

Radiation Effects on Polymeric Systems

Crosslinking and Scission

- **Both crosslinking and scission occur on irradiation of polymers; however, their relative importance varies from polymer to polymer**

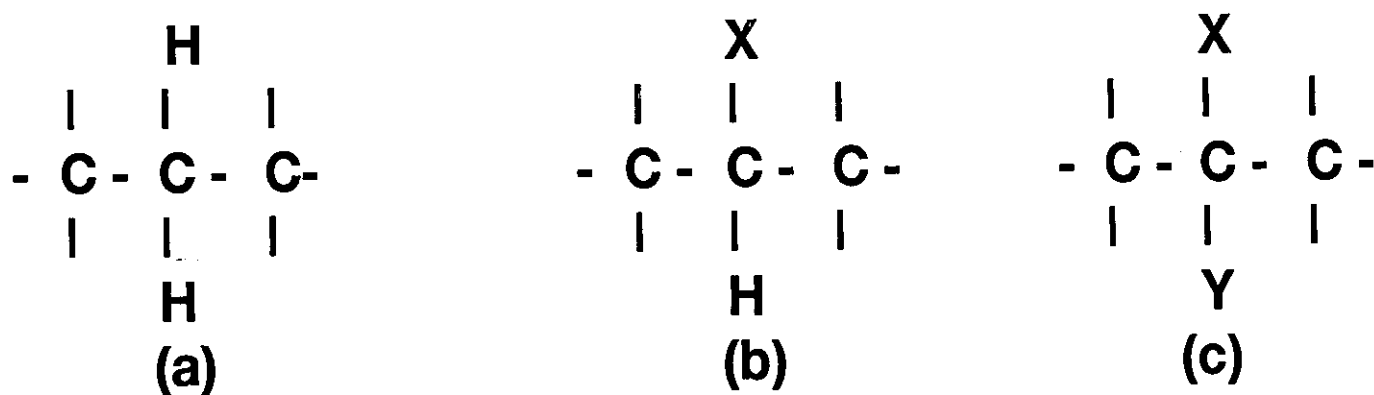
Predominant Processes in Irradiated Polymers

Crosslinking	Scission
<p>Polyethylene Polypropylene Polystyrene Polyacrylates Polyamides Polyesters Rubbers Polysiloxanes Polyacrolein Polymethylene Chlorinated polyethylene Polyacrylonitrile Polyethylene oxide</p>	<p>Polyisobutylene Poly-α-methylstyrene Polymethacrylates Polyvinylidene chloride Cellulose Cellulose acetate Polytetrafluoroethylene Polytrifluorochloroethylene Poly-α-methacrylonitrile Polyethylene terephthalate</p>

Polymer Structure

Crosslinking vs Scission

- As the hydrogen in the backbone of an organic polymer is replaced with heavier substituents, its tendency to crosslink decreases and its tendency to scission increases



X and Y, heavier than H, e.g., CH₃, Cl

Crosslinking a>b>c; Scission a<b<c

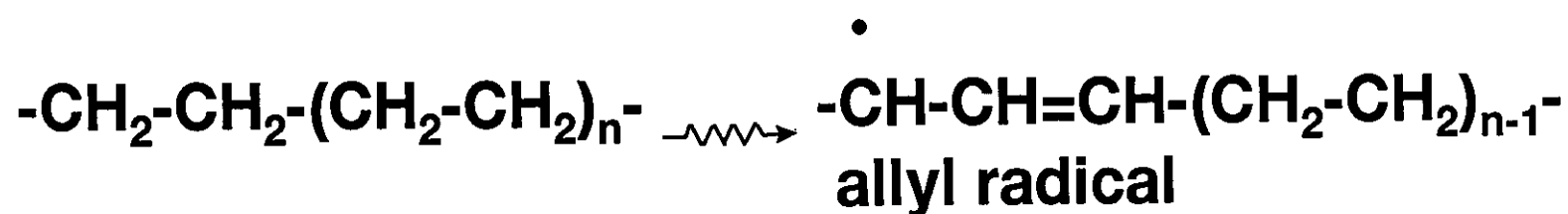
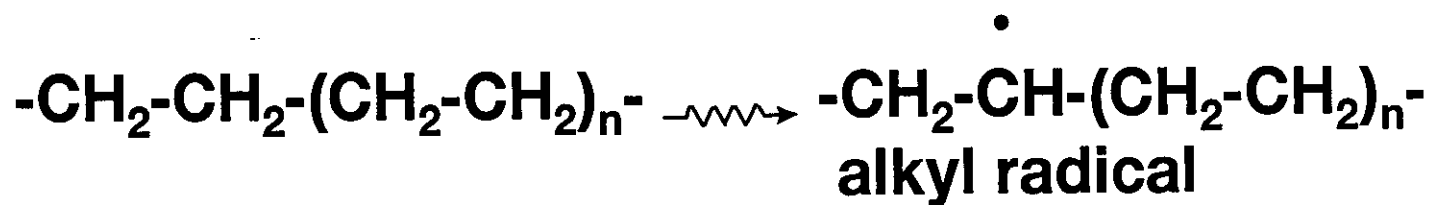
Yields of Gaseous Products from Irradiated Polymers^a

(γ - or electron irradi, room temp)

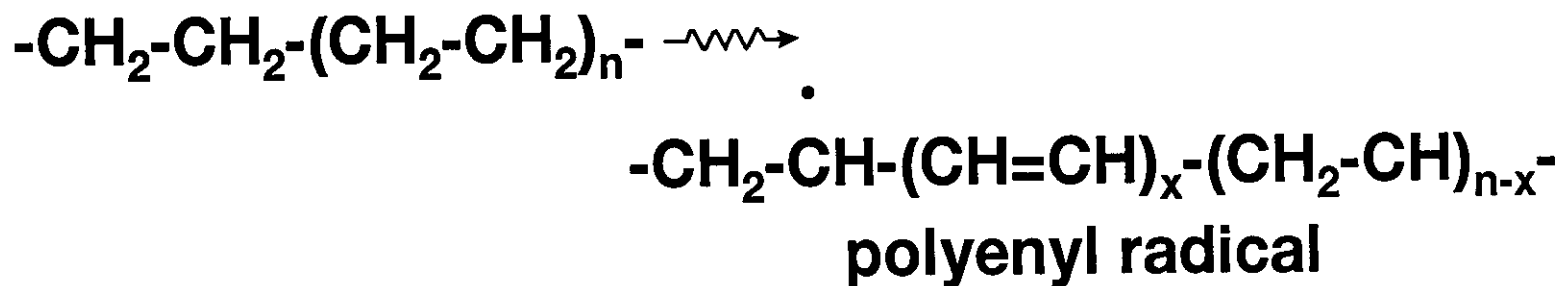
Polymer	Products G (product)(molecules/100 ev)
High-density PE	H ₂ ~3; CH ₄ ~0.002
Polypropylene	H ₂ ~2.5; CH ₄ ~0.1
Polyisobutylene	H ₂ ~1.5; CH ₄ ~0.5
Poly(vinyl chloride)	HCl ~2.7; H ₂ ~0.15; CH ₄ ~0.002
Poly(vinyl acetate)	H ₂ ~0.6; CH ₄ ~0.3; CO ~0.28; CO ₂ ~0.06
Poly(methyl methacrylate)	CH ₄ ~ 0.6; CO ~0.5; CO ₂ ~0.4; H ₂ ~0.2
Polystyrene	H ₂ ~0.03; CH ₄ ~ 1x10 ⁻⁵
Poly- α -methyl styrene	H ₂ ~0.04; CH ₄ ~0.003

^a Woods and Pikaev (1994)

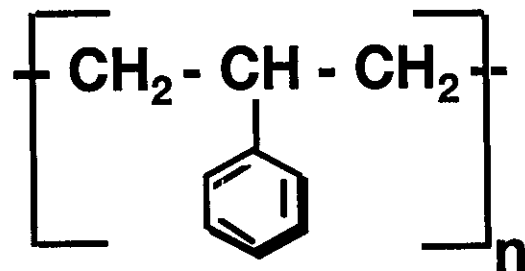
Free Radicals Formed on Irradiation of Polyethylene



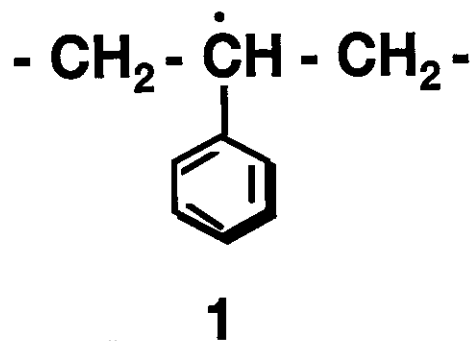
- At very high doses



Radiation Effect on Polystyrene

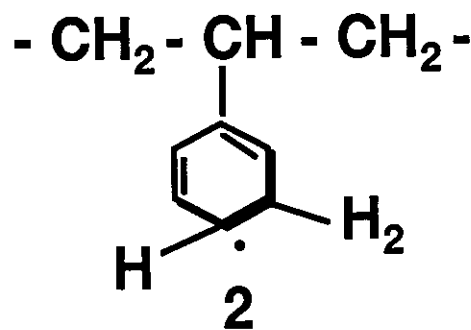


- Ions and radicals formed on irradiation
- Shows thermoluminescence on irradiation at -196°C and subsequent warming
- $G(\text{free radicals})$ low, ~ 0.2



Radiation stable in inert atmosphere

and

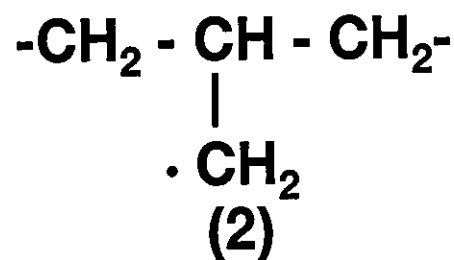
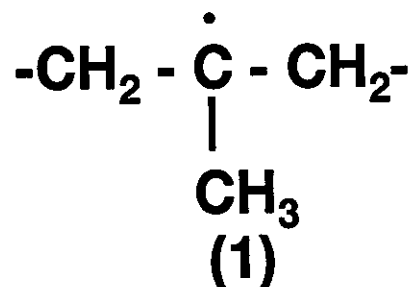


Radiation-induced oxidation in air

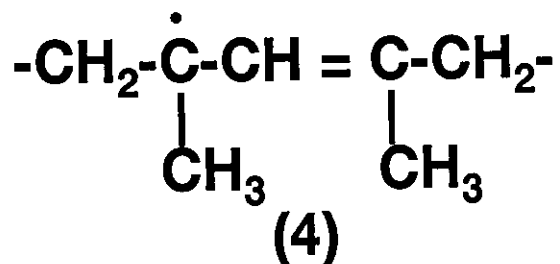
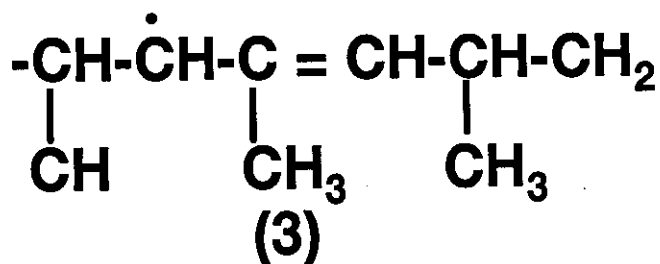
Radiation Effect on Polypropylene

- On irradiation, long-lived free radicals formed

Low temperature (-196°C)



Room temperature

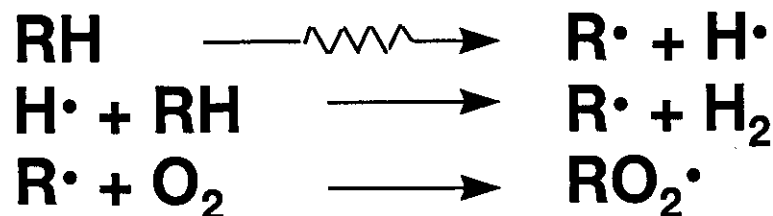


- Overall effect of irradiation: loss of mechanical strength

Dole (1973); Bradley (1984)

Chemical Basis of Oxidative Degradation

- **Initiation**



- **Crosslinking**

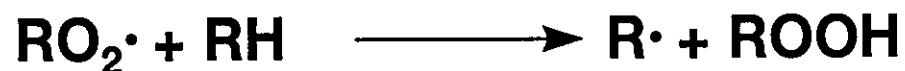


- **Degradation**

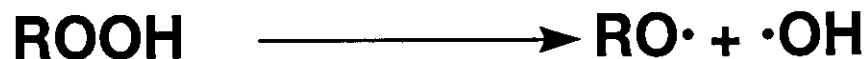


Propagation, Chain Reaction and Post-Irradiation Degradation of Polymers

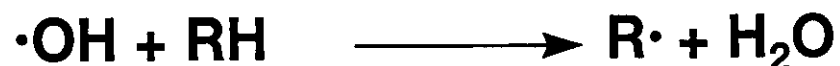
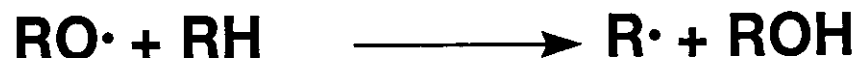
- Oxidative degradation of polymers reduces strength and flexibility, causes cracking, increases moisture uptake and degrades electrical insulation properties



Heat



Light

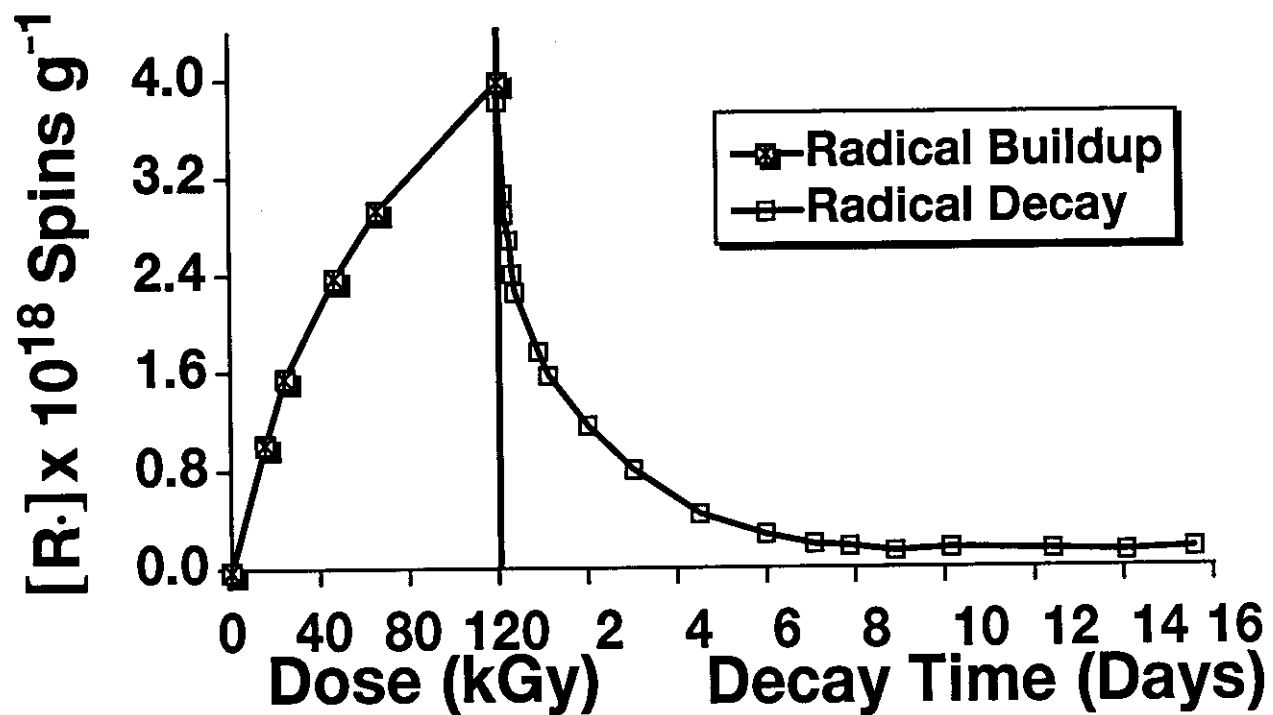


- Oxidative degradation usually continues for months after irradiation, e.g., initiated by the reactions of ROOH

Radiation Effects on Polyethylene

- **Known products on irradiation in air include H₂O, CO, CO₂, alcohols, ketones, hydroperoxides, peroxides and carboxylic acids**
- **Free radicals (alkyl and allyl) usually considered precursors of crosslinks**
- **Free radical migration from crystalline to amorphous regions**
- **Unsaturation in PE participates in crosslinking reactions**
- **Oxygen and additives excluded from the crystalline regions**
- **Roles of excited states and ionic reactions not well understood**

Radical Buildup and Decay in Gamma Irradiated Polypropylene in Air



Kashiwabara and Seguchi, 1992

Radiation-Induced Oxidation of Polymers

G-Value of Oxygen Consumption at Room Temperature under ~ 70 kPa Oxygen (Kashiwabara and Seguchi, 1992)

Polymer	Dose (kGy)	Dose Rate (kGy/h)	G(-O₂)
Low-density polyethylene	500-1000	10	14
High-density polyethylene	500-1000	10	18
Medium-density polyethylene	500-1000	10	18
Ethylene propylene rubber	100-500	2	8
Isotactic polypropylene	100-200	10	50
Polyvinyl chloride	100-200	10	29
Polyvinyl chloride (stabilized)	100-200	10	11

Polymer Degradation by Irradiation

- **Radiation degradation can be used to reduce the molecular weight of commercial polymers, e.g., polypropylene and polyethylene oxide**
 - **PP-vis-breaking, a patented process**
- **Teflon: scrap or waste Teflon is converted into useful powder and low MW products by irradiation (500 kGy), e.g., for producing lubricants and coated non-stick pans**

Effect of Additives

There are four main types of additives whose effect on irradiation of polymeric systems needs to be considered

- 1. Crosslinking agents: these are typically multifunctional monomers (such as di-and triacrylates) that reduce the dose required for crosslinking**
- 2. Degradation agents: primarily oxygen; it degrades polymers via the formation of peroxy radicals**
- 3. Protective agents: basically, there are two types of protectors- the anti-rads, which act as energy acceptors (such as pyrene and other aromatic hydrocarbons), and free radical scavengers or anti-oxidants, e.g., phenols, which protect the polymer via peroxy or carbon centred radical reactions**
- 4. Neutral additives: frequently, mineral powders or fibres are added to polymers; many of these have no effect on irradiation of polymers**

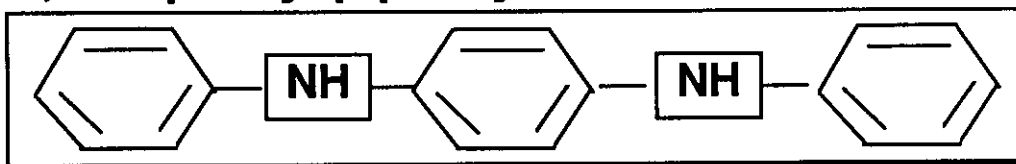
Chemical Formulae of Some Antioxidants (Kashiwabara and Seguchi, 1992)

Symbol

Name and formula

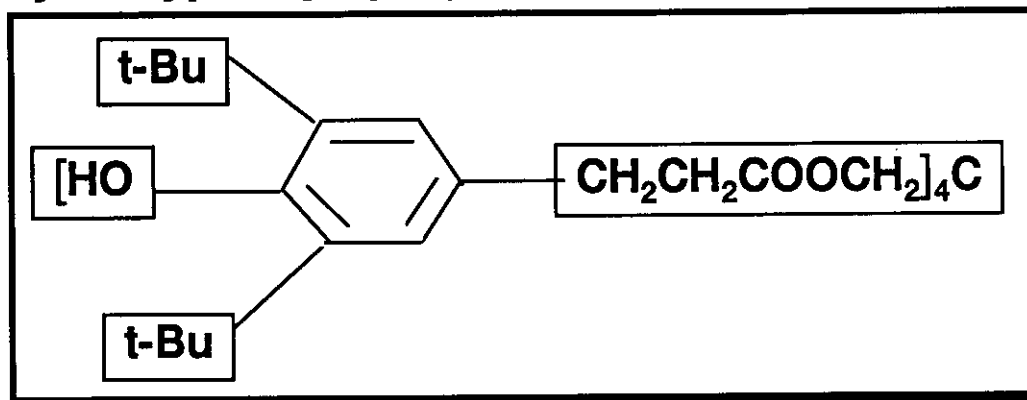
DPPD

N,N'-Diphenyl-p-phenylenediamine



Irganox 1010

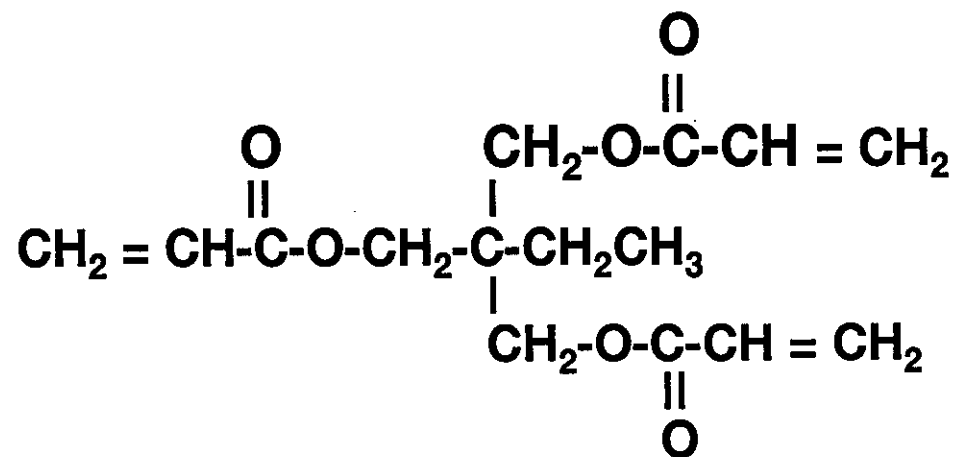
Tetrakis[methylene-3(3,5-di-t-butyl-4-hydroxyphenyl) propionate]methane



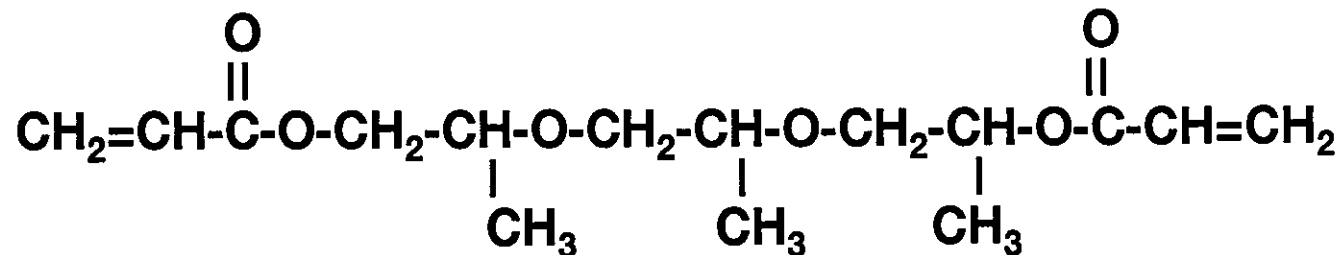
- Use of antioxidants, and mobilizers (e.g. mineral oils), reduces radiation-induced damage to most polymers

Multifunctional Monomers

Trimethylolpropane triacrylate (TMPTA)



Tripropylene glycol diacrylate (TPGDA)



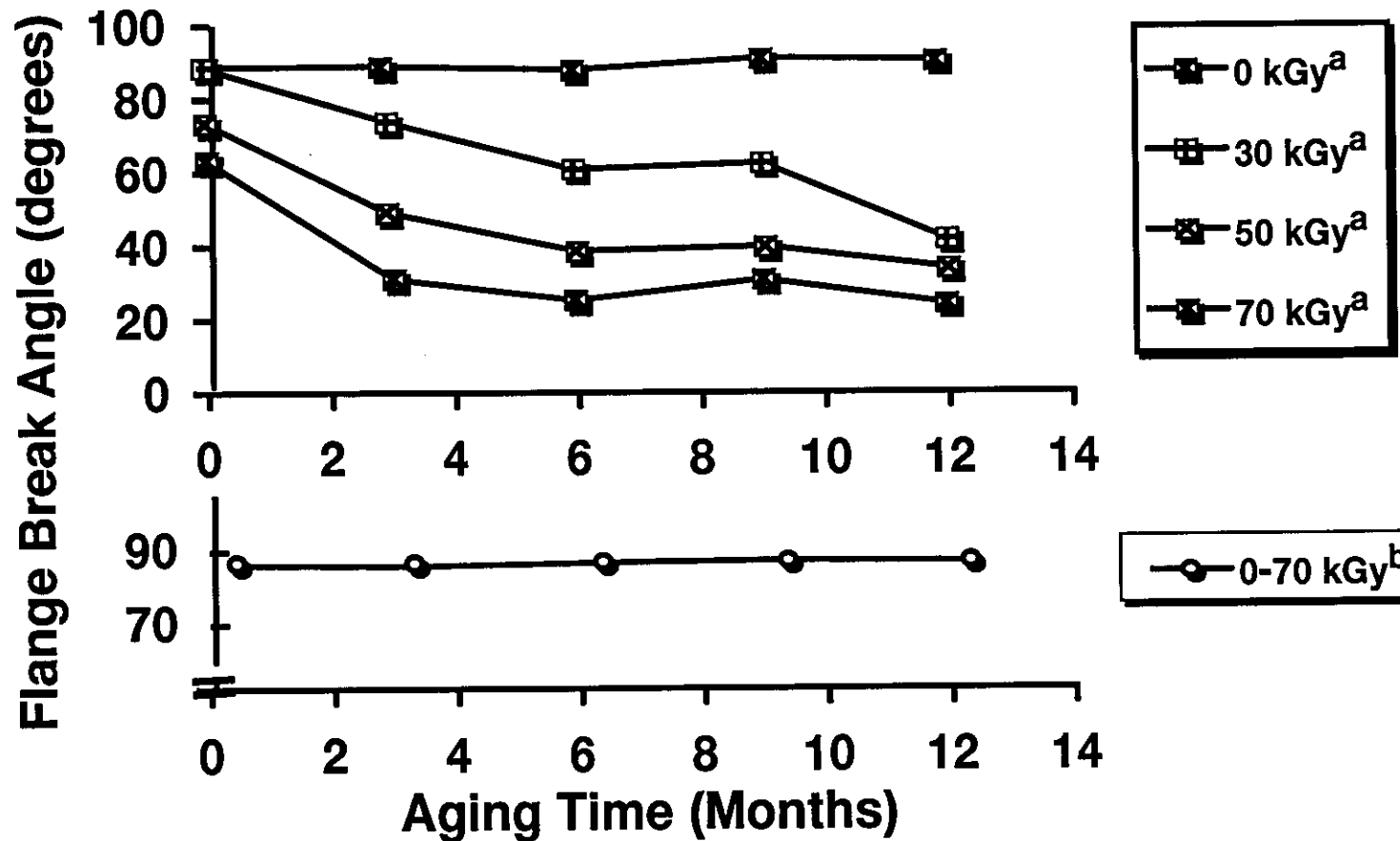
- These enhance crosslinking and grafting reactions

Effect of Electron and Gamma Irradiation on the Colour of Polycarbonate Resin

Dose (kGy)	Electron Yellowness Index	Gamma Yellowness Index
0	-	1.2
10	1.0	8.4
40	1.6	26.4

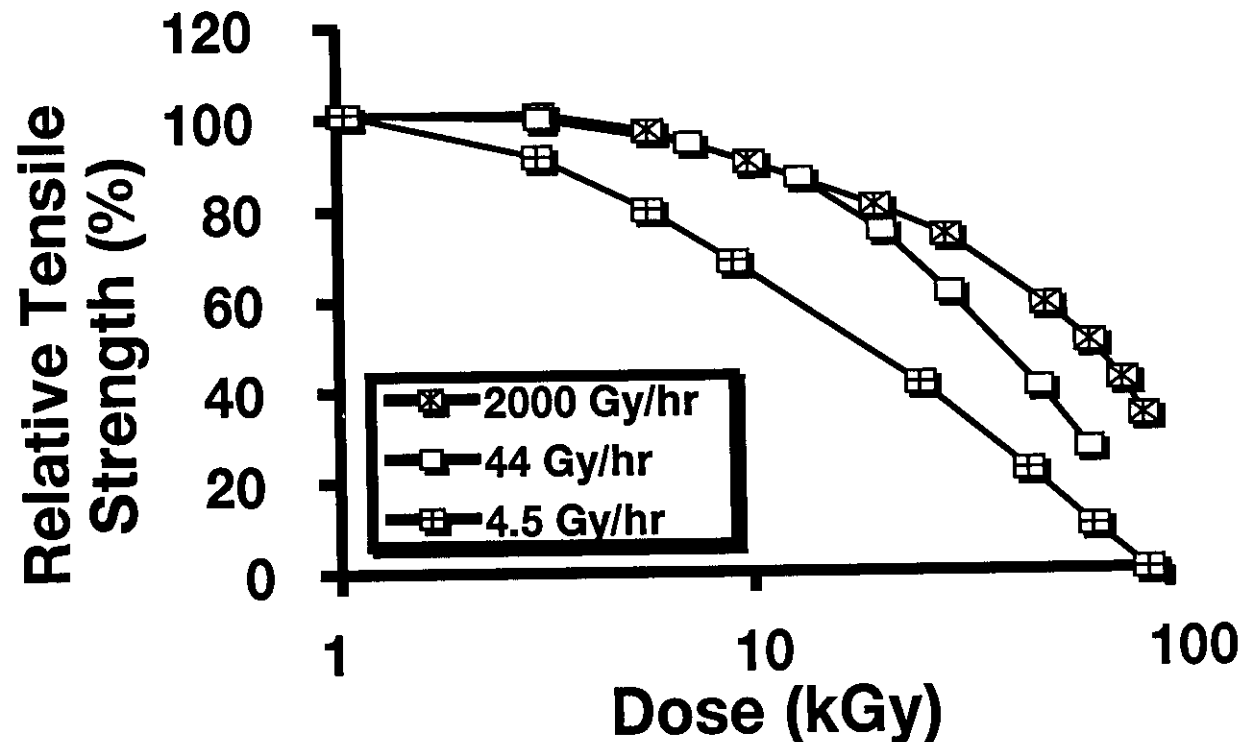
- **The level of colour developed varies from polymer to polymer, and also depends on the stabilizers used**

Effect of Radical Scavenger and Mobilizing Agent on Polypropylene



a. Radical scavenger, b. Radical scavenger + mobilizing agent

Effect of Dose and Dose Rate on the Tensile Strength of Polypropylene



- In general, the mechanical properties of polymers are less adversely affected on electron irradiation, as compared to gamma irradiation
- Satisfactory stabilized polymers for both types of irradiations are available