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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M. Ferry[1], M. Cornaton[1], D. Durand[1], V. Dauvois[1], S. Esnouf[1], J.L. Roujou[1], C. Aymes-Chodur[2] and Y. Ngono-Ravache[3]

[1] Den-Service d'Étude du Comportement des Radionucléides (SECR), CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France.
[2] Université Paris-Sud, SM2B/ICMMO, UMR CNRS 8182, F-91405, Orsay, France.
[3] CIMAP (CEA/CNRS/ENSICaen/UNICaen), CIMAP site GANIL, Caen, France.

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 ?

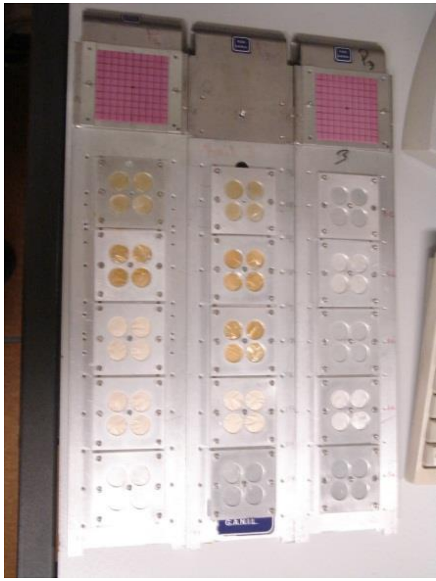
Influence of radiation-induced defects accumulation?

Influence of reactions with oxygen?

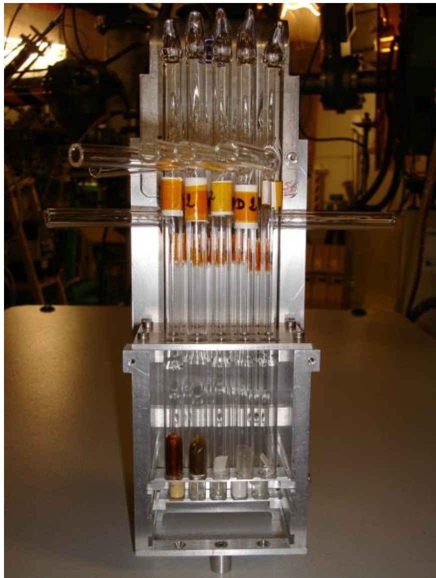
Schoepfle & Fellows, *Ind. Eng. Chem.* 23 (1931), 1396
Alexander & Charlesby, *Proc. R. Soc. London, Ser. A* 230 (1955), 136
Chang & LaVerne, *J. Polym. Sci.: Part A: Polym. Chem.* 38 (2000),1656

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



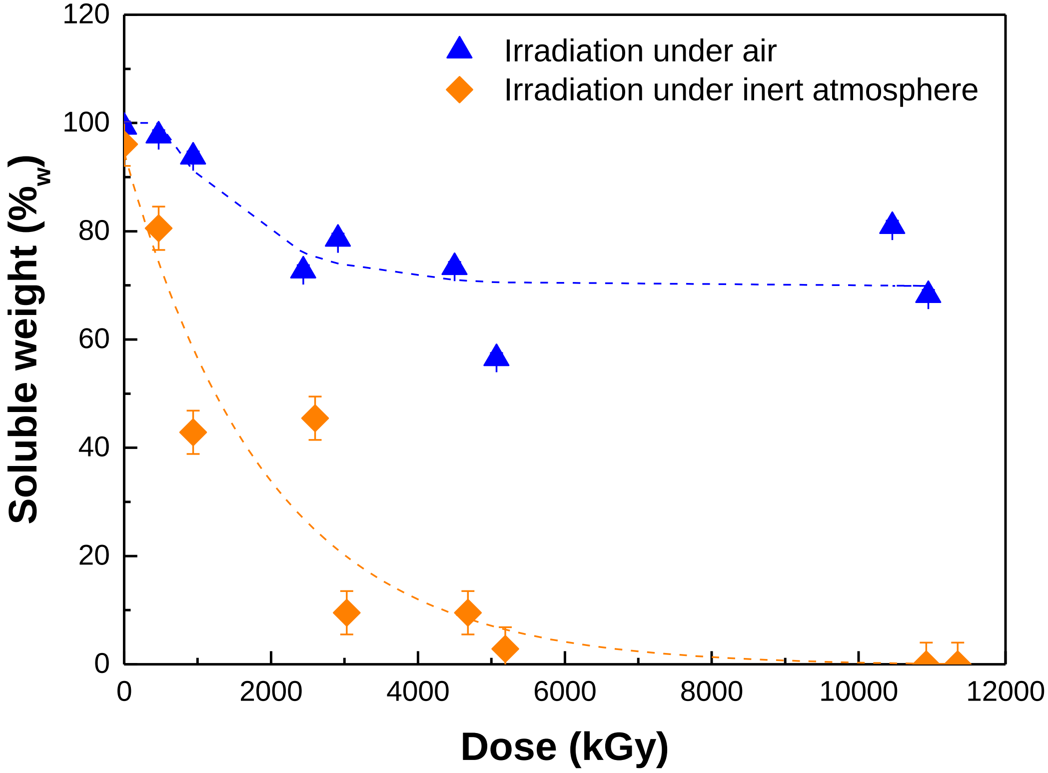
- Masses estimated to reach in closed containers
  - Final hydrogen content < 1 $\%_{vol}$ to avoid readdition
  - If present, final oxygen content > 10 $\%_{vol}$
    - To ensure homogeneous oxidation conditions

Results

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

Materials evolution

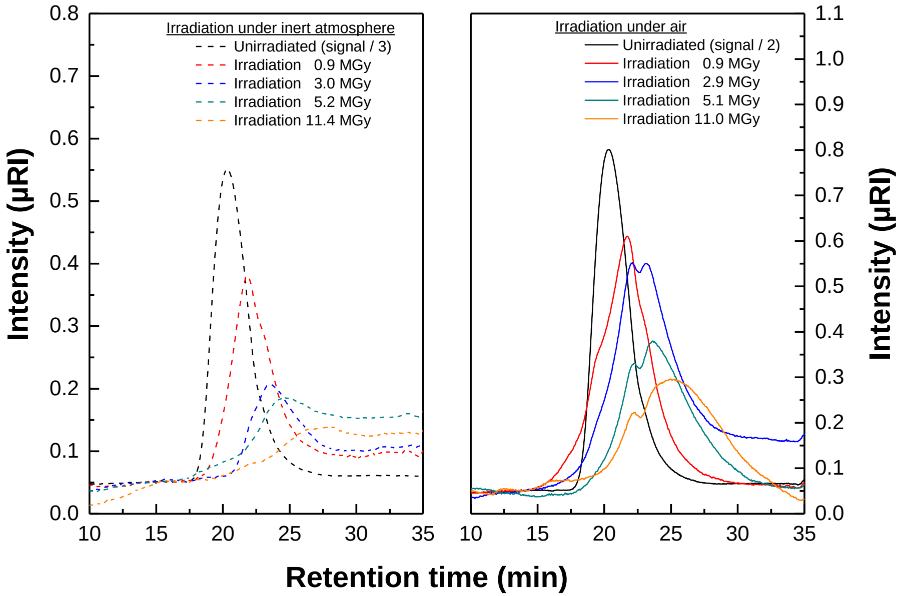
Soluble fraction in THF

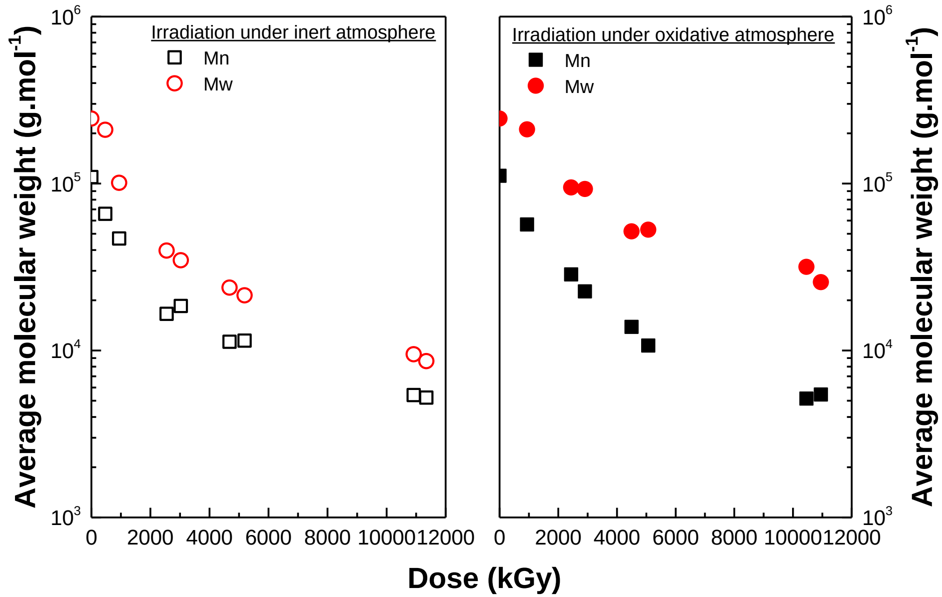


- Under inert atmosphere
  - Insoluble gel formation
  - Confirmation of crosslinking as the predominant mechanism
- Under oxidative atmosphere
  - Solubility remains important
  - Scission predominant mechanism

Materials evolution

Average Molecular Weights





- Average molecular weights *of the soluble fractions*
- 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

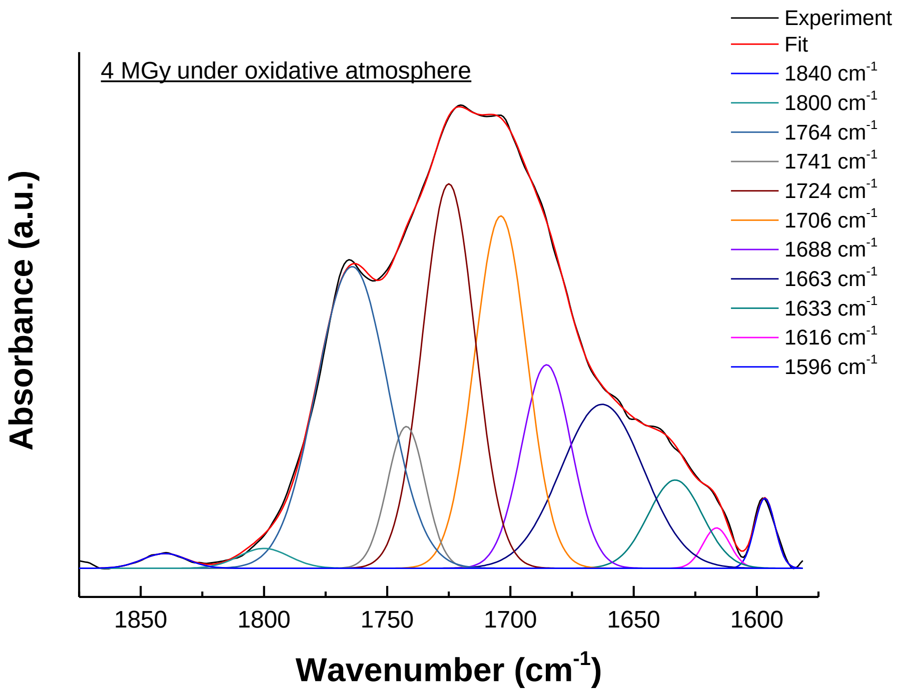
- Under inert atmosphere
  - From literature : G(S) << 4 * G(X)
    => Predominant mechanism: *crosslinking*
  - Insoluble fraction already formed at low doses
    => G(S) overestimated (about one order of magnitude)

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

<u>Saito</u>, *Statistical theories of crosslinking*, Academic Press (1972)

Materials evolution

Deconvolution of the FTIR massif (C=O area)

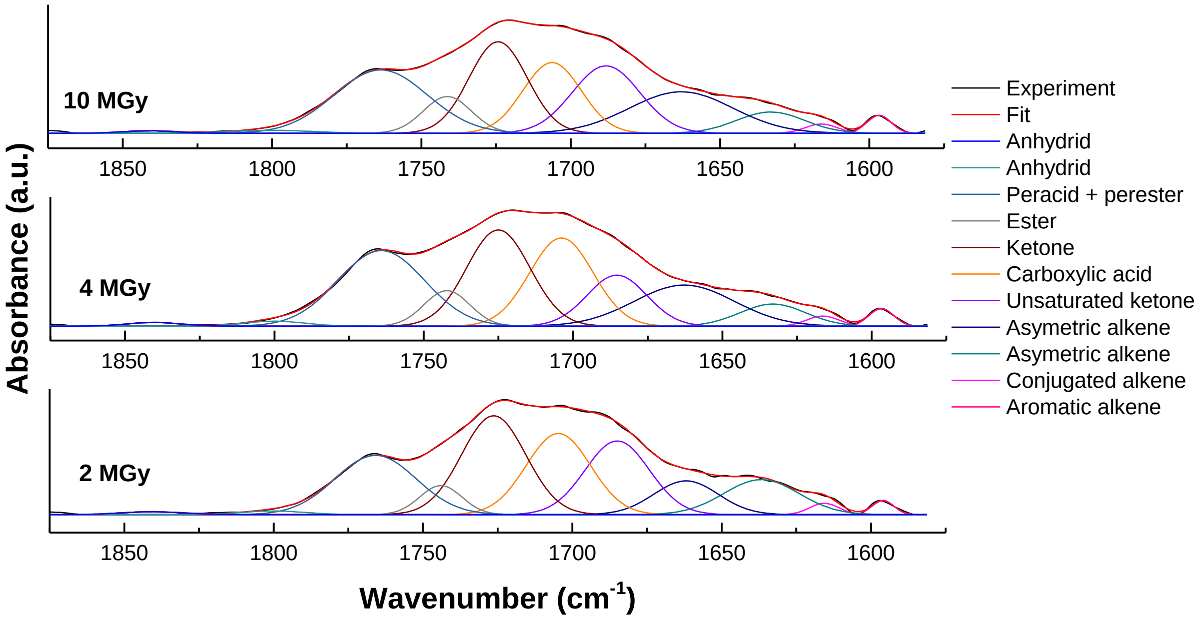


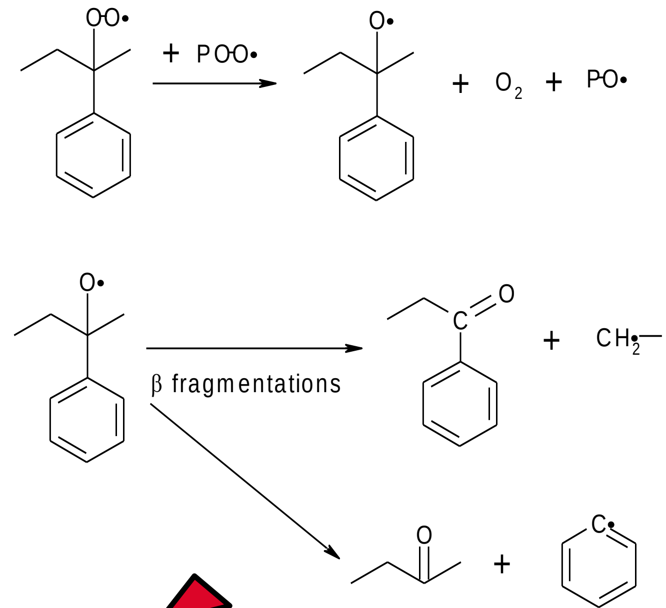
ATR mode infrared spectra with subtraction of the pristine PS spectrum

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

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



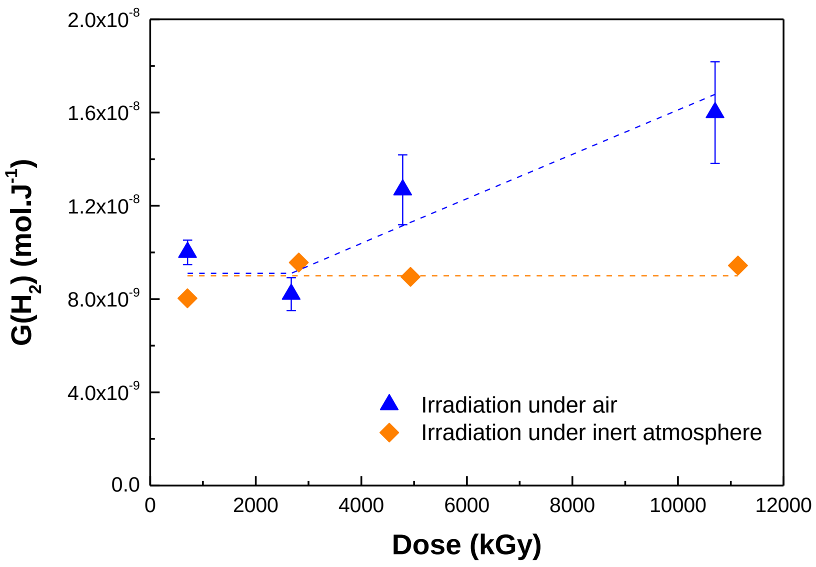


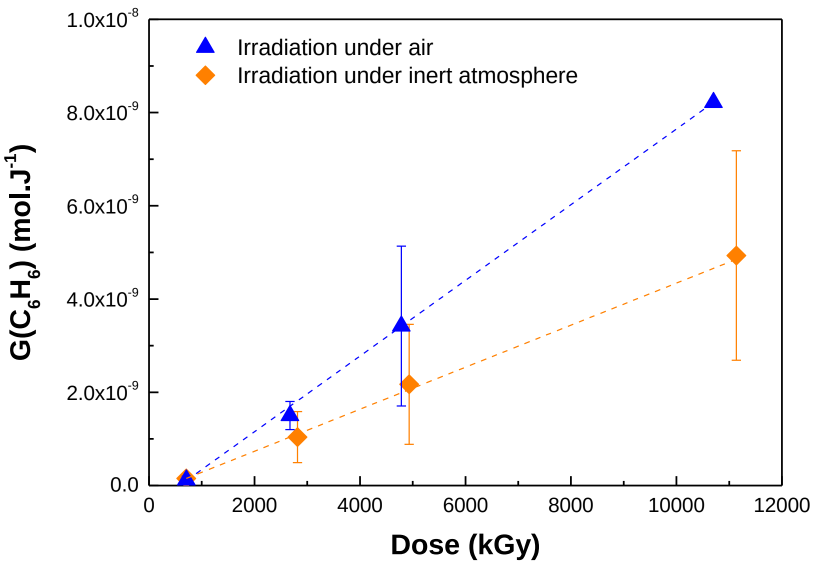
- No dose threshold
  - Defects probably equivalent under low LET ionizing rays and SHI
- Very important ketone contribution whatever D
  - Saturated ketones
  - Conjugated ketones

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

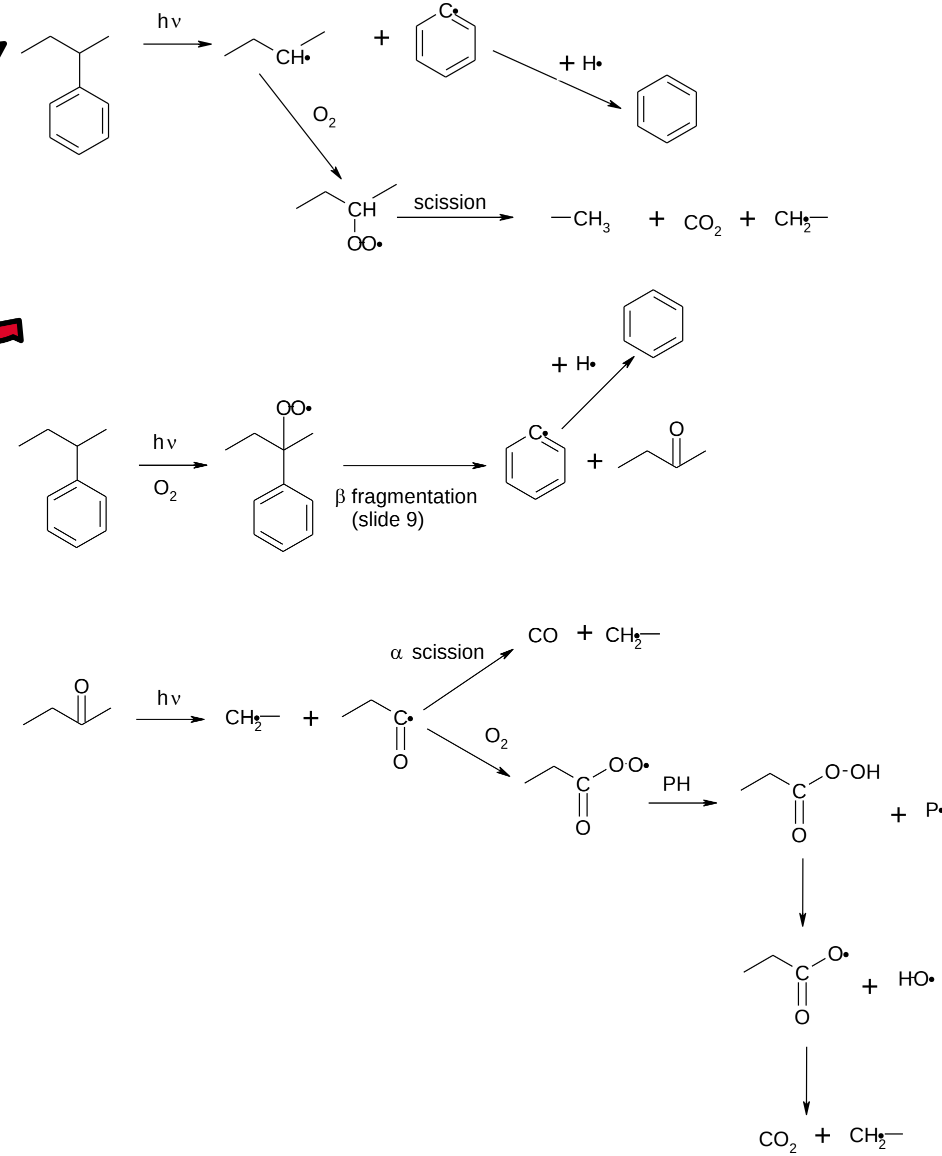
- Under oxidative atmosphere
  - Hydrogen release ↗ from 2 MGy : $G(H_2)_{ox} \sim 2 * G(H_2)_{inert}$ at 10 MGy
  - Benzene release ↗ 2 times faster
    - In-chain reactions strongly sensitize polystyrene
    - Oxygen ↘ radiation-induced protection: attack on the tertiary carbon

Gases evolution

Oxidized specific gases

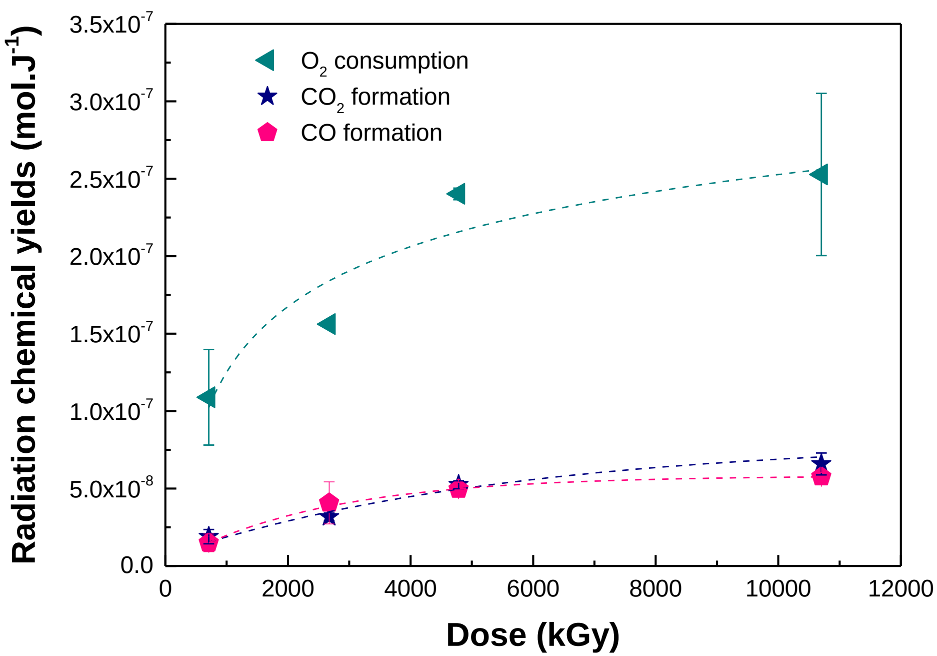
From benzene release

From literature

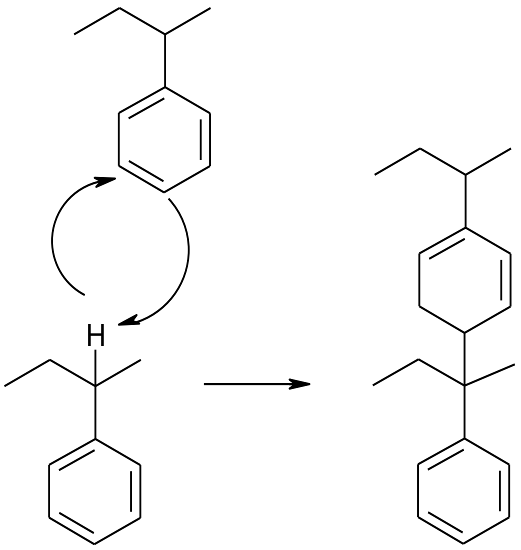


Rabek, Photodegradation of Polymers, *Physical Characteristics and Applications*, Springer (1996), 60

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