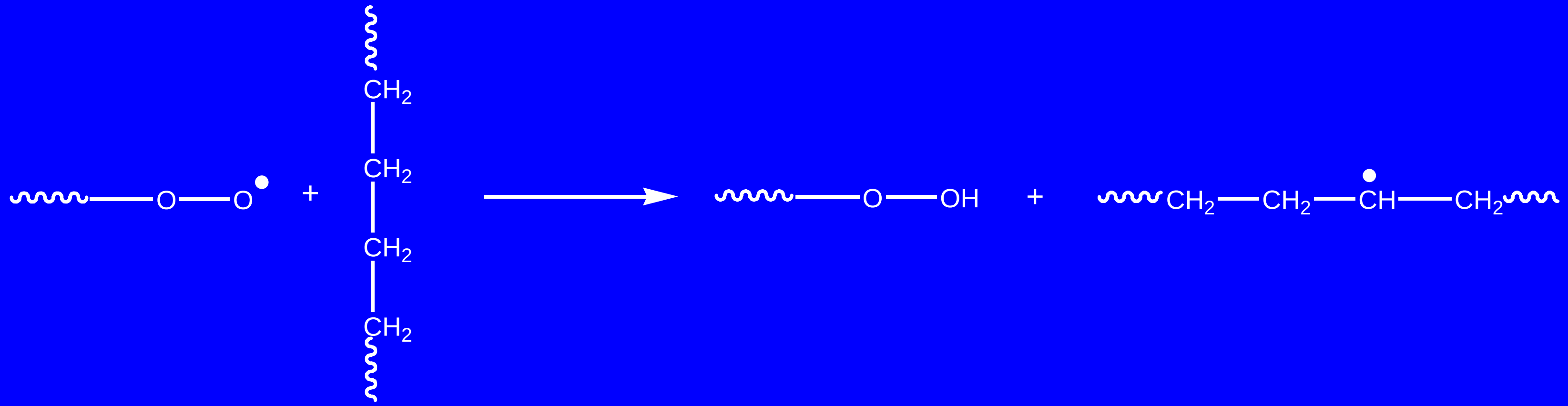
Reaction with oxygen

- Oxygen is always present in a polymer exposed to air
- Solubility is *ca* 1 mmol kg^{-1} in the amorphous polymer and zero in the crystalline
- Reacts instantaneously with carbon radicals on encounter



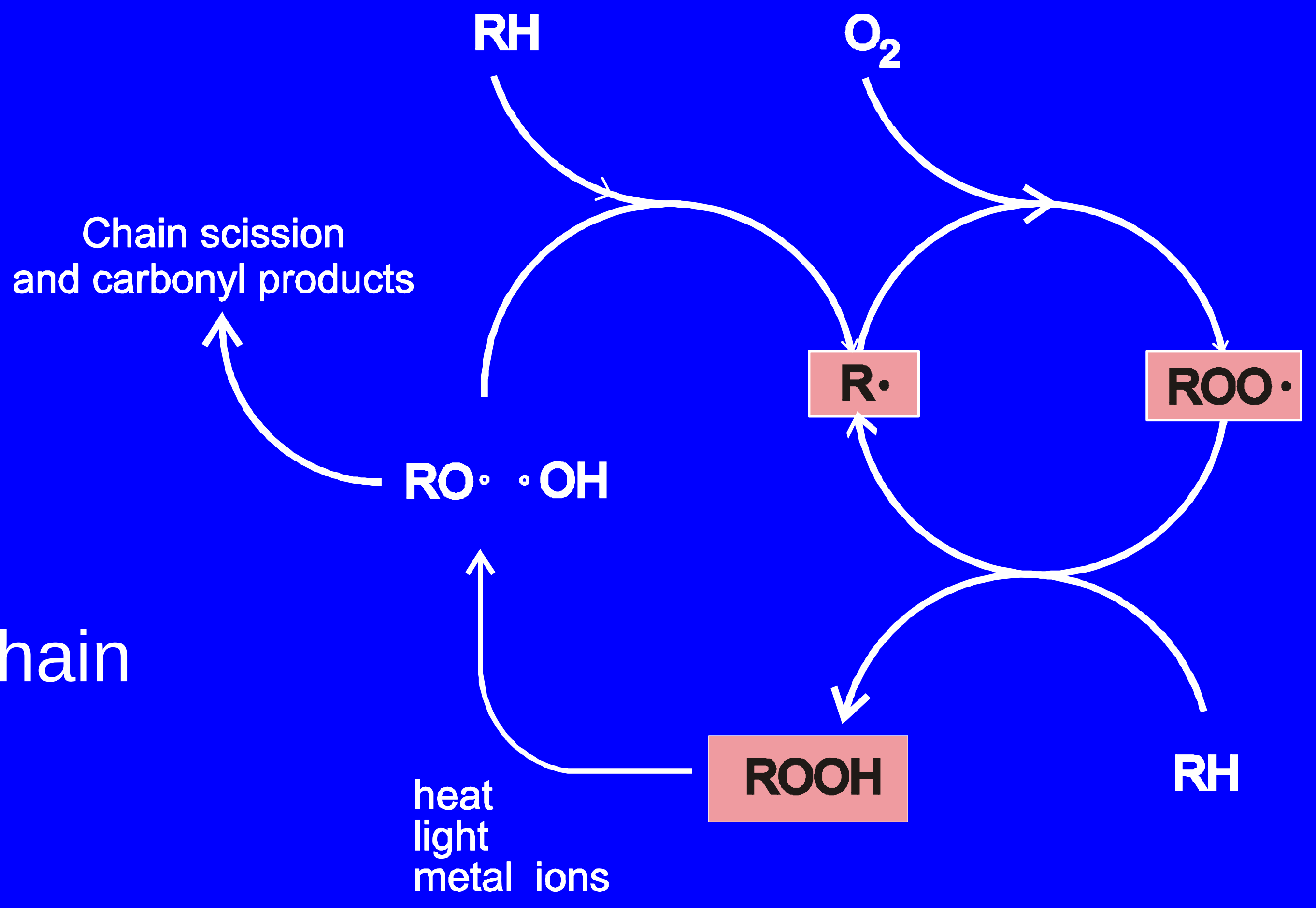
Reaction with oxygen II

- Peroxyl radicals are relatively stable but abstract hydrogen to make new C-centred radicals



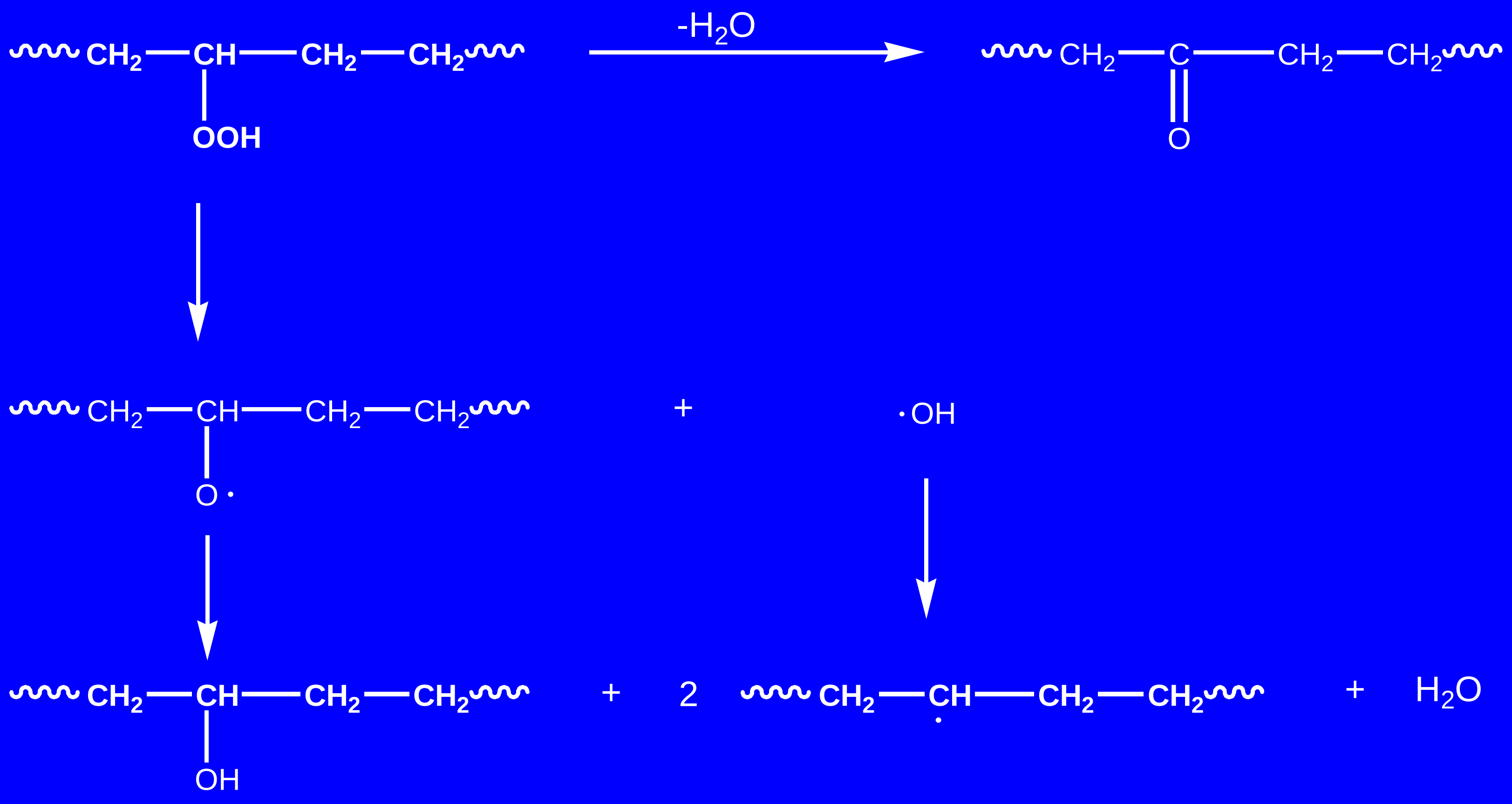
- Overall we have a *chain reaction*

The oxidation cycle



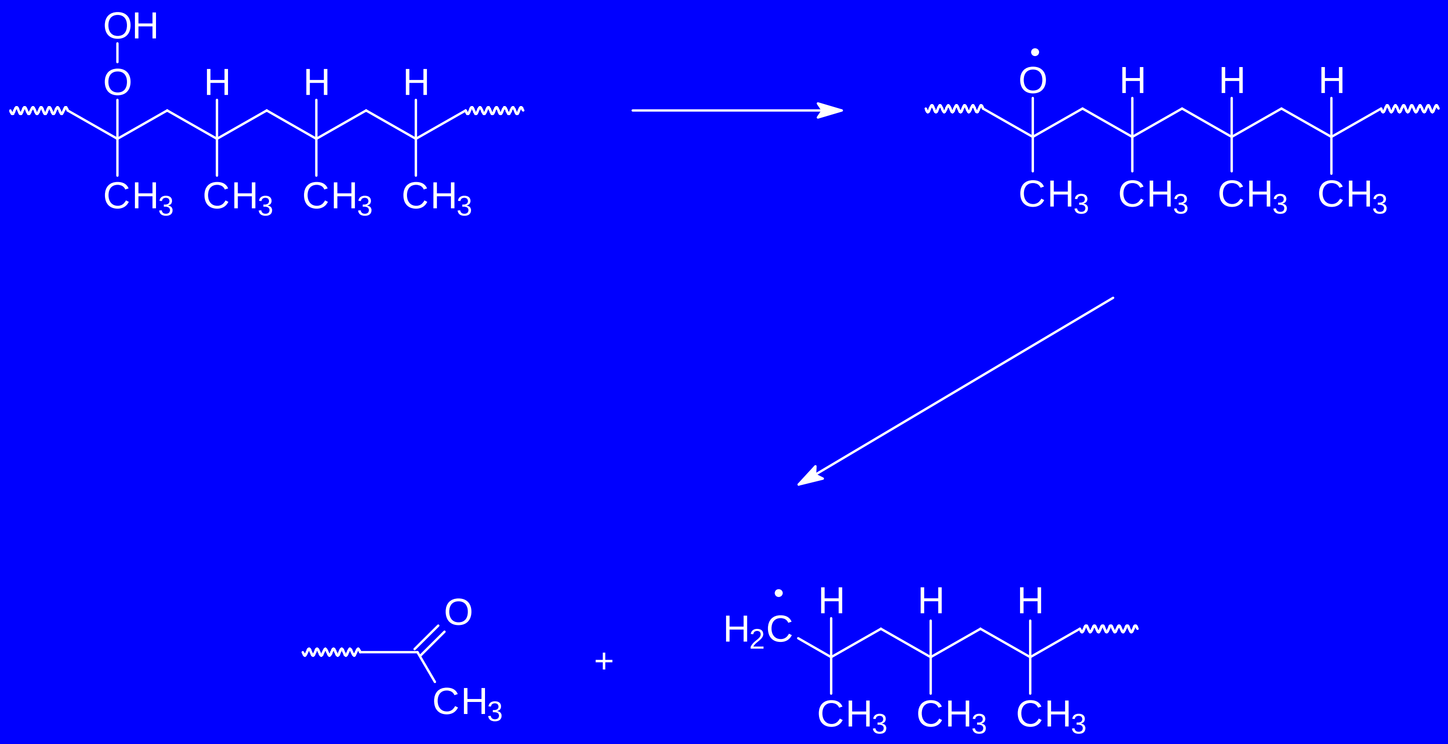
Kinetic chain length?

Decomposition of hydroperoxides

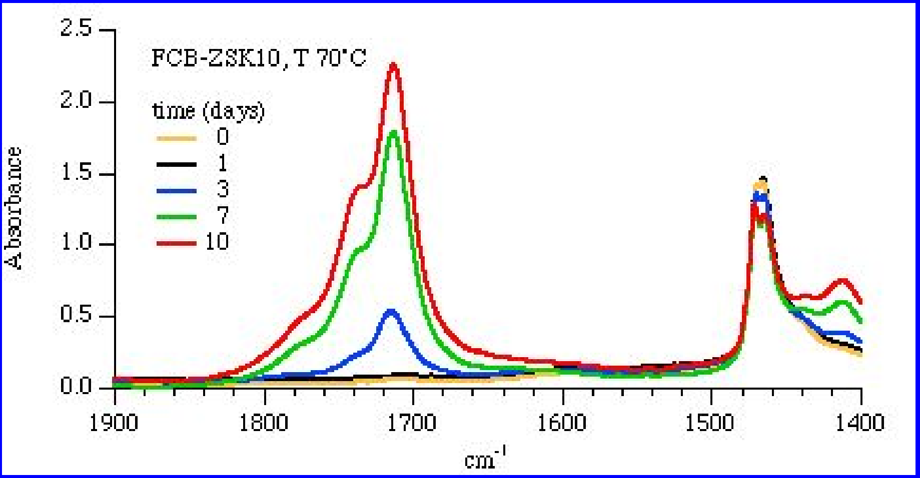


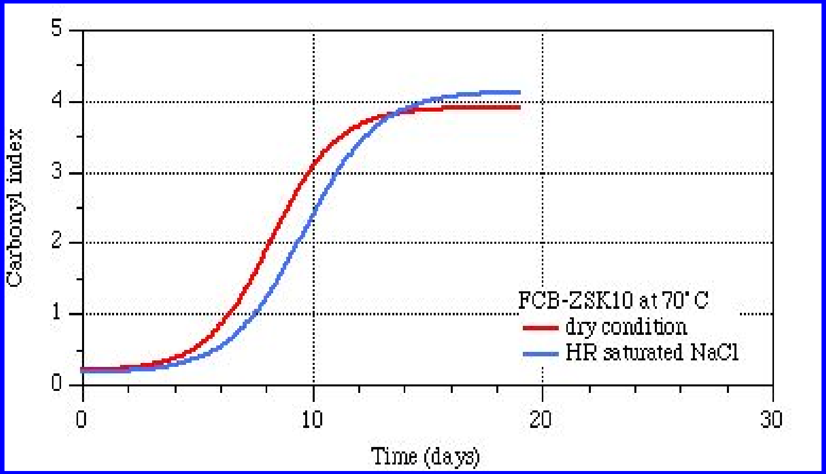
AUTOACCELERATION

Chain scission reactions of alkoxy radicals



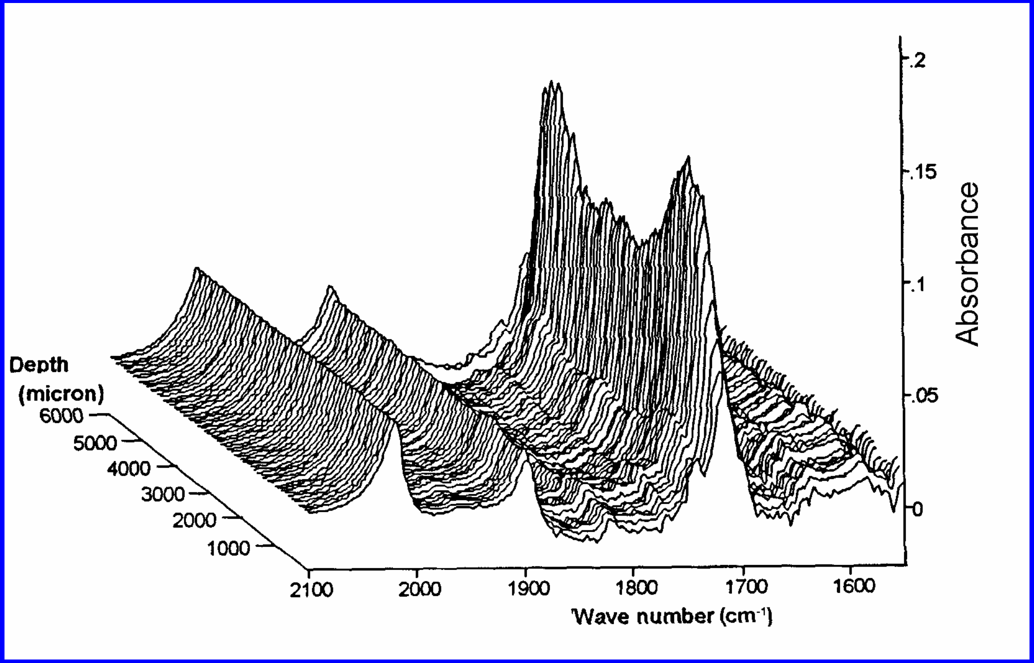
Infra-red analysis of oxidation





- Development of bands in region 1700 – 1750 cm^{-1} is characteristic of carbonyl-containing products of oxidation (ketones, acids and esters.

Diffusion limited oxidation



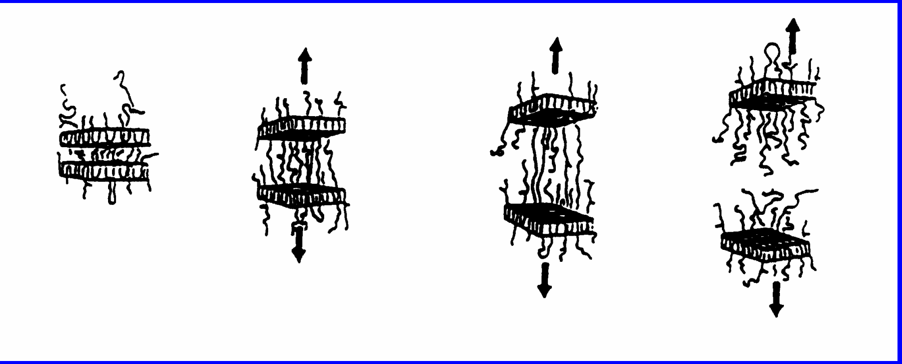
Oxygen diffusion controls distribution of oxidation products through thick sections

Effects of oxidation

- Oxygen incorporation increases density and hydrophilicity
- Chain scission allows recrystallisation – “chemicrystallisation”
- Increased density and crystallinity leads to surface cracking
- Polymer changes from tough to brittle

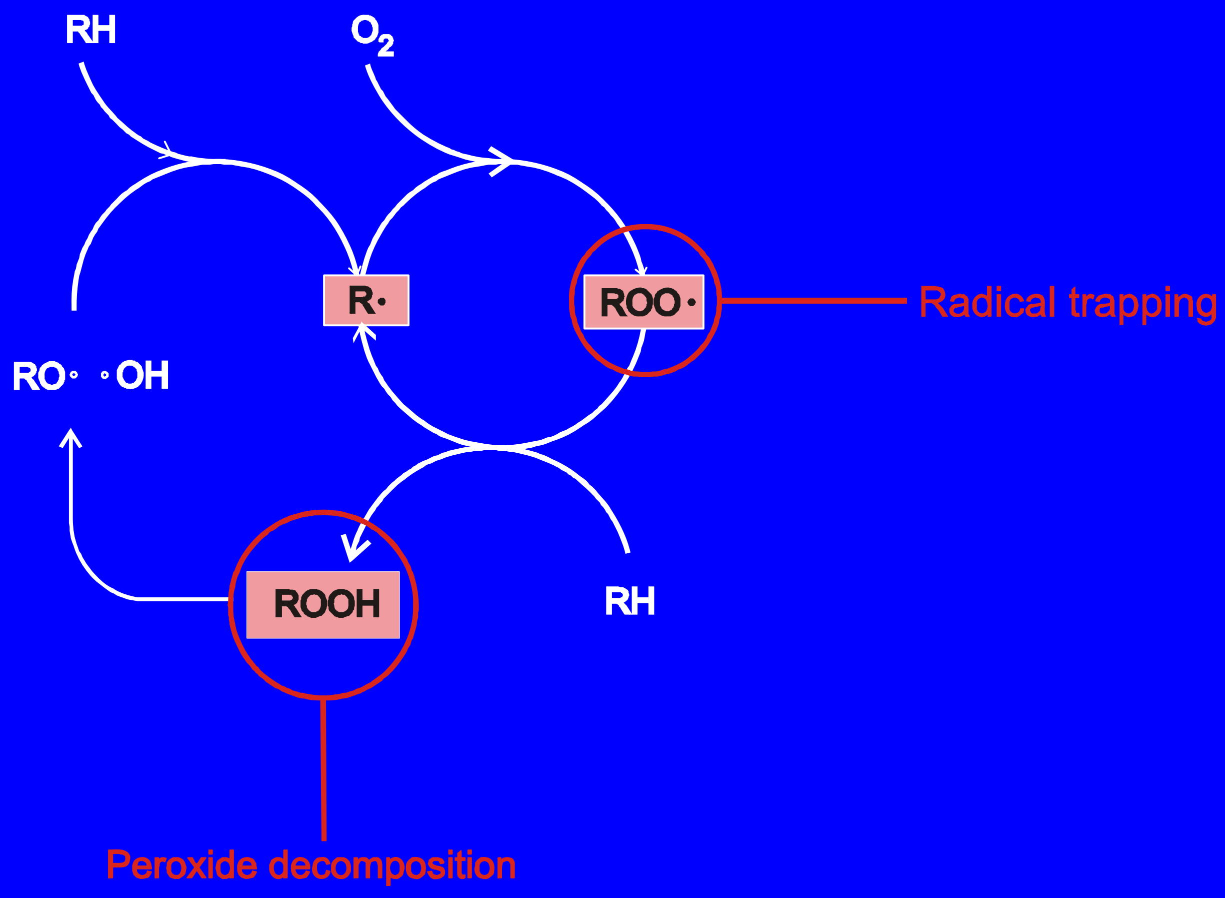
Mechanical Properties

- Increased density and crystallinity leads to surface cracking
- Cleavage of tie molecules stops load transfer via crystals
- Overall – loss of toughness

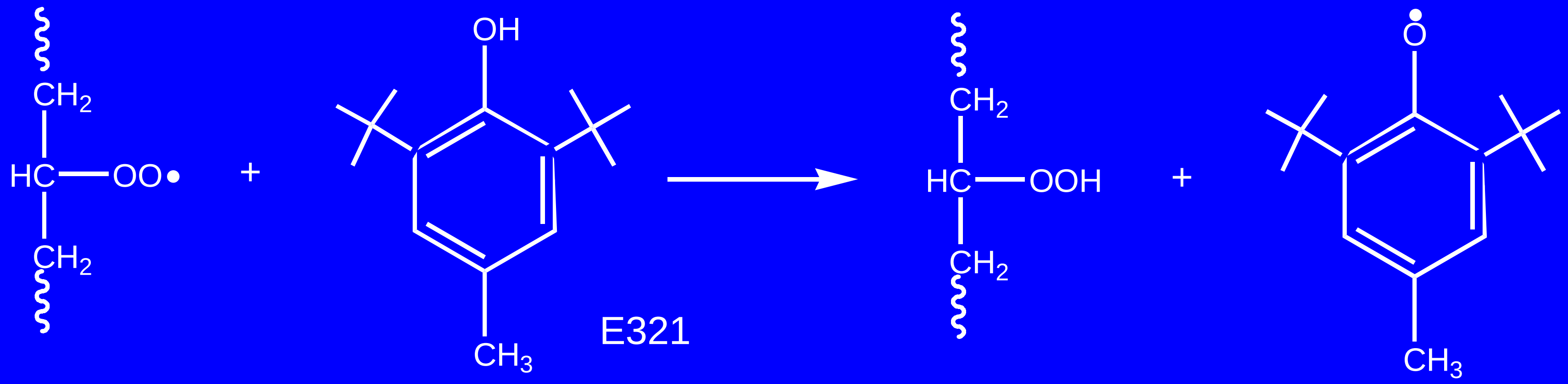


Note that a polymer whose MW is reduced by degradation can be brittle even though a normal sample of same MW is tough

Potential routes for stabilisation



Simple phenolic antioxidant - BHT



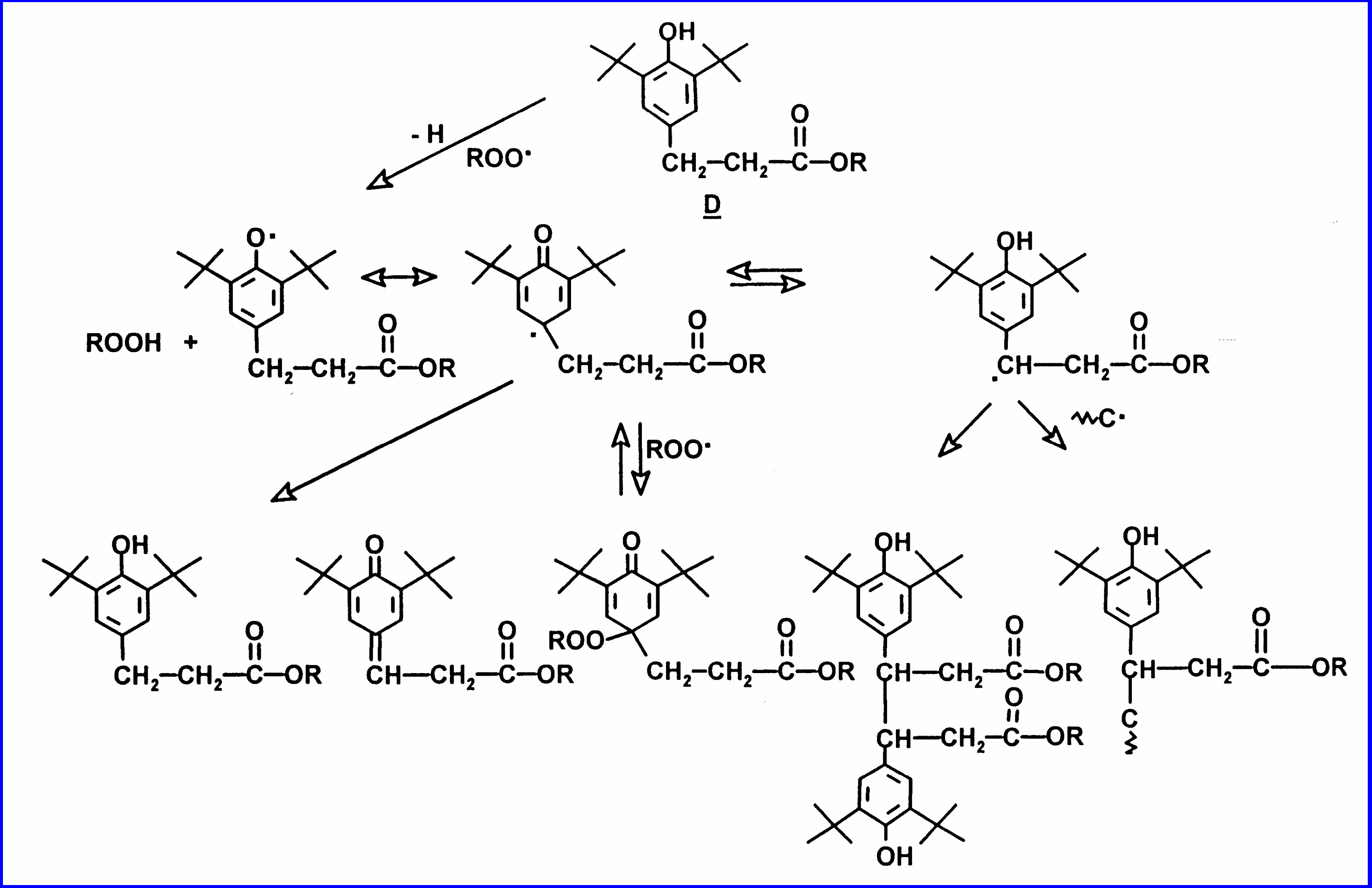
- Able to trap peroxy radical
- Producing new radical too stable to reinitiate

Requirements of an antioxidant

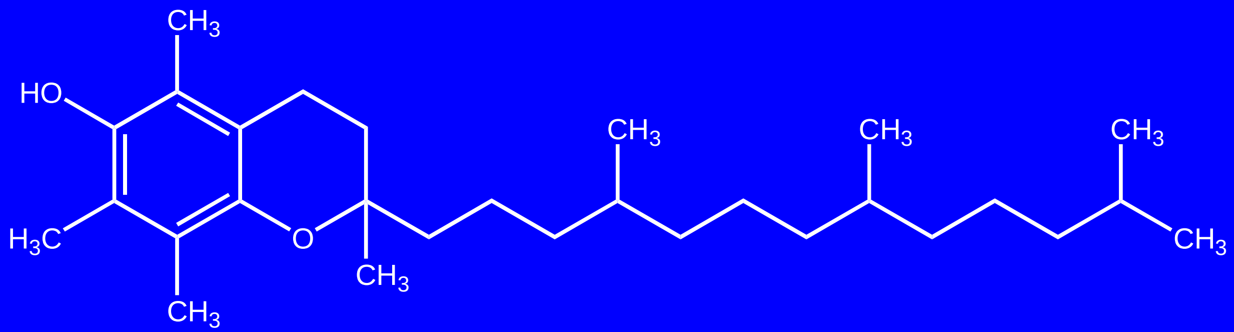
In addition to chemical reactivity an antioxidant must have:

- Thermal stability to survive processing
- Good solubility in hydrocarbon polymer
- Low volatility
- Low extractability into contacting liquids
- Low toxicity, especially in food contact

Reaction products of phenolics



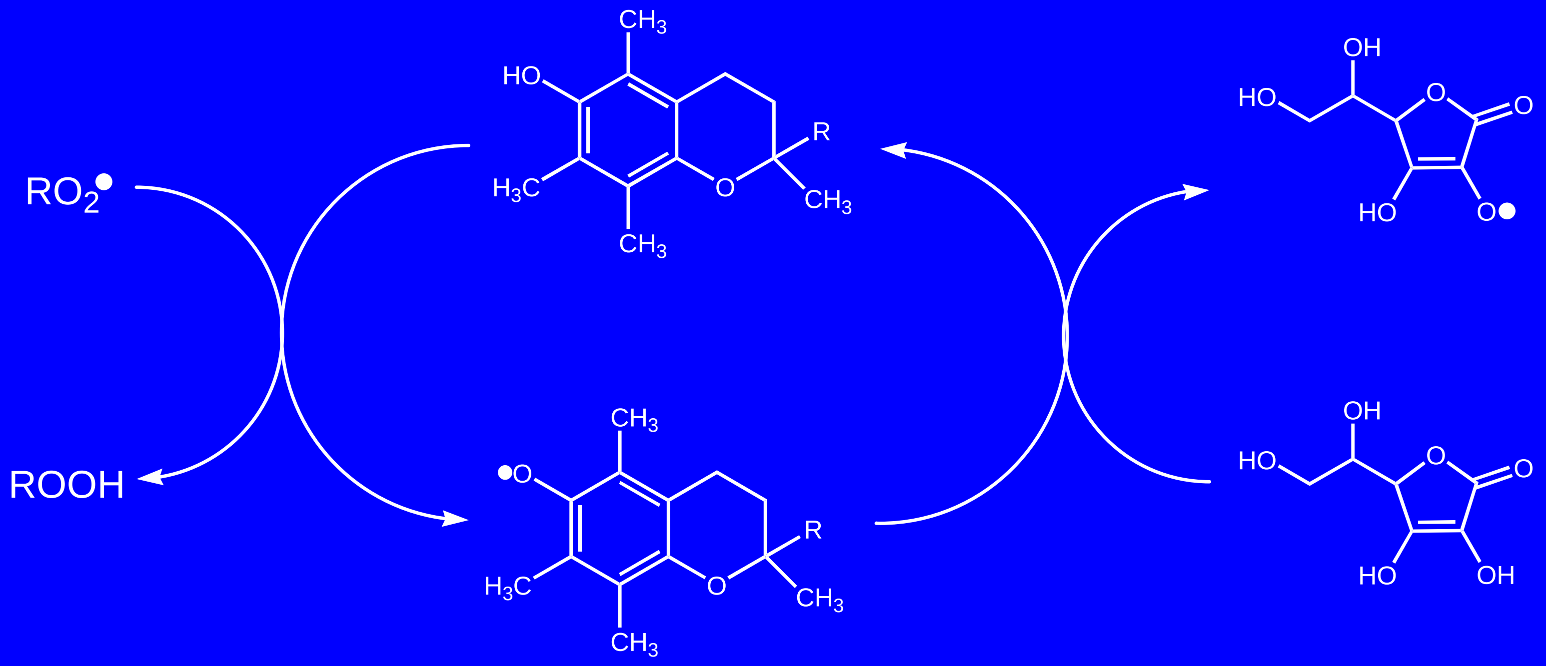
Natural antioxidants



α-tocopherol Vitamin E E307 Oil soluble

ascorbic acid Vitamin C E300 Water soluble

Antioxidant synergism *in-vivo*

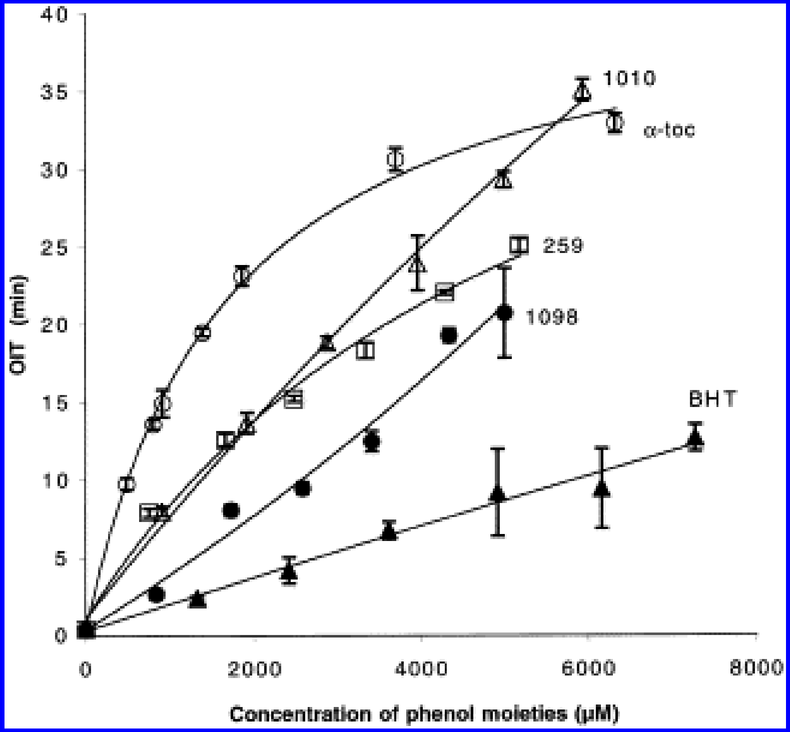


Cell membrane

Plasma

Niki, E, *Ann. NY Acad. Sci* 498, 186, 1987

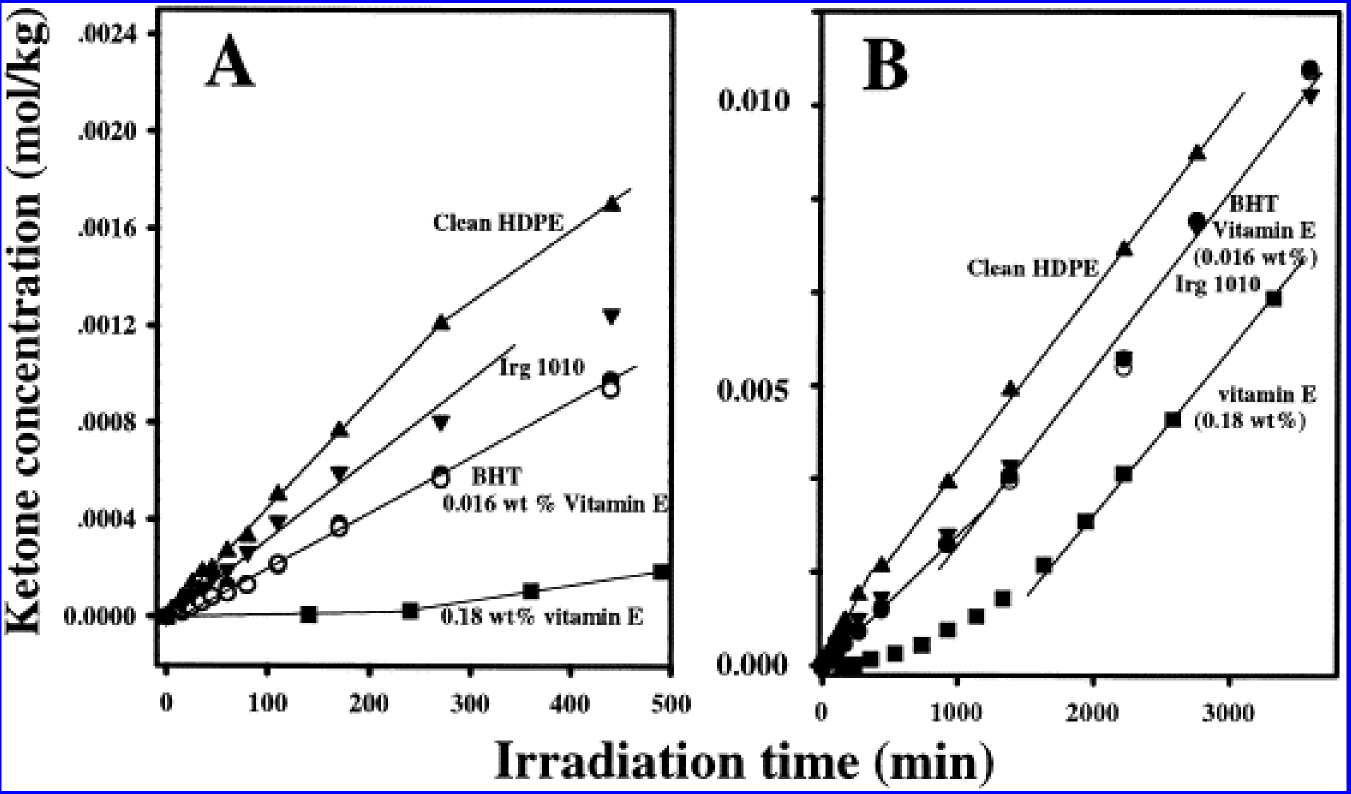
Oxidation inhibition in hydrocarbons at 190^{o}C



Breese, K D, Lamethe, JF, and DeArmitt, C, *Polym. Deg. Stab.,* 70, 89, 2000

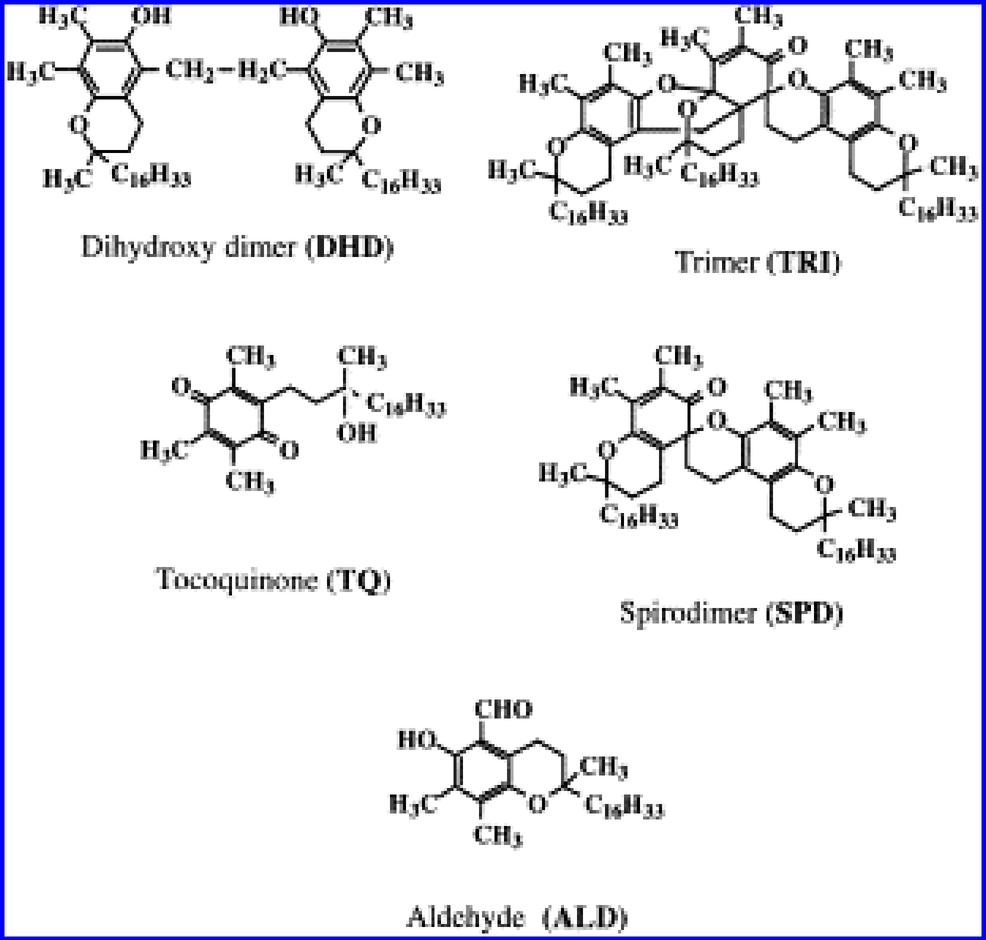
Stabilising effect of Vitamin E

Gamma induced oxidation of HDPE



Mallegol, J, Carlsson, DJ, Deschenes, L, *Polymer Deg. Stab.* 73 (2), 259-267, 2001

Oxidation products of tocopherol



Al-Malaika, S, Goodwin, C, Issenhuth, S, Burdick, D, *Poly. Deg. Stab.* 64, 145, 1999

Conclusions

- Polyethylene gets its mechanical properties from the combination of long chain length and semi-crystalline morphology
- Chemically insignificant amounts of oxidative degradation affect mechanical properties profoundly by cleaving the important “tie molecules”
- Oxidative degradation is easily initiated by γ or e-beam radiation

Conclusions II

- Detailed mechanisms may depend on local solid-state mobility – especially UHMWPE
- Antioxidants are added to essentially all PE products to inhibit oxidation during processing and end use
- Most commercial antioxidants would be excluded from use in medical devices due to potential migration and toxicity
- Vitamin E has potential for medical applications