Atmosphere and dose effects on the irradiation at high LET of polystyrene

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DE LA RECHERCHE À L'INDUSTRIE

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Introduction & context

- Polystyrene
  - Very resistant under irradiation
  - Radiation protection conferred by the side-chain aromatic ring
  - Phenomenon assigned to “sponge-type” mechanism
    - Energy dispersion by conjugated double bonds delocalization

- LET effect on G_0 from PS irradiated under inert atmosphere/vacuum
  - LET ↗ <=> radiation resistance ↘

- Literature
  - Polymer studied at different LET but always at low doses
  - No study on the atmosphere & dose effects ?

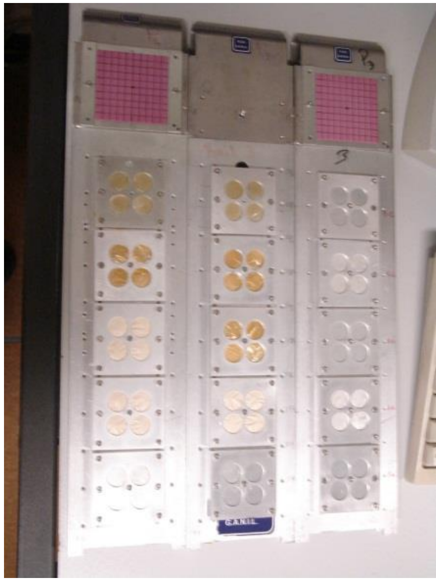
Influence of radiation-induced defects accumulation?

Influence of reactions with oxygen?

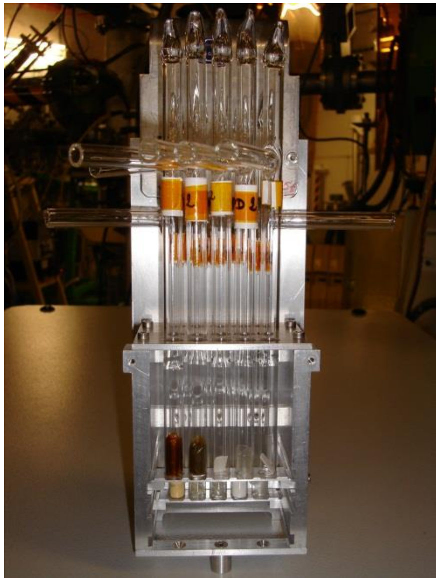
Schoepfle & Fellows, *Ind. Eng. Chem.* 23 (1931), 1396
Alexander & Charlesby, *Proc. R. Soc. London, Ser. A* 230 (1955), 136
Chang & LaVerne, *J. Polym. Sci.: Part A: Polym. Chem.* 38 (2000),1656

Gas radiation chemical yields determination
A two steps irradiation

- Pre-ageing step in closed containers in large excess of gas
  - SME line of GANIL
    - ^{16}O ions irradiation ($E_i \approx 7$ MeV/A)
    - LET ~ 6.5 $MeV.mg^{-1}.cm^{-2}$
    - Atmosphere: nitrogen / oxygen
    - Doses : 2 – 4 – 10 MGy



- Second step in closed glass ampoules
  - HE line of GANIL to go through thin glass walls
    - ^{36}Ar ions irradiation ($E_i \approx 95$ MeV/A)
    - LET ~ 2.5 $MeV.mg^{-1}.cm^{-2}$
    - Atmosphere: helium / reconstituted air (with tracer)
    - Doses : 500 – 1000 kGy



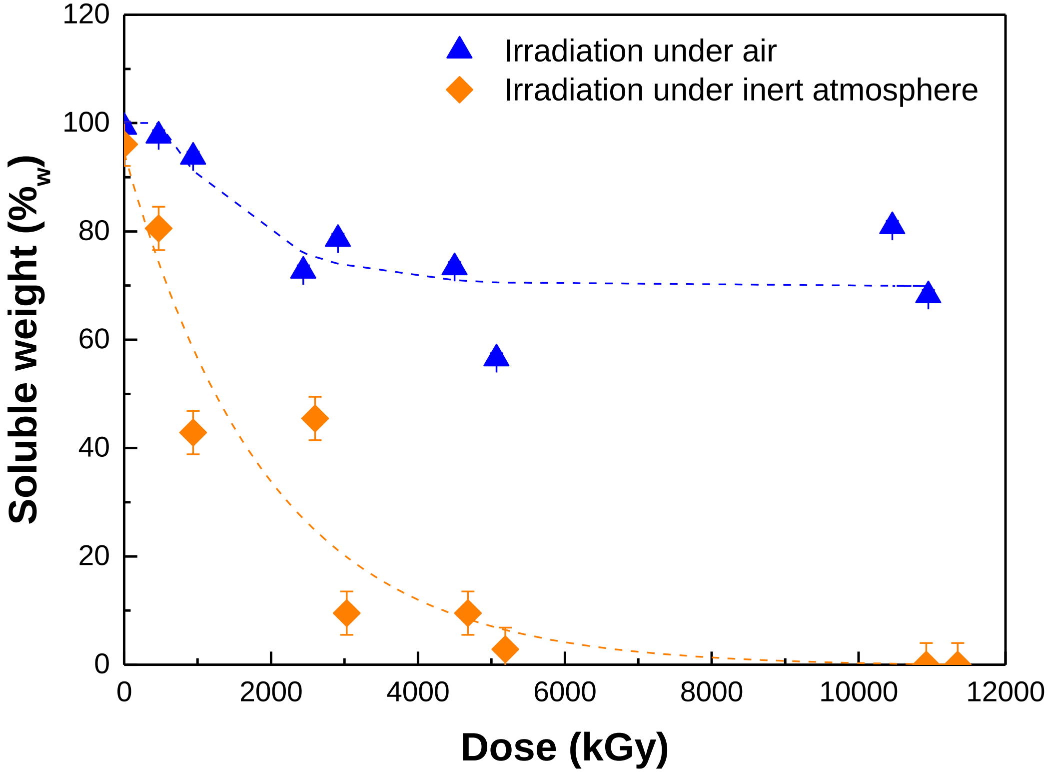
- Masses estimated to reach in closed containers
  - Final hydrogen content < 1 $\%_{vol}$ to avoid readdition
  - If present, final oxygen content > 10 $\%_{vol}$
    - To ensure homogeneous oxidation conditions

Results

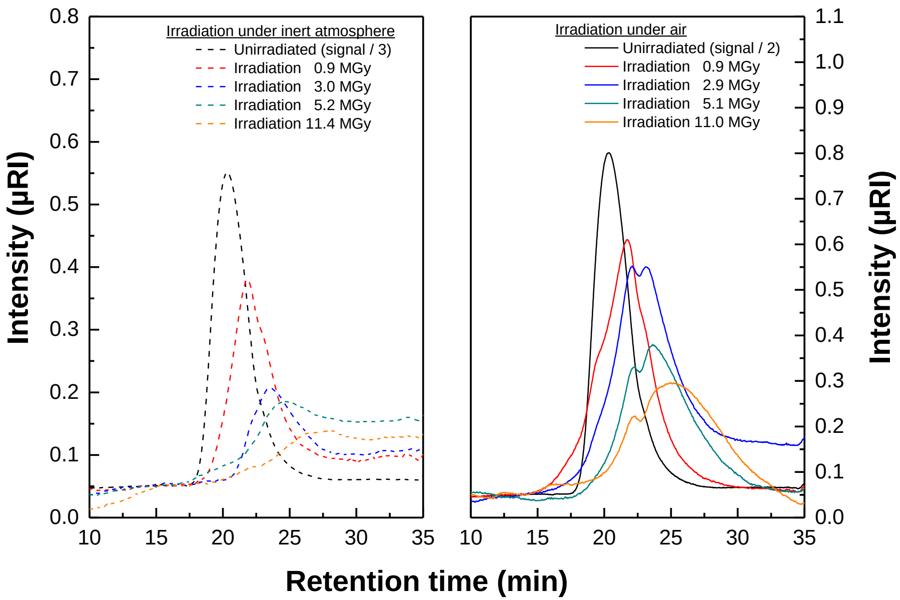
1. Crosslinking vs Scissions
2. Molecular evolution
3. Gas release

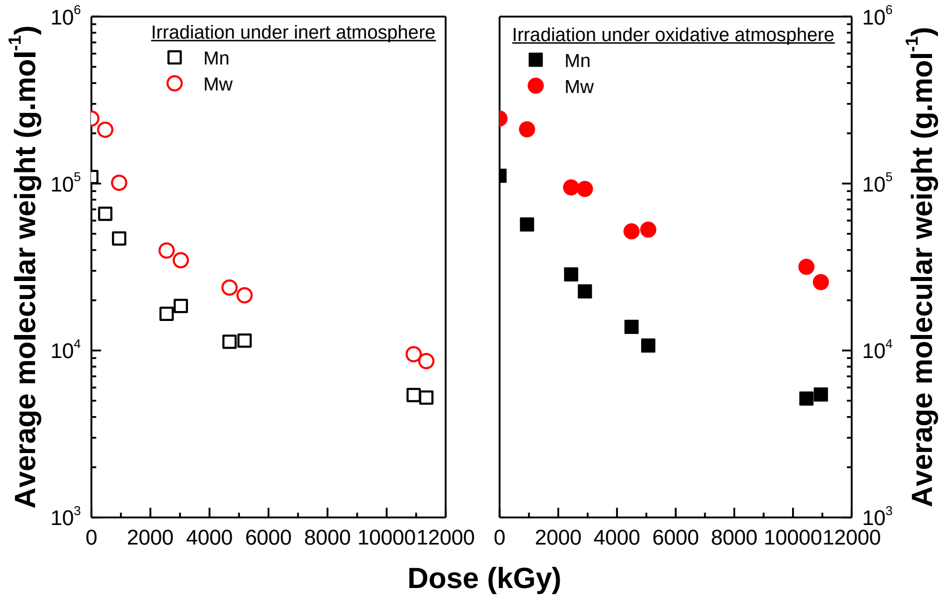
Materials evolution

Soluble fraction in THF



- Under inert atmosphere
  - Insoluble gel formation
  - Confirmation of crosslinking as the predominant mechanism
- Under oxidative atmosphere
  - Solubility remains important
  - Scission predominant mechanism





- Average molecular weights <u>*of the soluble fractions*</u>
- Under inert atmosphere, SEC peaks almost disappear at the highest doses
  - Confirmation of crosslinking as predominant mechanism
- At low doses, application of the Saito's equation
  - Under inert atmosphere: a part of polymer already insoluble
    - Saito's equation hypothesis not verified
      => Results given for information purposes only

Materials evolution

Scissions vs crosslinking

	G(X) (10^{-7} mol.J^{-1})	G(S) (10^{-7} mol.J^{-1})	G(S) / 4 G(X)
Oxidative atmosphere	0.02	0.12	1.5
Inert atmosphere	~~0.03~~	~~0.16~~	-
Inert atmosphere / Literature	0.03	0.02	0.17

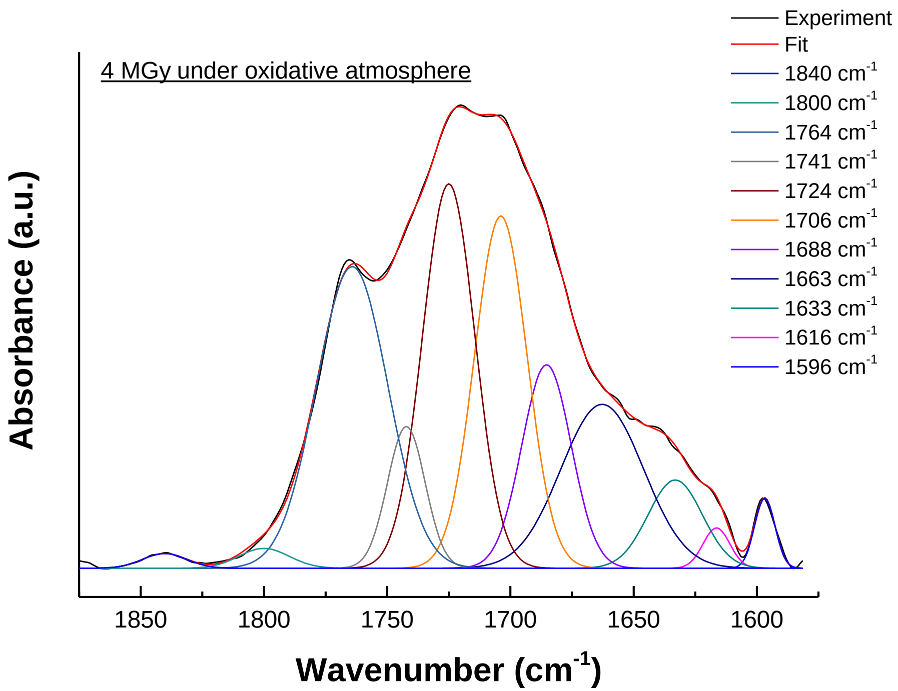
- Under inert atmosphere
  - From literature : G(S) << 4 * G(X)
    => Predominant mechanism: *crosslinking*
  - Insoluble fraction already formed at low doses
    => G(S) overestimated (about one order of magnitude)

- Under oxidative atmosphere
  - This work: G(S) > 4 * G(X)
    => Predominant mechanism: *chain scissions*

Saito, *Statistical theories of crosslinking*, Academic Press (1972)

Materials evolution

Deconvolution of the FTIR massif (C=O area)



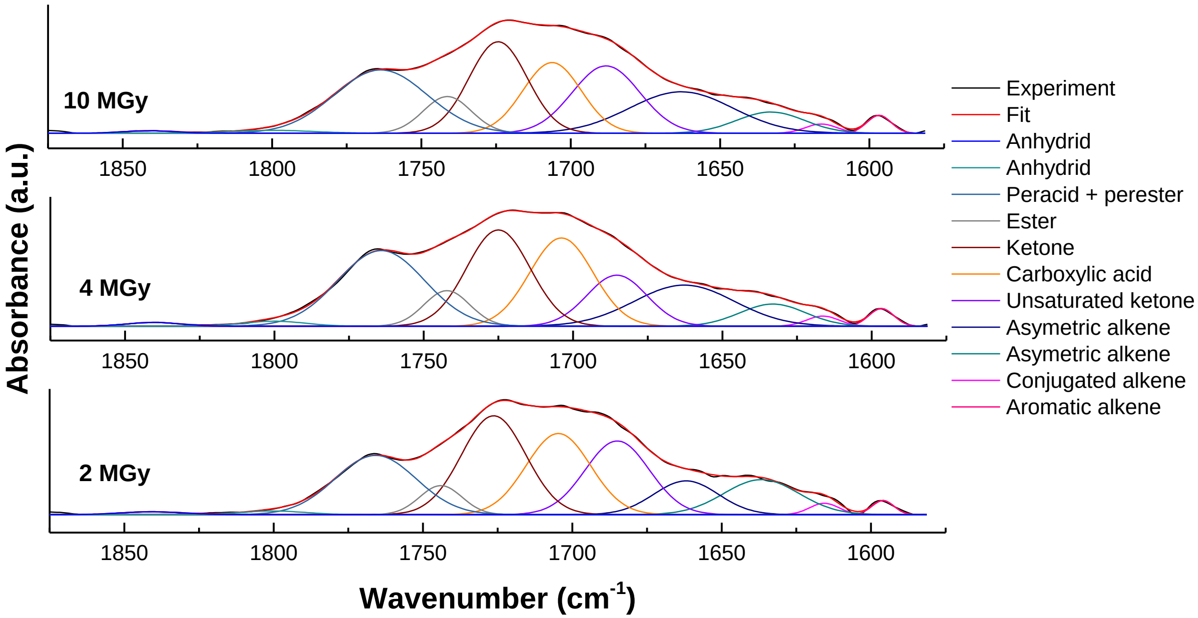
Wavenumber (cm^{-1})	Attribution
1840	Anhydrid
1800	Anhydrid
1764	Peracid + perester
1741	Ester
1724	Ketone
1706	Carboxylic acid
1688	Conjugated ketone
1663	Asymetric alkene
1633	Asymetric alkene
1616	Conjugated alkene
1596	Aromatic alkene

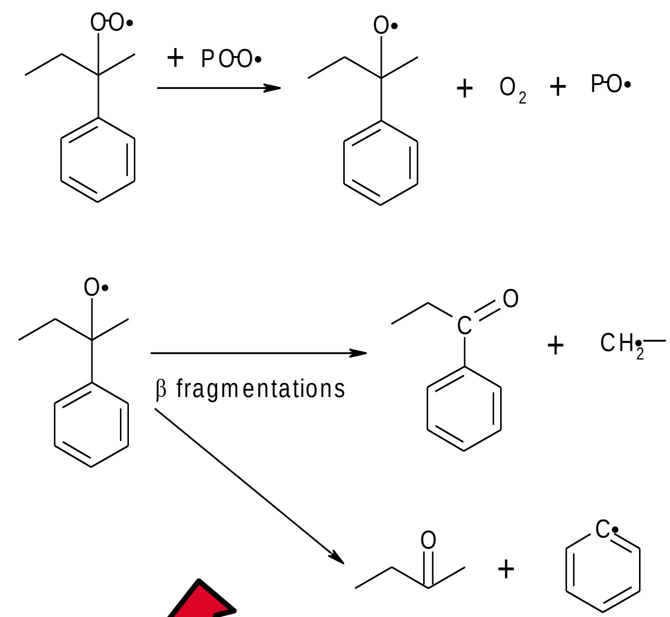
ATR mode infrared spectra with subtraction of the pristine PS spectrum

Liang & Krimm, *J. Polym. Sci.* 27 (1958), 241
Luongo, *J. Polym. Sci.* 42 (1960), 139
Ngono-Ravache et al., *Polym. Deg. Stab.* 111 (2015), 89

Materials evolution

At a molecular level



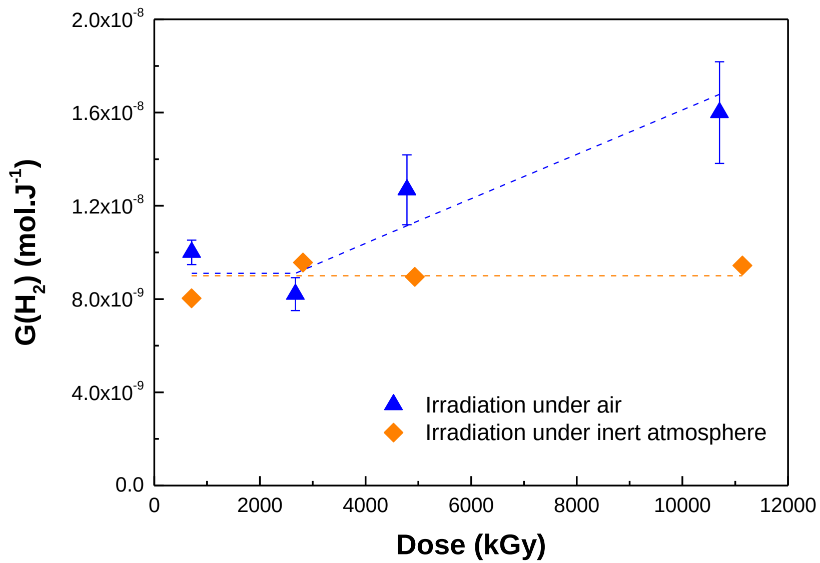


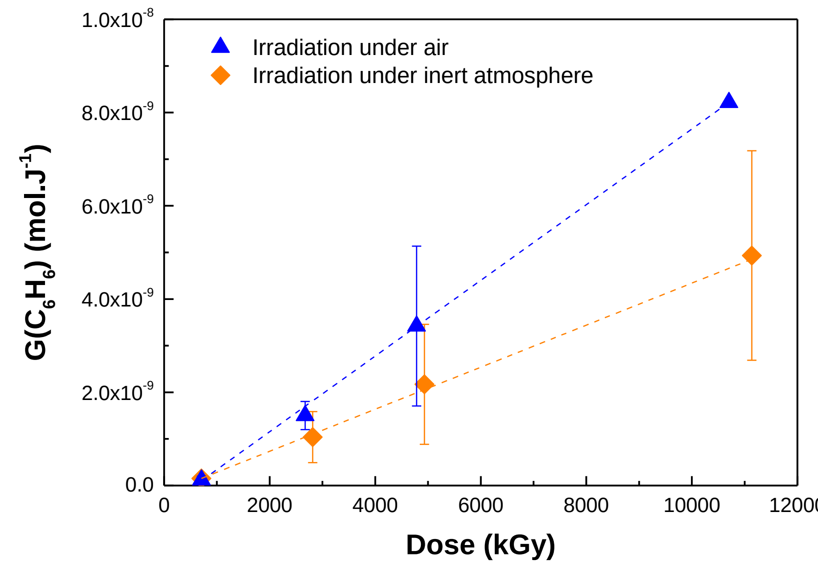
- No dose threshold
  - Defects probably equivalent under low LET ionizing rays and SHI
- Very important ketone contribution whatever D
  - Saturated ketones
  - Conjugated ketones

Cambon, PhD thesis, University of Clermont-Ferrand, France (2001)

Gases evolution

Hydrogen and benzene emission





- Under inert atmosphere
  - Hydrogen release ≈ and benzene release ↗
  - Energy transfers
    - Efficient in the dose range studied
    - At the expense of the side-chain

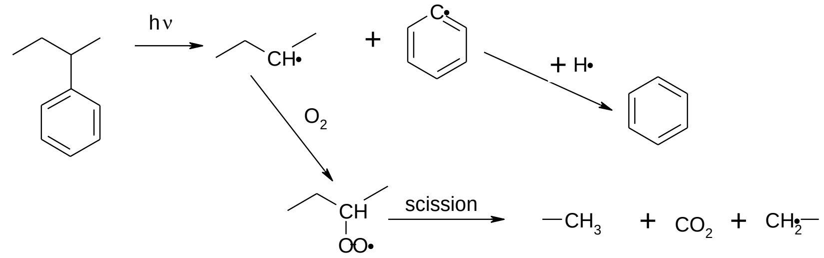
- Under oxidative atmosphere
  - Hydrogen release ↗ from 2 MGy : $G(H_2)_{ox} \sim 2 * G(H_2)_{inert}$ at 10 MGy
  - Benzene release ↗ 2 times faster
    - In-chain reactions strongly sensitize polystyrene
    - Oxygen ↘ radiation-induced protection: attack on the tertiary carbon

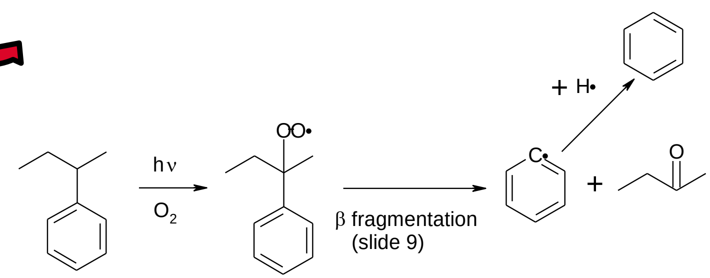
Gases evolution

Oxidized specific gases

From benzene release

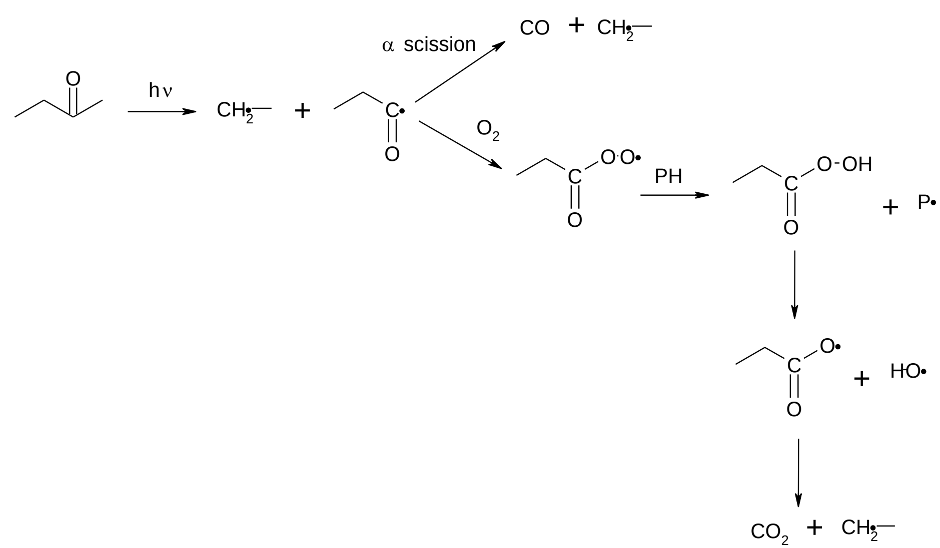
From literature

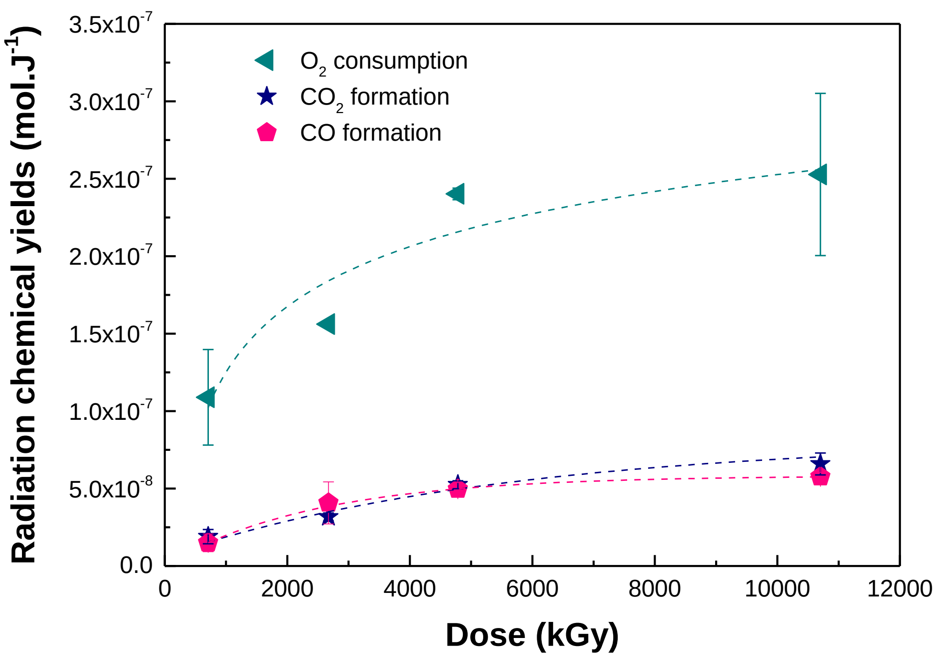




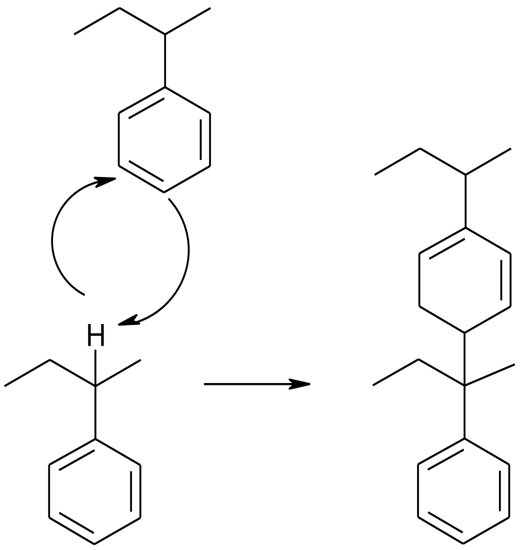
Rabek, Photodegradation of Polymers, *Physical Characteristics and Applications*, Springer (1996), 60

Matsuo & Dole, *J. Phys. Chem.* 63 (1959),837





Conclusion



- Under inert atmosphere: *crosslinking*
  - Via the aromatic ring, *i.e.* without loss of benzene / conjugated C=C
  - No hydrogen release
  - Protection active up to high doses (10 MGy)

- Under oxidative atmosphere: *scissions*
  - Radical's formation on the tertiary carbon
    - Subsequent O_2 consumption and in-chain oxidation reactions
    - Loss of benzene => loss of radiation protection

      Preliminary mechanism to be completed
  - Loss of radiation protection begins at lower doses (2 MGy)
    - Atmosphere is of high importance to evaluate the loss of radiation protection with dose ↗

Puglisi et al., *Radiat. Eff. Defects Solids* 98 (1986), 161

Thank you for your attention