Corrosion of polymers

- corrosion = deterioration by electrochemical reaction with water, alkali, or acid
- C–C, C–X, C–O bonds are resistant to corrosion.
- Polymers containing amide, ester, or urethane may be attacked by hot acids or alkalies, and hydrolyzed.
  - due to C=O
  - backbone or side-chain

Thermal stability

- resistance to degradation by heat [열안정성]
  - heat resistance [내열성]
    - resistance to softening by heat
    - depends on T_g or HDT
- groups
  - time-temperature zones
  - 50% property in air
  - Table 1.13

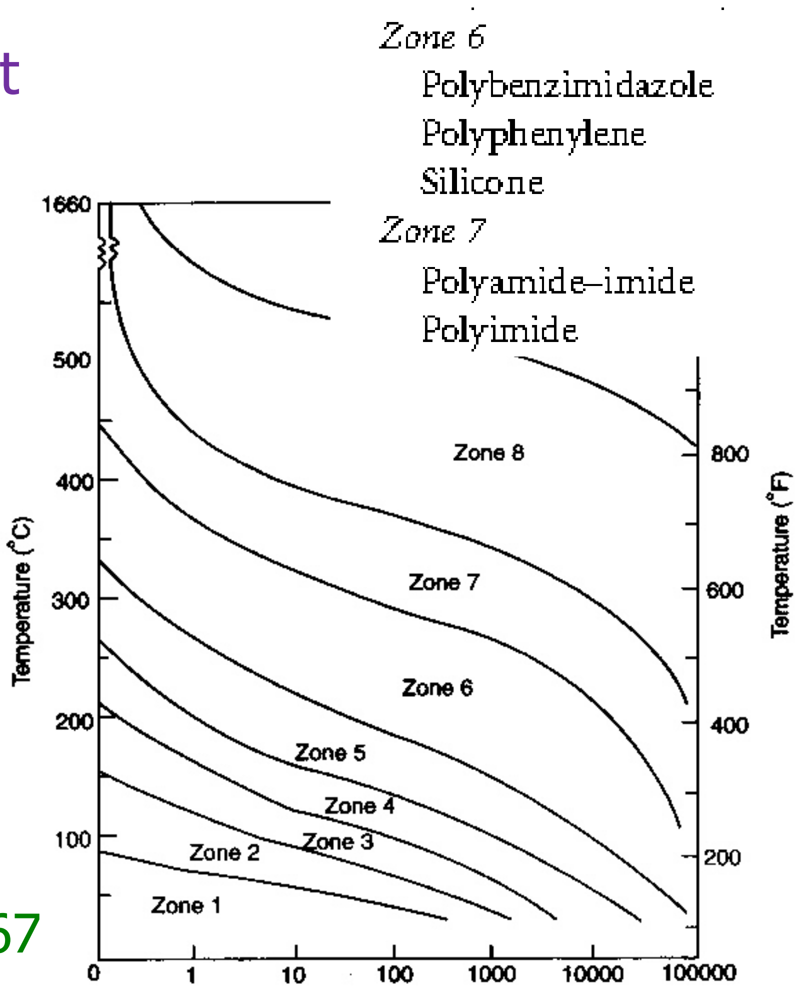
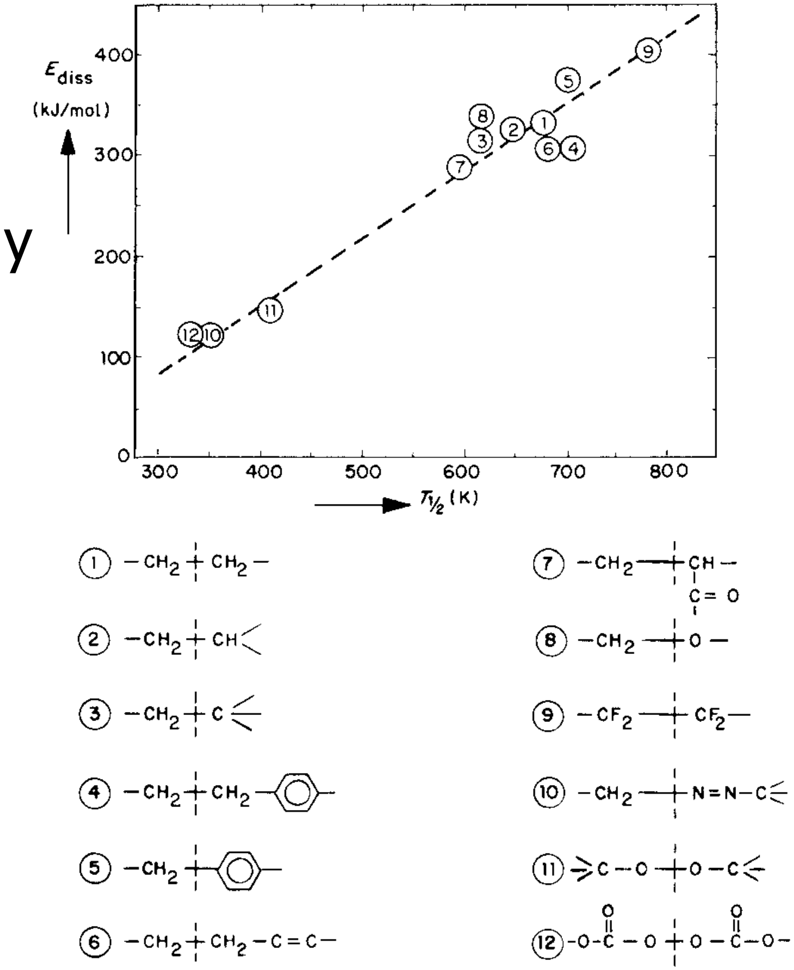
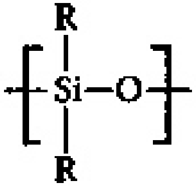


Fig 1.67

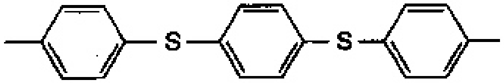
- thermal stability depends on the dissociation energy of the weakest bond
    - E_{diss} vs $T_{1/2}$
        - E_{diss} = bond dissociation energy
        - $T_{1/2}$ = half weight at ½ hr

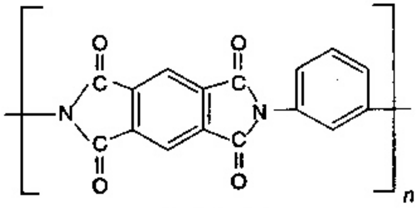


- high-temperature polymer
  - highly heat-resistant? thermally stable? parallels!
  - polymers with high (aromatic) ring content
    - polyphenylene, PPS, PPO
    - aromatic polyesters (Vectra)
    - aromatic polyamides (Kevlar)
    - polyimides
    - polybenzimidazoles
  - ladder polymers
  - inorganic atom ~ Si, P, ---

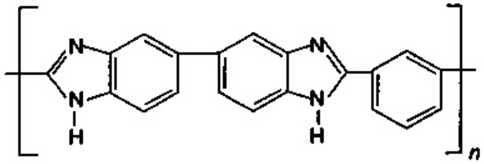


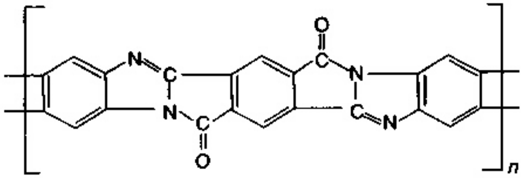
$$\left[\mathrm{Si(R)_2{-}O}\right]$$



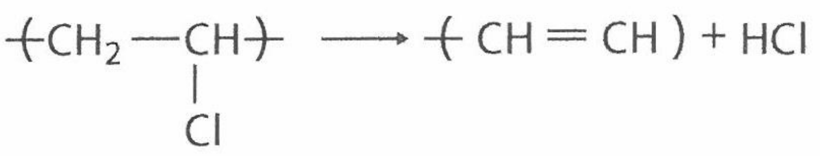


Polyimide



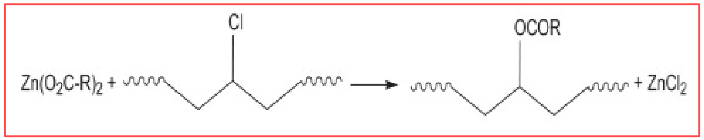


- thermal degradation mechanisms (of vinyl polymers)
  - side-chain cleavage
    - yellowing



$$\left(CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} \right) \longrightarrow \left(CH = CH \right) + HCl$$

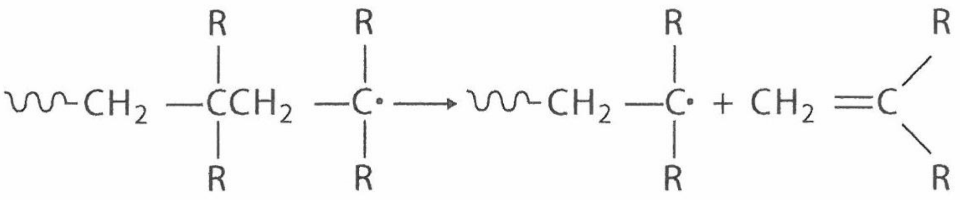
heat stabilizer for PVC



  - random chain scission

$$\sim\sim CH_2CH_2CH_2CH_2 \sim\sim \longrightarrow \sim\sim CH_2\dot{C}H_2 + \cdot CH_2CH_2 \sim\sim \longrightarrow \sim\sim CH{=}CH_2 + CH_3CH_2 \sim\sim$$

  - depropagation [depolymerization]
    - 1,1-disubstituted ~ low $\Delta H_{polym'n}$ ~ low T_c



$$\sim\sim CH_2 - \underset{R}{\overset{R}{C}}CH_2 - \underset{R}{\overset{R}{C}}\cdot \longrightarrow \sim\sim CH_2 - \underset{R}{\overset{R}{C}}\cdot + CH_2 = C\begin{matrix} R \\ R \end{matrix}$$

- other polymers? p100-101

Flame [fire] retardation

- burning: 2-step process
  - pyrolysis [decompose] → 'char' + gas – Q_1
  - combustion [ignite-inflame] → combustion product + Q_2

- for flame retardation [high LOI]
  - adding flame retardants later
  - fire-resistant polymers
    - low gas [Q_2] and high char yield = lower H/C ~ rings
      - High-Temp polymers are fire-resistant.
    - inhibiting gas ~ PVC

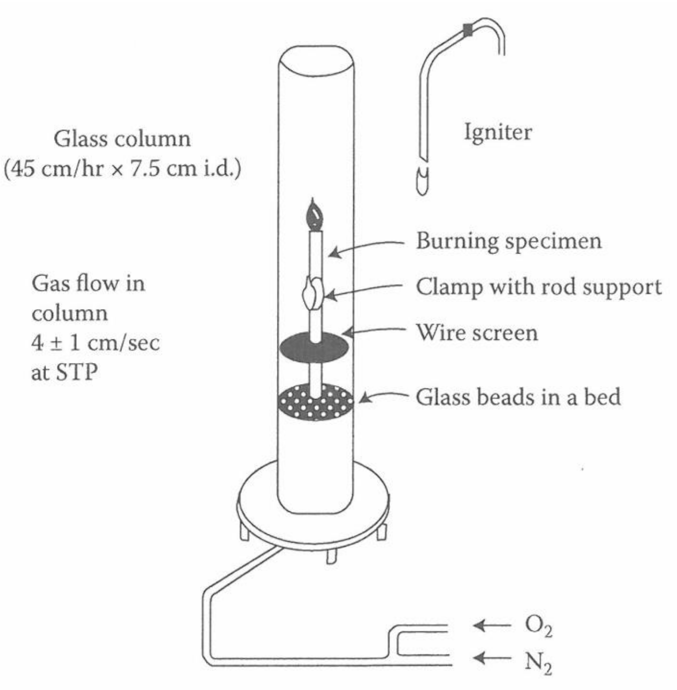


Fig 3.80 p390

Ablation

- heat protection by sacrificial loss of material
- ablative material
  - decompose to gas and porous char (protective layer)
  - absorb and dissipate energy
  - useful in space shuttles
  - phenolic resins
- intumescent coating
  - fire-protection by swelling

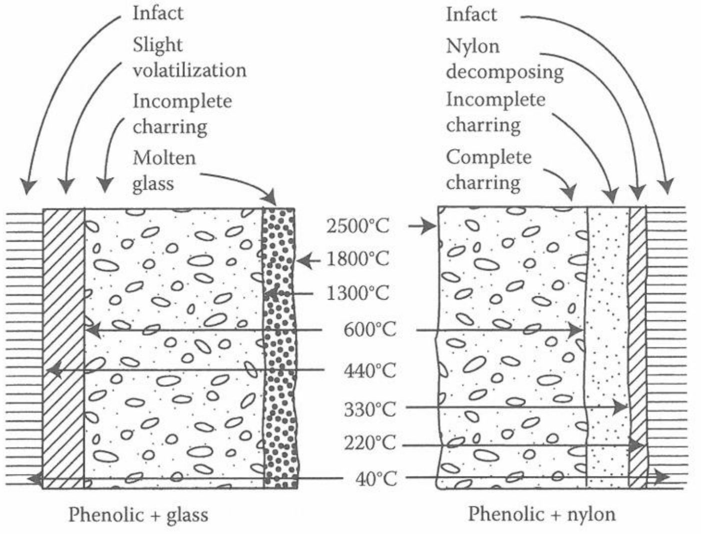
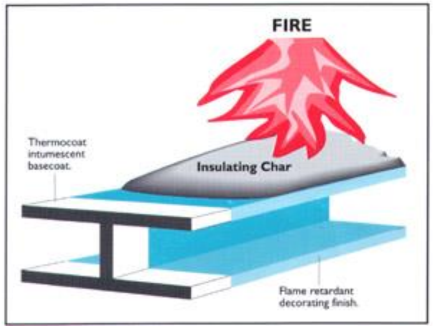


Fig 1.72



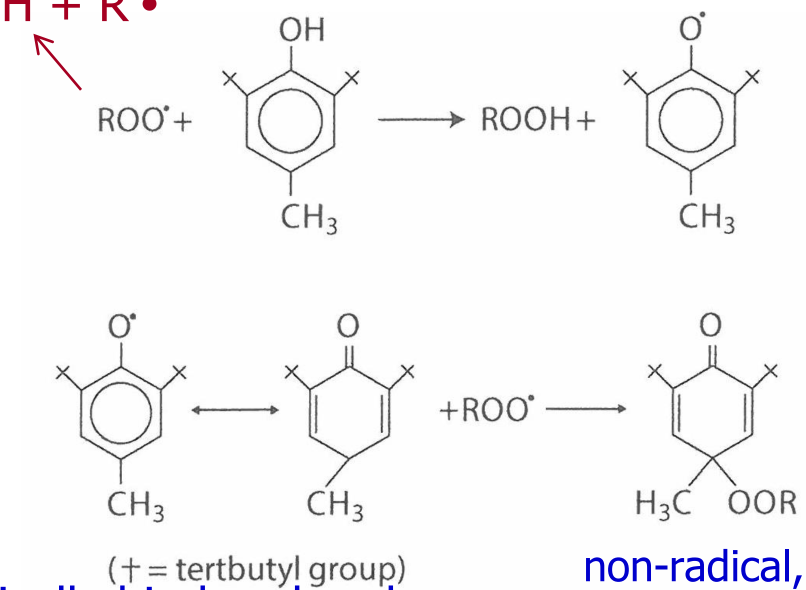
Deterioration of polymers

- loss of property and/or dimension by
  - heat
  - UV or other radiation
  - O_2 or O_3 ~ usually combined with heat or radiation
  - water or chemicals
  - bacteria
- deterioration through
  - degradation
  - oxidative degradation (eqn 1.101-108) ~ chain reaction
    - $R\bullet + O_2 \rightarrow ROO\bullet \rightarrow ROOH + R'\bullet \rightarrow RO\bullet + \bullet OH$
  - hydrolysis ← hydrolyzable group [ester, amide, --]
  - crosslinking

Stabilization 1: antioxidants

- 2 types of AO [산화안정[방지]제]
  - primary antioxidants = radical scavenger
    - stop chain reaction
    - hindered phenols, 2° aromatic amines

ROOH + R'•



non-radical, stable

sterically hindered and resonance-stabilized

Eqn 1.111,112

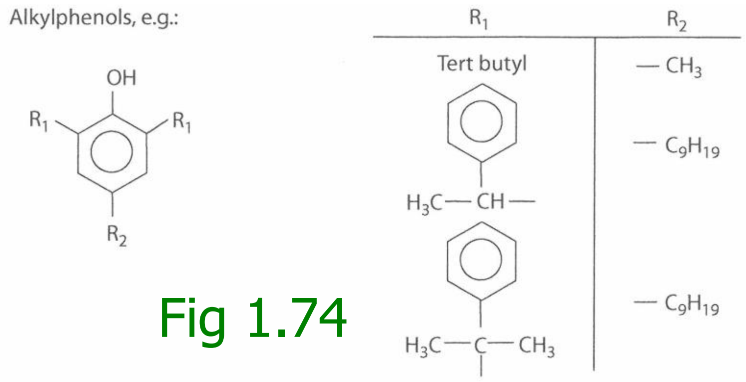
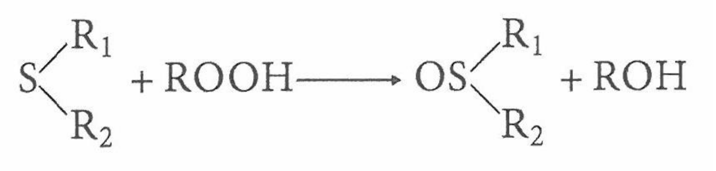


Fig 1.74

Stabilization 1: antioxidants

- 2 types (cont'd)
  - secondary antioxidants (= hydroperoxide scavenger)
    - decompose hydroperoxide
    - thioethers, thioesters, phosphates



$$\mathrm{S}\langle^{R_1}_{R_2} + \mathrm{ROOH} \longrightarrow \mathrm{OS}\langle^{R_1}_{R_2} + \mathrm{ROH}$$

$$\mathrm{P(OR')_3 + ROOH \rightarrow OP(OR')_3 + ROH}$$

Eqn 1.113,114

(a) Thioethers, e.g.:

(b) Phosphites and phosphonites, e.g.:

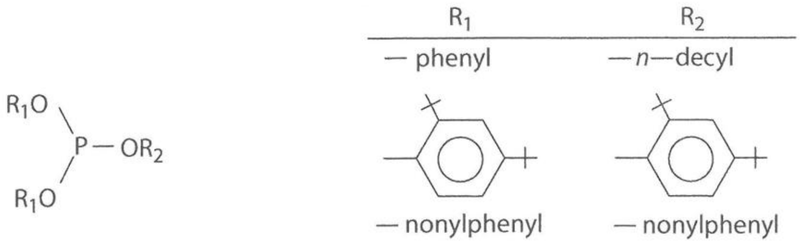
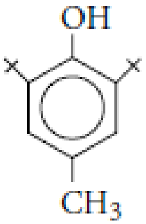
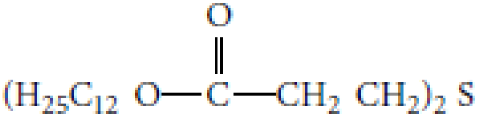


Fig 1.75

- synergistic AO
  - homosynergism
    - 2 or more AOs with the same mechanism (1° or 2°)
  - heterosynergism
    - combination of 1° and 2° AOs (2° AO called synergist)
      - BHT/DLTDP ~ most popular combination, approved by FDA





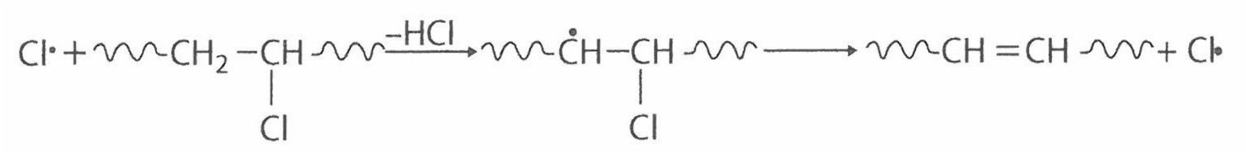
$$(H_{25}C_{12}\,O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2\,CH_2)_2\,S$$

- combination of AO and other stabilizer(s) (like UV stabilizer)

- AO for polymers pp110-118
  - polyolefins
    - mixture of phenols and phosphates, commonly
    - HDPE < PP ≈ LDPE ← tertiary C, Xtallinity
  - styrenics
    - 'crystal' PS < ABS ≈ HIPS ← double bonds
  - PC
    - yellowing ~ phosphates
  - polyacetal ~ depolym'n
    - hindered phenol + amines ~ amine react with CH_2O

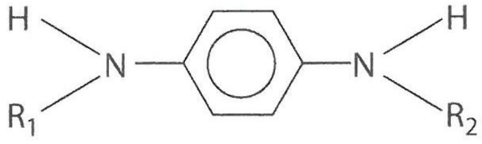
AO for polymers (cont'd)

- PVC
  - HCl, =, • ~ Pb comp'ds, reactive plasticizers



$$Cl^{\bullet} + \sim CH_2-\underset{\underset{Cl}{|}}{CH}\sim \xrightarrow{-HCl} \sim \dot{C}H-\underset{\underset{Cl}{|}}{CH}\sim \longrightarrow \sim CH=CH\sim + Cl^{\bullet}$$

- rubber
  - ozonolysis of double bond when stretched
  - staining [color, C] or non-staining



R_1, R_2 = Alkyl

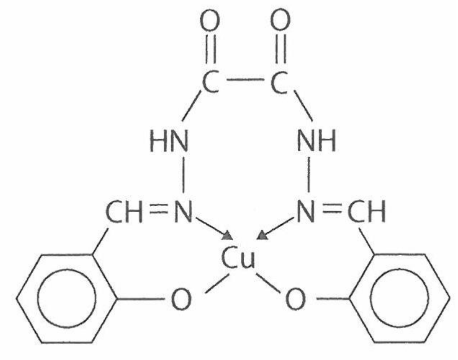
Metal deactivators

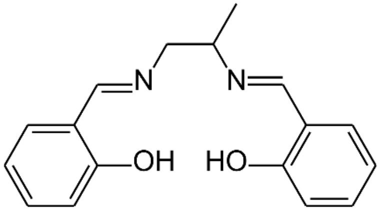
- Transition metals catalyze radical rxn of hydroperoxide (even with AO).

$$\mathrm{ROOH} + \mathrm{M}^{n+} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{M}^{(n+1)+} + \mathrm{OH}^{-}$$

$$\mathrm{ROOH} + \mathrm{M}^{(n+1)+} \rightarrow \mathrm{ROO}^{\bullet} + \mathrm{M}^{n+} + \mathrm{H}^{+}$$

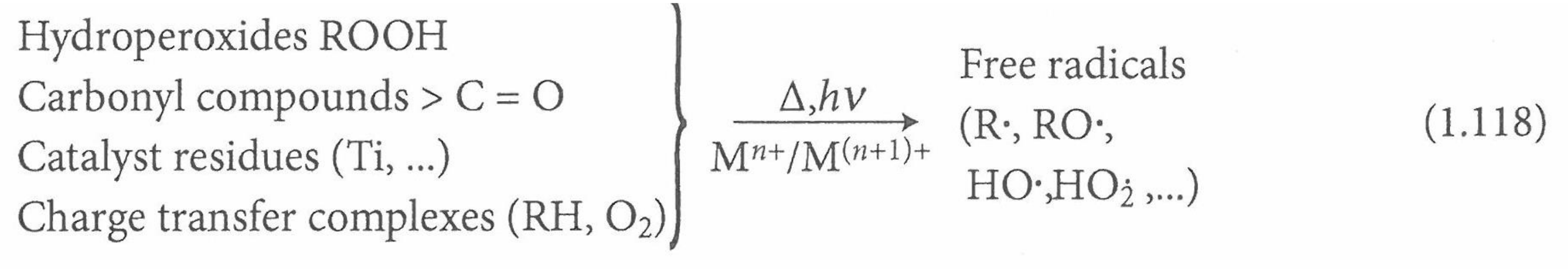
  - induce metal-catalyzed oxidation of polymers
  - esp critical in polyolefin cable insulation
- needs metal deactivators
  - chelating agents
  - ‘copper inhibitor’ in cable insulating PO





Stabiliz’n 2: Light [UV] stabilizer

- photo-oxidation by UV (around 300 nm)

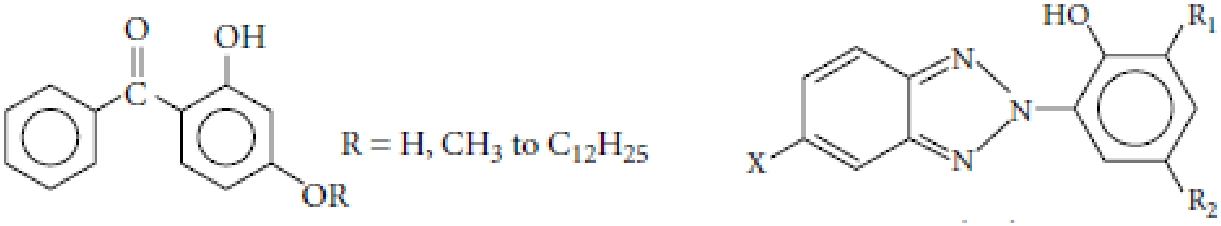


$$\left.\begin{array}{l}\text{Hydroperoxides ROOH}\\ \text{Carbonyl compounds} > C=O\\ \text{Catalyst residues (Ti, ...)}\\ \text{Charge transfer complexes } (RH, O_2)\end{array}\right\} \xrightarrow[M^{n+}/M^{(n+1)+}]{\Delta, h\nu} \begin{array}{l}\text{Free radicals}\\ (R\cdot, RO\cdot,\\ HO\cdot, HO_2^{\cdot}, ...)\end{array} \qquad (1.118)$$

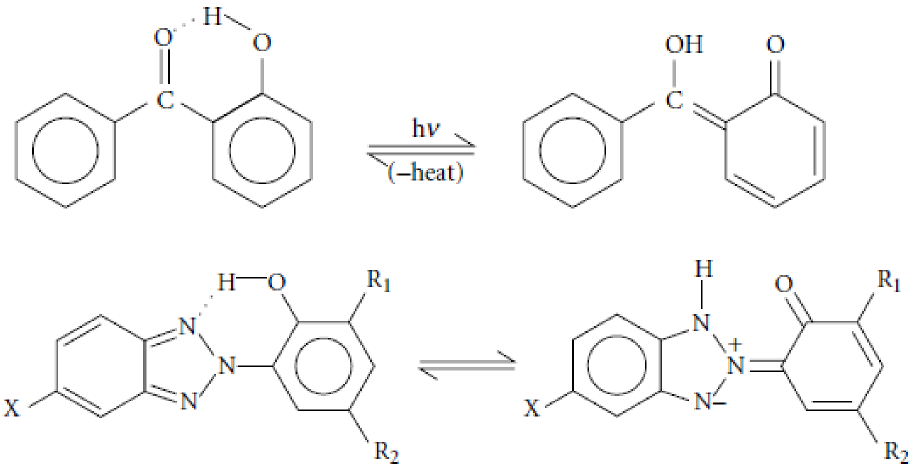
  - critical in outdoor use

- protect with 광안정제 by
  - preventing UV absorption ← UV absorber
  - deactivation of initiation ← ‘quencher’
  - decomposing ROOH ~ same to AO
  - scavenging radical ~ same to AO

- UV absorber
  - hydroxybenzophenones, hydroxyphenyl benzotriazoles



    - R determines ~~absorption wavelength~~ compatibility
    - UV energy consumed by reaction, (and not produce •)



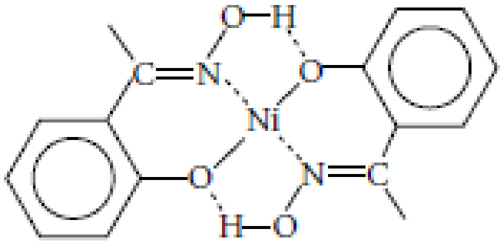
- quencher [Q]
  - takes over energy from K*
    - K ~ chromophore
    - by ‘Forster mechanism’
  - then, release energy
    - by heat or fluorescence
  - metal [Ni or Co] - phenol complexes

eqn 1.128-131

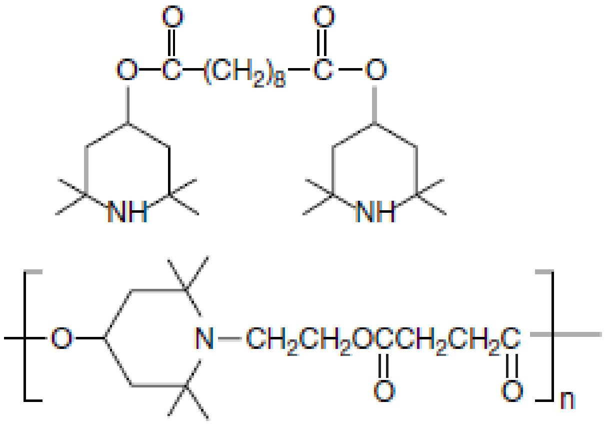
$K + h\nu \rightarrow K^*$

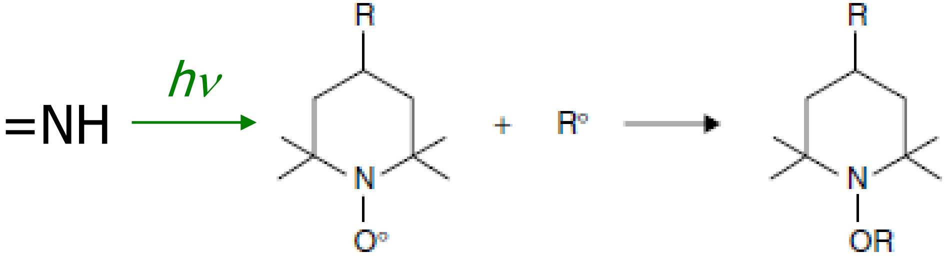
$K^* + Q \rightarrow K + Q^*$

$Q^* \rightarrow Q + \text{heat or } h\nu'$

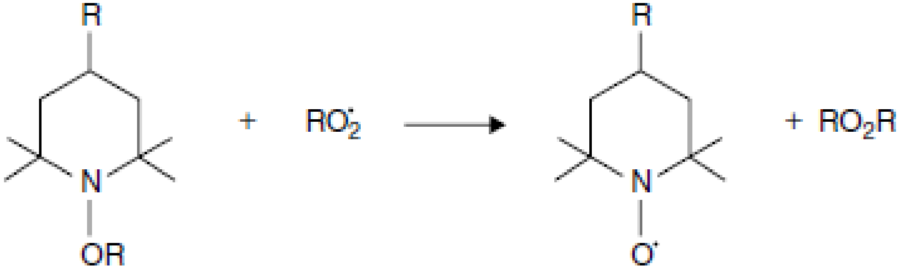


- carbon black
  - sometimes useful
- HALS
  - hindered amine light stabilizer
  - very effective
  - stabilize by 'Denisov cycle'



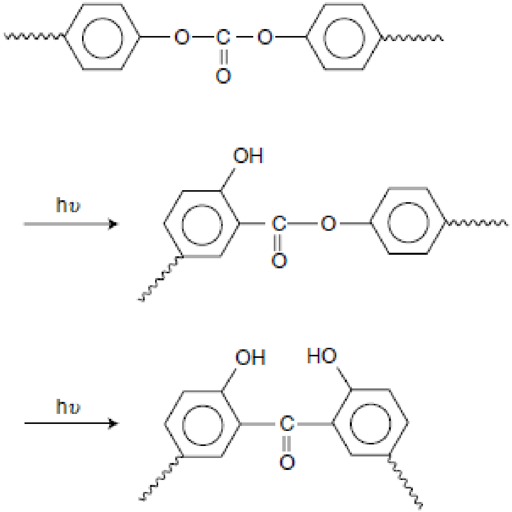


eqn (1.136)



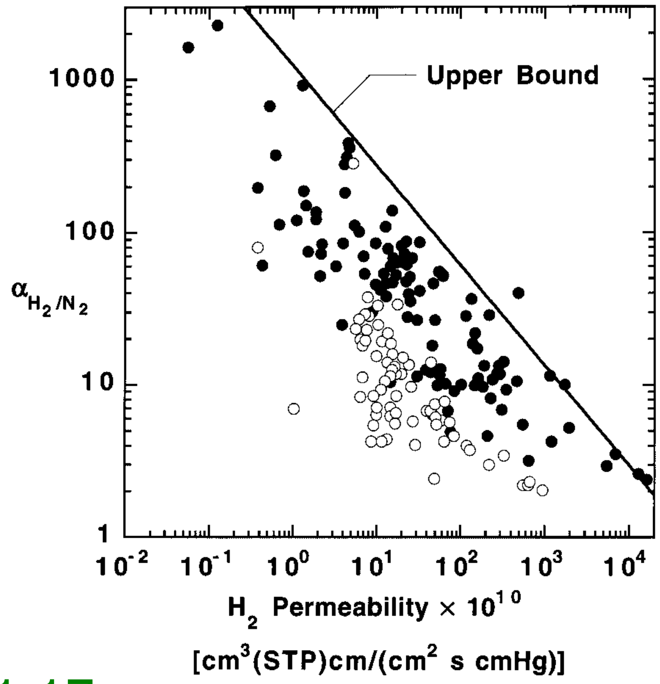
eqn (1.137)

- UV stabilizers for polymers pp128-131
  - polyolefins ~ UV absorber + Ni quencher used; HALS more effective
  - styrenics ~ HIPS and ABS for indoor use only; UV absorber + HALS can be used for outdoor use
  - PVC ~ UV absorber for outdoor; HALS not effective
  - PC ~ yellowing; UV absorber effective
  - PMMA ~ more stable [transparent]; absorber and HALS effective
  - polyacetal ~ unstable; carbon black; absorber/HALS
  - PU ~ aliphatic DI/ester diol stable; HALS effective



Diffusion and permeability

- important in
  - processing ~ plastisol, casting, lubrication
  - usage ~ membrane (selectivity), packaging (barrier)
- diffusivity
  - size of gas (and liquid)
  - state of polymer ~ Xtallinity, T_g
- permeability
  - absorption-diffusion-desorption
  - $P = D\ S$ Table 1.17
  - $P = F_{polymer}\ G_{gas}\ H_{p\text{-}g}$ Table 1.18
    - G ~ size, bp, polarity
  - permeability and selectivity Table 1.17
    - trade-off between P and α



Compounding

= mixing polymer with other ingredients

  - stabilizers
  - modifiers

- fillers [충진제]
  - for reinforcing [보강제] a/o cost
  - organic or inorganic
  - fibrous [FRP] or particulate
  - macro-, micro-, or nano-composite
  - Table 1.19-20

Plasticizers [가소제]

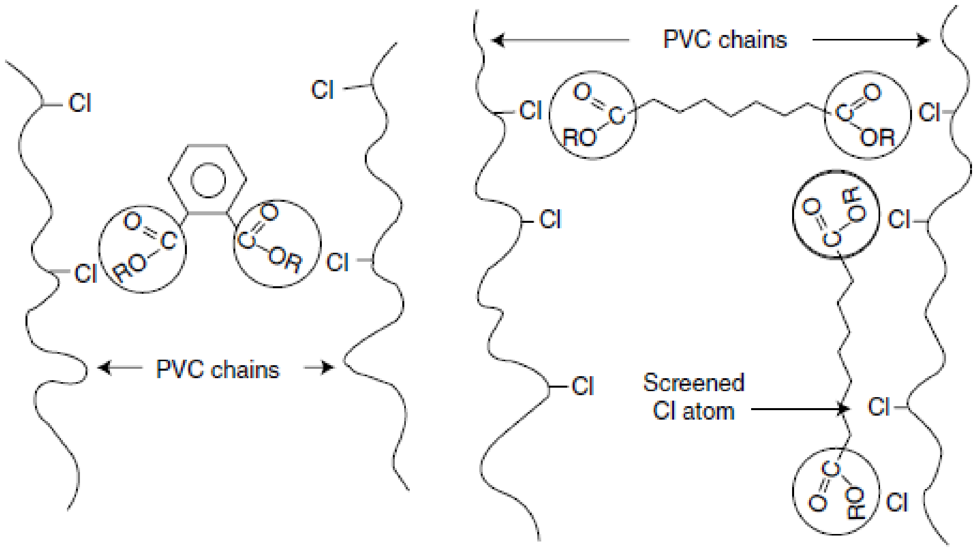
= organic or polymeric compound

- to improve flexibility and/or processability
- to lower T_g a/o ductile-brittle transition temp

- primary vs secondary plasticizer
  - primary ~ fully miscible with polymer
  - secondary plasticizer
    - partially miscible to polymer, miscible to 1° plasticizer
    - used with primary plasticizer
    - extender plasticizer, internal lubricant
    - to optimize cost, viscosity and processability
    - chlorinated HC, linseed oil

- most extensively used for PVC
  - UPVC ~ T_g = 80 °C
  - two categories
    - solvent-type ~ aromatic, easy gelation
    - oil-type ~ aliphatic, screening, cold-resistant
    - in practice, intermediate betw the two ~ DOP, DBP etc

plasticizers =
environmental hormones

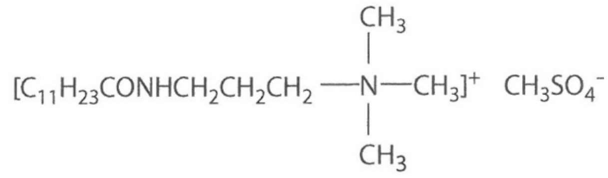


- choice of plasticizer
  - solubility parameter ~ not too far, not too close
- popular plasticizers
  - phthalates ~ DOP, DDP, ---
  - phosphates ~ TCP, TOP, ---
  - fatty acid esters ~ sebacates, adipates, ---
  - polymeric ~ oligomeric; polymeric
  - HC and Cl-HC ~ extenders
- antiplasticizer

Antistatic agents

- Polymers are insulators.
  - low surface conductivity → build-up of static [frictional] electricity → shock, dust, clinging
- AA ~ conducting or hygroscopic compounds
- external vs internal
  - external ~ applied on the surface
  - internal ~ compounded during or before processing
    - has to be migrated to the surface ~ partial miscibility
- ionic vs non-ionic
  - ionic ~ N, S, or P compounds
  - non-ionic ~ organic-OH

p144-146



$$[C_{11}H_{23}CONHCH_2CH_2CH_2-\overset{CH_3}{\underset{CH_3}{N}}-CH_3]^+ \quad CH_3SO_4^-$$

Flame retardants

- burning
  - pyrolysis → combustible gas + char
  - combustion → heat
- flame retardants Appendix A3
- halogen comp'ds
  - halogenated HC, --- ~ releasing HX
  - HX stop radical chain reaction and block oxygen

$$\text{Inhibition} \quad HO^{\cdot} + HBr = H_2O + Br^{\cdot}$$

  - efficiency ~ dep on C-X bond strength

Aliphatic bromides > aliphatic chlorides = aromatic bromides > aromatic chlorides

  - not for indoor use

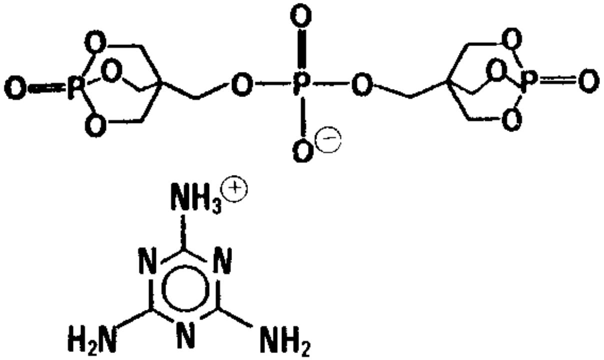
- P comp'd
  - carbonization [charring] + forming protective layer
    - by the reaction with polymer
    - more effective for polar polymers, less for POs
  - phosphates, phosphites, ---
  - sometimes (for non-polar) with halogenated HC + Sb_2O_3 ~ synergistic
- X/Sb mixture
  - Sb_2O_3 as a synergist
  - reduces the amount of halogen

$$Sb_2O_3 + 2HCl \rightarrow 2SbOCl + H_2O$$

- inorganics
  - MDH, ATH, --

$$2\mathrm{Al(OH)_3} \rightarrow \mathrm{Al_2O_3} + 3\mathrm{H_2O}$$

  - nanoclays, layered double hydroxide [LDH]
    - layering in the char
- intumescent
  - forming gas ~ H_2O, NH_3
  - helps carbonization



Smoke suppressants

- smoke
  - polymer as a fuel → CO and black smoke
  - small in PO, depolymerization polymers
  - large in PVC, aromatic polymers
- SS
  - inducing crosslinking (→ char) ~ Mo, Zn comp'd

$$2ZnO.3B_2O_3 + 12HCl \rightarrow Zn(OH)Cl + ZnCl_2 + BCl_3 + 3HBO_2 + 4H_2O$$

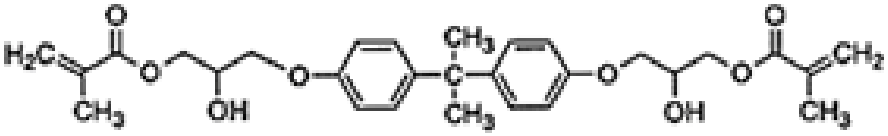
    - $ZnCl_2$ ~ a Lewis acid ~ catalyst of Friedel-Craft alkylation
  - producing H_2O ~ ATH
    - SS awa FR

Antimicrobials

- has to be migrated onto the surface
- protective or biocidal
- types
  - organics or organometallics
    - some toxic
    - some leaching out
  - inorganics
    - metals [Ag, Zn, Ti, ---] on substrates [zeolites, silica, ---]
    - not toxic
    - long-lasting

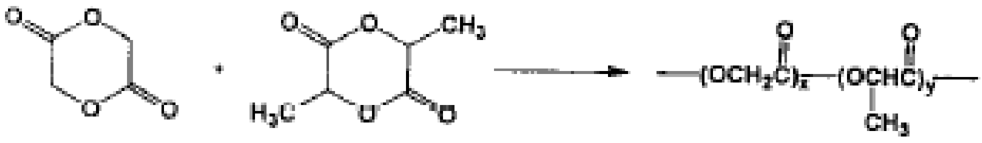
Toxicity

- Most polymers are <u>not</u> toxic.
  - Residual monomers, catalysts, and additives may be toxic.
- biomedical polymers
  - packaging, tubing, bags ~ PE, PP are OK; PVC
  - implants ~ epoxy, PU, silicone
  - adhesives ~ cyanoacrylates; butyl, octyl, not methyl
  - dental materials ~ bis-GMA



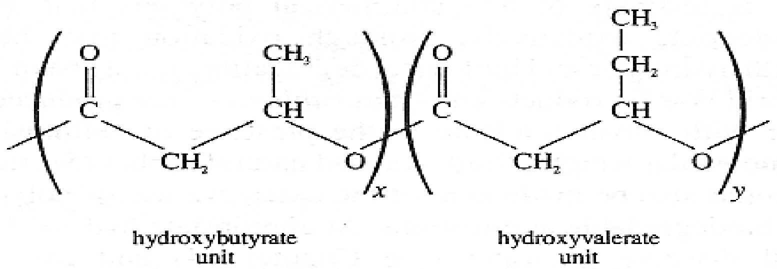
  - nanomedicine
  - drug delivery

- biodegradable polymers
  - in medicine [sutures, scaffolds, DDS] ~ PLA, PGA, PGL



글리콜라이드 락타이드

  - in waste
    - PHV, PHB, PBV



    - oxo-(bio)degradation
      - adding degradent ~ programmed degradation
      - complete degradation to H_2O + CO_2