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

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

\[
\begin{align*}
\text{H} & \quad \text{X} & \quad \text{X} \\
\text{C-C-C} & \quad \text{C-C-C} & \quad \text{C-C-C} \\
\text{H} & \quad \text{H} & \quad \text{Y} \\
(\text{a}) & \quad (\text{b}) & \quad (\text{c})
\end{align*}
\]

\(X\) and \(Y\), heavier than \(H\), e.g., \(\text{CH}_3\), \(\text{Cl}\)

Crosslinking \(a>b>c\); Scission \(a<b<c\)
Yields of Gaseous Products from Irradiated Polymers\textsuperscript{a}
(\(\gamma\)- or electron irrad, room temp)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Products</th>
<th>G (product) (molecules/100 ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-density PE</td>
<td>(H_2 \sim 3;) CH(_4) \sim 0.002)</td>
<td></td>
</tr>
<tr>
<td>Polypropylene</td>
<td>(H_2 \sim 2.5;) CH(_4) \sim 0.1)</td>
<td></td>
</tr>
<tr>
<td>Polyisobutylene</td>
<td>(H_2 \sim 1.5;) CH(_4) \sim 0.5)</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>HCl \sim 2.7;) (H_2) \sim 0.15; (CH_4) \sim 0.002)</td>
<td></td>
</tr>
<tr>
<td>Poly(vinyl acetate)</td>
<td>(H_2) \sim 0.6;) (CH_4) \sim 0.3; CO \sim 0.28; (CO_2) \sim 0.06)</td>
<td></td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>CH(_4) \sim 0.6; CO \sim 0.5; (CO_2) \sim 0.4; (H_2) \sim 0.2)</td>
<td></td>
</tr>
<tr>
<td>Polystyrene</td>
<td>(H_2) \sim 0.03;) CH(_4) \sim 1 \times 10^{-5})</td>
<td></td>
</tr>
<tr>
<td>Poly-(\alpha)-methyl styrene</td>
<td>(H_2) \sim 0.04;) CH(_4) \sim 0.003)</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Woods and Pikaev (1994)
Free Radicals Formed on Irradiation of Polyethylene

-CH₂-CH₂-(CH₂-CH₂)ₙ- \rightarrow -CH₂-CH-(CH₂-CH₂)ₙ- alkyl radical

-CH₂-CH₂-(CH₂-CH₂)ₙ- \rightarrow -CH-CH=CH-(CH₂-CH₂)ₙ₋₁ allyl radical

- At very high doses
-CH₂-CH₂-(CH₂-CH₂)ₙ- \rightarrow -CH₂-CH-(CH=CH)ₓ-(CH₂-CH)ₙ₋ₓ polyenyl radical
Radiation Effect on Polystyrene

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

1. Radiation stable in inert atmosphere
2. Radiation-induced oxidation in air
Radiation Effect on Polypropylene

- On irradiation, long-lived free radicals formed

*Low temperature (-196°C)*

\[ -\text{CH}_2 - \overset{\cdot}{\text{C}} - \text{CH}_2 - \]
\[ \text{CH}_3 \]

\[(1)\]

*Room temperature*

\[ -\text{CH} - \overset{\cdot}{\text{CH}} = \text{CH} - \text{CH}_2 - \]
\[ \text{CH} \quad \text{CH}_3 \quad \text{CH}_3 \]

\[(3)\]

\[ -\text{CH}_2 - \overset{\cdot}{\text{C}} - \text{CH} = \text{C} - \text{CH}_2 - \]
\[ \text{CH}_3 \quad \text{CH}_3 \]

\[(4)\]

- Overall effect of irradiation: loss of mechanical strength

Dole (1973); Bradley (1984)
Chemical Basis of Oxidative Degradation

- **Initiation**
  
  \[
  \begin{align*}
  RH & \rightarrow R^\cdot + H^\cdot \\
  H^\cdot + RH & \rightarrow R^\cdot + H_2 \\
  R^\cdot + O_2 & \rightarrow RO_2^\cdot
  \end{align*}
  \]

- **Crosslinking**
  
  \[
  R^\cdot + R^\cdot \rightarrow R-R
  \]
  (not favoured in air/oxygen)

- **Degradation**
  
  \[
  RO_2^\cdot, ROOH \rightarrow \text{Chain scission, degradation, alcohols, ketones}
  \]
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.

\[
\begin{align*}
RO_2^\cdot + RH & \rightarrow R^\cdot + ROOH \\
\text{Heat} & \\
ROOH & \rightarrow RO^\cdot + \cdot OH \\
\text{Light} & \\
RO^\cdot + RH & \rightarrow R^\cdot + ROH \\
\cdot OH + RH & \rightarrow R^\cdot + H_2O
\end{align*}
\]

- 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 $\text{H}_2\text{O}$, $\text{CO}$, $\text{CO}_2$, alcohols, ketones, hydroperoxides, peroxides and carboxylic acids.
- Free radicals (alkyl and allyl) usually considered precursors of crosslinks.
- Free radical migration form 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)

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

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Name and formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPPD</td>
<td>N,N'-Diphenyl-p-phenylenediamine</td>
</tr>
<tr>
<td>Irganox 1010</td>
<td>Tetrakis[methylene-3(3,5-di-t-butyl-4-hydroxyphenyl) propionate]methane</td>
</tr>
</tbody>
</table>

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

Trimethylolpropane triacrylate (TMPTA)

\[
\text{O} \\
\text{O} \\
\text{CH}_2\text{-O-C-CH} = \text{CH}_2 \\
\text{CH}_2 = \text{CH-C-O-CH}_2\text{-C-CH}_2\text{CH}_3 \\
\text{CH}_2\text{-O-C-CH} = \text{CH}_2 \\
\text{O}
\]

Tripropylene glycol diacrylate (TPGDA)

\[
\text{O} \\
\text{O} \\
\text{CH}_2=\text{CH-C-O-CH}_2\text{-CH-O-CH}_2\text{-CH-O-CH}_2\text{-CH-O-C-CH} = \text{CH}_2 \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
\]

- These enhance crosslinking and grafting reactions
Effect of Electron and Gamma Irradiation on the Colour of Polycarbonate Resin

<table>
<thead>
<tr>
<th>Dose (kGy)</th>
<th>Electron Yellowness Index</th>
<th>Gamma Yellowness Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>1.2</td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
<td>8.4</td>
</tr>
<tr>
<td>40</td>
<td>1.6</td>
<td>26.4</td>
</tr>
</tbody>
</table>

- 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

Flange Break Angle (degrees)

0 2 4 6 8 10 12 14

Aging Time (Months)

- 0 kGy^a
- 30 kGy^a
- 50 kGy^a
- 70 kGy^a
- 0-70 kGy^b

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