Free Radical Polymerization

Group Meeting

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Timeline of Polymer Science and Technology: To 1950

1839  Charles Goodyear vulcanized natural rubber with sulfur
1869  John Wesley Hyatt introduced celluloid (camphor-plasticized nitrocellulose, mainly use in film industries)
1892  Viscose rayon (cellulose fiber) invented
1907  Leo Baekeland invented 'Bakelite' phenol-formaldehyde resins (first synthetic polymer)
1920  Hermann Staudinger introduced 'macromolecular hypothesis' (Nobel Prize, 1953)
1926  Waldo Semon invented plasticized poly(vinylchloride) (B. F. Goodrich)
1929  SBR (styrene-butadiene rubber) invented (commercialized by Farben)
1932  Poly(methylmethacrylate) sheet developed by Walter Bauer
1933  Palmer Griffith invented melamine resins (American Cyanamid)
1934  Werner Kuhn started publishing on polymer chain statistics
1935  Wallace Carothers invents nylon 6,6 (DuPont)
1937  Polystyrene commercialized (Farben)
1938  Roy Plunkett accidentally invented Teflon (DuPont, commercialized 1941)
1939  ICI commercialized LDPE (invented by Fawcett and Gibson)
1941  Poly(dimethylsiloxane) developed (commercialized 1943)
1941  PET developed (commercialized 1953/54)
1942  Paul Flory and Maurice Huggins independently publish on polymer solution thermodynamics (Nobel Prize to Flory, 1974)
1942  US Synthetic Rubber Project begins; yielded SBR, nitrile rubber and butyl rubber
1950  Bayer commercialized polyurethanes
Timeline of Polymer Science and Technology: Post 1950

1953 Karl Ziegler prepares HDPE (Nobel Prize 1963)
1954 Researchers, notably Ziegler, Natta, and Ed Vandenberg, synthesize isotactic polypropylene
1955 Williams, Landel, and Ferry publish WLF equation for time-temperature superposition
1957 Fox invented bisphenol-A polycarbonate
1964 Ethylene/methacrylic acid ionomers (random chain) introduced (DuPont)
1965 DuPont invented first polyaramid (Kevlar)
1970 Union Carbide introduces UNIPOL process for LLDPE
1972 ICI introduced poly(ether ether ketone) , PEEK
1973 Julia Higgins et al. (Strasbourg) proved that polymers in bulk are random coils
1975 Thermotropic liquid crystalline polyesters commercialized
1976 Hideki Shirakawa, Alan MacDiarmid, and Alan Heeger (Penn) doped polyacetylene with bromine to produce the first conductive polymer (Nobel Prize, 2000)
1979 Polymer blending now commonplace
1982 Poly(etherimide) was introduced
1982 First artificial heart implanted, polyurethane and PET were used for blood-contacting surfaces
1987+ Schrock and Grubbs demonstrated 'living' ROMP (Nobel Prize, 2005)
1989 IBM developed chemically-amplified photoresists
1990 Richard Friend (Cambridge) demonstrated a polymeric LED
1991 Dow and Exxon introduced metallocene catalysts for olefin polymerization (principally LLDPE, ULDPE,..)
1993+ 'living' radical polymerizations emerge: NMP (Georges, XRCC, 1993), ATRP (Matyjaszewski, CMU, 1995), RAFT (Moad, CSIRO, 1998)
Mechanistic Classification of Polymerization Processes

Chain-growth polymerization
- Radical Polymerization
- Coordination Polymerization
- Ionic Polymerization

Step-growth polymerization
- Polycondensation
- Polyaddition

Nesvadba, P. *Encyclopedia of Radicals in Chemistry, Biology and Materials*
Polymers produced by radical polymerization (RP) represent ~40-50% of all industrial polymers

- RP tolerates trace impurities (e.g., oxygen and monomer stabilizers), so ultrapure materials aren't required
- RP tolerates protic solvents, so it can be conducted in water (important for industry-scale synthesis)

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**Global primary plastic production (2015)**

- PP: 68 million tonnes
- LD, LDPE: 64 million tonnes
- PP&A fibers: 59 million tonnes
- HDPE: 62 million tonnes
- PVC: 38 million tonnes
- PET: 33 million tonnes
- PUT: 27 million tonnes
- Additives: 25 million tonnes
- PS: 25 million tonnes

LDPE (Low-density polyethylene); HDPE (High-density polyethylene); PP (Polypropylene); PS (Polystyrene); PVC (Polyvinyl chloride); PET (Polyethylene terephthalate); PUT (Polyurethanes); and PP&A fibres (Polyphthalamide fibres).

Part I: Conventional Free Radical Polymerization

Free Radical Polymerization Introduction

Mechanism, Thermodynamics and Kinetics of FRP

   Initiation

   Propagation

   Chain Transfer

   Termination

   Industrial Polymer Synthesis Process

Part II: Reversible Deactivation Radical Polymerization

Stable-Radical-Mediated Polymerization

Atom Transfer Radical Polymerization (ATRP)

Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization
Monomers Amenable/Not Amenable to RP

Polystyrene or PS

**NOT amenable to RP**

Poly(vinylchloride) or PVC
- Plastic Pipes, Tygon tubing (plasticized)

Poly(methyl methacrylate) or PMMA
- Lucite (DuPont/Mitsubishi Rayon)
- Plexiglas (Rohm & Haas/Arkema)
  - Acrylates and methacrylates are basis of nearly all latex paints/coatings

Poly(acrylonitrile) or PAN
- Acrylic fibers (former DuPont Orlon)
- Carbon Fiber Precursor

Polybutadiene or PB
- Synthetic rubber, especially as copolymer with styrene (SBR)

Poly(tetrafluoroethylene) or PTFE
- DuPont Teflon

**Only amenable to RP at high P**

- \( \alpha \)-olefins
- Internal olefins
- 1,1-disubstituted olefins
- Vinyl ethers
- Ethylene (>1000 atm)
Key Mechanistic Steps of RP

**Initiation**

\[ \text{I} \text{I} \xrightarrow{k_d} 2 \text{R}^* \]

\[ k_d \approx 10^{-6} - 10^{-4} \text{ s}^{-1} \]

\[ ([\text{I}] = 10^{-4} - 10^{-2} \text{ M}) \]

\[ \text{R}^* + \text{X} \xrightarrow{k_i} \text{R}_X \text{X}^* \]

\[ k_i \approx k_p \approx 10^{2} - 10^{4} \text{ M}^{-1} \text{ s}^{-1} \]

\[ ([\text{M}] = 10^{-1} - 10 \text{ M}) \]

**Propagation**

\[ \text{R}_X \text{X}^* + \text{X} \xrightarrow{k_p} \text{R}_X \text{X}_{XX}^* \]

**Chain transfer**

\[ \text{R}_X \text{X}^* + \text{Y} \text{H} \xrightarrow{} \text{R}_X \text{X} + \text{Y}^* \]

**Termination**

\[ \text{R}_X \text{X}^* + \text{R}_X \text{X}^* \xrightarrow{k_{\text{tc}}} \text{R}_X \text{X}_{XX} + \text{R}_X \text{X}_{XX} \]

\[ (more \ common) \]

\[ k_{\text{tc}} \approx k_{\text{td}} \approx 10^{6} - 10^{8} \text{ M}^{-1} \text{ s}^{-1} \]

\[ ([\text{R}^*_n] = 10^{-7} - 10^{-9} \text{ M}) \]

Nesvadba, P. *Encyclopedia of Radicals in Chemistry, Biology and Materials*
**Initiation**

Initiator efficiency \((f)\): the proportion of radicals that escape the solvent cage to form initiating radicals. Typically \(f\) should be 0.6 – 1 for useful initiators.

\[
f = \frac{\text{rate of initiation}}{n \times \text{rate of initiator decay}}
\]

where, \(n\) = moles of radicals generated per mole of initiator

Note: \(f\) should take into account all side reactions that lead to decay of initiator; thus \(f\) is not a constant and typically decreases with conversion.

Nesvadba, P. *Encyclopedia of Radicals in Chemistry, Biology and Materials*
**Initiation**

Thermal Autoinitiation – Styrene and its derivatives are the most prominent examples of monomers that generate the initiating radicals by a purely thermal reaction without the use of other reagents. This process is used industrially to prepare extremely pure PS devoid of any initiator and derived functional groups.

*Mayo's proposed mechanism*

Nesvadba, P. *Encyclopedia of Radicals in Chemistry, Biology and Materials*
Azoinitiators

Examples of azoinitiators with indicated temp. for $\tau_{1/2} = 10$ hr (required for conventional RP)

65 °C  30 °C  88 °C  111 °C

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Azoinitiators

Cage reactions

- depend on rate of diffusion of the radicals away from one another
- lower the initiation efficiency and produce ranges of by-products
- affect the polymer structure and properties
- can be alleviated by reducing medium viscosity (e.g., conducting polymerization in solution rather than in bulk)

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Peroxides Initiators

- Peroxides are the most important industrial radical initiators, exceeding the production volume of azoinitiators by order of magnitude.

Dicumylperoxide

Dibenzoylperoxide

t-Butylperoxypivalate

t-Butylhydroperoxide

1,1-Di-t-butylperoxycyclohexane

Persulfate anion

- important initiators for aqueous emulsion polymerization

Nesvadba, P. Encyclopedia of Radicals in Chemistry, Biology and Materials
Diacylperoxides are also susceptible to radical-induced decomposition resulting from homolytic attack of a radical on the O–O bond, leading to chain transfer from the growing chain and incorporation of benzoyloxy group into the polymer (negatively affect stability of polymer.)
Initiation–Reaction with Monomers

Interaction of radicals and monomers heavily depends on the structure of both radical and monomer.

- For reactions with styrene, specificity order: cyanoisopropyl~methyl~t-butoxy>phenyl>benzoyloxy

**Examples:**

\[
\begin{align*}
\text{NC} & \cdot \text{CH}_3 & \rightarrow & \text{S} \\
\text{NC} & \cdot \text{CH}_3 & \rightarrow & \text{Ph} \\
\text{Ph} & \cdot & \rightarrow & \text{S} \\
\text{Ph} & \cdot & \rightarrow & \text{Ph} \\
1\% & & \text{b-scission} & & \text{80\%} & \text{tail addition} & & \text{6\%} & \text{head addition} \\
\end{align*}
\]

- PS prepared by using BPO as initiators is less thermally stable and less resistant to weathering and yellowing than that prepared using other initiators

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Initiation–Reaction with Monomers

Interaction of radicals and monomers heavily depends on the structure of both radical and monomer.

For reactions with MMA, specificity order: cyanoisopropyl~methyl>phenyl>benzoyloxy>t-butoxy

Examples:

\[
\begin{align*}
\text{CH}_3^+ & \quad \text{CH}_3^+ \\
\text{MMA} & \quad \text{H}_3\text{C}^+ \quad \text{H}_3\text{C}^+ \\
& \quad \text{CH}_3 \quad \text{CH}_3 \\
\end{align*}
\]

4% β-scission

Judicious choice of initiators for a given monomer system is needed to avoid formation of undesired end groups

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Propagation–Regiosequence Isomerism

Monoene polymers

- **Isoregic:** head-to-tail linkage
- **Syndioregic:** head-to-head or tail-to-tail linkage
- **Aregic:** random arrangement of connections

The preponderance of head-to-tail linkages in polymers is determined largely by steric and polar factors.

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Side reactions competitive with addition reaction—Proposed mechanism for ‘defect group’ formation that results in poor thermal stability of PVC

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Conjugated diene polymers

Propagation–Regiosequence Isomerism

• Mixture of products is obtained, in which 1,4-addition is favored (especially for 2-substituted dienes)
• Little is known about the microstructure of diene polymers other than PB, polyisoprene and polychloroprene

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Isomers can have very different physical properties

**cis-polyisoprene (natural rubber)**

- $T_g = -67 \, ^\circ C$ (excellent rubber; used in treads and belt-edge section)

**trans-polyisoprene**

- Crystalline, $T_m = 80 \, ^\circ C$ (hard plastic; formerly used for root canal fill, golf ball covers)

**vinyl polyisoprene (1,2 + 3,4)**

- Amorphous, $T_g = 20 \, ^\circ C$ (leathery, no commercial use)
Tacticity Terminology

diad: smallest structural unit containing stereochemical information
  • $m$: two chirality centers have like configuration. $P(m)$ is the probability of finding
    a $m$ diad.
  • $r$: two chirality centers have opposite configuration. $P(r)$ is the probability of finding
    a $r$ diad.

General observations

• Polymers formed from monosubstituted monomers appear almost atactic with only slight preference
  for syndiotacticity ($P(m) \sim 0.45–0.52$).
• For 1,1-disubstituted monomers, polymeric products typically have $P(m) \sim 0.2–0.5$.
• Tacticity is solvent and temperature dependent (e.g., syndiotacticity is enhanced in fluoroalcohol
  solvents and by lower temperatures.
• Achieving stereochemical control over propagation in RP remains important challenge in the field.
Propagation–Structural Isomerism

Cyclopolymerization

\[ \text{ring} \cdot + \text{alkene} \rightarrow \text{cycloalkene} \]

Ring-opening polymerization

*Interest in ROP stems from the volume expansion upon polymerization → applications in dental composite and adhesive compositions*

\[ \text{ring} \cdot + \text{cycloalkene} \rightarrow \text{alkene} \]

- Typical monomers are methylene-substituted cyclic or strained cyclic (e.g., bicyclobutane) compounds
- \( k_\beta >> k_p \). Typically \( k_\beta > 10^5–10^6 \text{ s}^{-1} \). ROP can be favored with low concentration and high temperatures

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Intramolecular HAT (backbiting)

- Backbiting occurs to some extent during polymerization of most monosubstituted monomers, especially VAc, VC, and acrylate esters

- Addition-abstraction polymerization: monomers are designed to give quant. rearrangement of the initially formed adduct via 1,5-HAT

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Table 2  Thermodynamic parameters for polymerization of selected monomers (CH$_2$=CRX)

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$X$</th>
<th>$R$</th>
<th>$\Delta H_p$ (kJ mol$^{-1}$)</th>
<th>$\Delta S_p$ (J mol$^{-1}$ K$^{-1}$)</th>
<th>$T_c$ (°C)</th>
</tr>
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<tr>
<td></td>
<td>$\text{a}$</td>
<td>$\text{b}$</td>
<td>$\text{c}$</td>
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<td></td>
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<tr>
<td>AA</td>
<td>CO$_2$H</td>
<td>H</td>
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<td>–</td>
<td>–</td>
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<tr>
<td>MAA</td>
<td>CO$_2$H</td>
<td>CH$_3$</td>
<td>43</td>
<td>65</td>
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<tr>
<td>MA</td>
<td>CO$_2$CH$_3$</td>
<td>H</td>
<td>78</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MMA</td>
<td>CO$_2$CH$_3$</td>
<td>CH$_3$</td>
<td>56 (58)</td>
<td>55</td>
<td>118$^{170,171}$</td>
</tr>
<tr>
<td>EMA</td>
<td>CO$_2$C$_2$H$_5$</td>
<td>H</td>
<td>60 (58)</td>
<td>–</td>
<td>124$^{172}$</td>
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<tr>
<td>BMA</td>
<td>CO$_2$C$_4$H$_9$</td>
<td>CH$_3$</td>
<td>58 (60)</td>
<td>–</td>
<td>–</td>
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<tr>
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<td>22</td>
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<tr>
<td>AN</td>
<td>CN</td>
<td>H</td>
<td>75$^f$</td>
<td>–</td>
<td>109$^{169}$</td>
</tr>
<tr>
<td>MAN</td>
<td>CN</td>
<td>CH$_3$</td>
<td>57</td>
<td>64$^{174}$</td>
<td>142$^{174}$</td>
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<tr>
<td>St</td>
<td>Ph</td>
<td>H</td>
<td>69 (73)</td>
<td>70</td>
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<tr>
<td>AMS</td>
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<tr>
<td>VAc</td>
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<td>88 (90)</td>
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<td>–</td>
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<tr>
<td>VC</td>
<td>Cl</td>
<td>H</td>
<td>96</td>
<td>112</td>
<td>–</td>
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</tbody>
</table>

Abbreviations: AA, acrylic acid; AMS, α-methylstyrene; AN, acrylonitrile; BMA, butyl methacrylate; MA, methyl acrylate; MAA, methacrylic acid; MAN, methacrylonitrile; MEA, methyl ethacrylate; MMA, methyl methacrylate; St, styrene; VAc, vinyl acetate; VC, vinyl chloride.

- In most RPs, propagation steps are facile and highly exothermic.
- Steric factors are dominant in determining $\Delta H_p$ and $\Delta S_p$ (e.g., the presence of α-methyl substituents cause the propagation in RP of MAA to be less exothermic than that of AA by >20 kJ/mol).

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<td>b</td>
<td>c</td>
</tr>
<tr>
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<td>H</td>
<td>67</td>
<td>–</td>
<td>–</td>
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<tr>
<td>MAA</td>
<td>CO$_2$H</td>
<td>CH$_3$</td>
<td>43</td>
<td>65</td>
<td>–</td>
</tr>
<tr>
<td>MA</td>
<td>CO$_2$CH$_3$</td>
<td>H</td>
<td>78</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MMA</td>
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<td>CH$_3$</td>
<td>56 (58)</td>
<td>55</td>
<td>56$^{170,171}$</td>
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<tr>
<td>EMA</td>
<td>CO$_2$C$_2$H$_5$</td>
<td>CH$_3$</td>
<td>60 (58)</td>
<td>–</td>
<td>–</td>
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<tr>
<td>BMA</td>
<td>CO$_2$C$_4$H$_9$</td>
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<td>–</td>
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<tr>
<td>MEA$^{172}$</td>
<td>CO$_2$CH$_3$</td>
<td>C$_2$H$_5$</td>
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<td>CN</td>
<td>H</td>
<td>75$^i$</td>
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<td>–</td>
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<tr>
<td>MAN</td>
<td>CN</td>
<td>CH$_3$</td>
<td>57</td>
<td>64$^{2,174}$</td>
<td>109$^{169}$</td>
</tr>
<tr>
<td>St</td>
<td>Ph</td>
<td>H</td>
<td>69 (73)</td>
<td>70</td>
<td>73$^{175}$</td>
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<td>88 (90)</td>
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<td>–</td>
</tr>
<tr>
<td>VC</td>
<td>Cl</td>
<td>H</td>
<td>96</td>
<td>112</td>
<td>–</td>
</tr>
</tbody>
</table>

**Table 2** Thermodynamic parameters for polymerization of selected monomers (CH$_2$-CRX)

*Abbreviations: AA, acrylic acid; AMS, α-methylstyrene; AN, acrylonitrile; BMA, butyl methacrylate; MA, methyl acrylate; MAA, methacrylic acid; MAN, methacyronitrile; MEA, methyl ethacrylate; MMA, methyl methacrylate; St, styrene; VAc, vinyl acetate; VC, vinyl chloride.*

- Propagation is reversible. The temperature at which rate of propagation and depopagation are equal is the ceiling temperature ($T_c$). Above $T_c$ there will be net depolymerization.
- $T_c$ depends on the monomer concentration.
- Monomers with α-alkyl substituents have lower $T_c$ than monosubstituted monomers (e.g., AMS has $T_c < 30^\circ$C and is not readily polymerizable by RP).

\[
T_c = \frac{\Delta H_p}{\Delta S_p + R \ln[M]}
\]
Table 4: Rate constants (25 °C) and Arrhenius parameters for propagation of monomers \( CH_2 = CR^1R^2 \) compared with rate constants for addition of small radicals.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>( k_p ) (M(^{-1}) s(^{-1}))</th>
<th>Log A</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
<th>Model</th>
<th>( k_a ) (M(^{-1}) s(^{-1}))</th>
<th>Log ( A^b )</th>
<th>( E_a ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>77</td>
<td>7.27</td>
<td>34.3</td>
<td>( \cdot CH_3 )</td>
<td>12000</td>
<td>8.5</td>
<td>28.2</td>
</tr>
<tr>
<td>St</td>
<td>340</td>
<td>7.63</td>
<td>32.5</td>
<td>( \cdot CH_2Ph )</td>
<td>4700</td>
<td>8.5</td>
<td>30.8</td>
</tr>
<tr>
<td>MA</td>
<td>28000</td>
<td>7.22</td>
<td>17.7</td>
<td>( \cdot 47 )</td>
<td>1100000</td>
<td>8.5</td>
<td>15.6</td>
</tr>
<tr>
<td>AN</td>
<td>(-)</td>
<td>(-)</td>
<td>(-)</td>
<td>( \cdot CH_2CN )</td>
<td>410000</td>
<td>8.5</td>
<td>18.4</td>
</tr>
<tr>
<td>MMA</td>
<td>820</td>
<td>6.43</td>
<td>22.4</td>
<td>( \cdot 49 )</td>
<td>9700</td>
<td>7.5</td>
<td>22.4</td>
</tr>
<tr>
<td>MAN</td>
<td>59</td>
<td>6.42</td>
<td>29.7</td>
<td>( \cdot C(CH_3)_2CN )</td>
<td>2300</td>
<td>7.5</td>
<td>26.4</td>
</tr>
</tbody>
</table>

Abbreviation: AN, acrylonitrile; E, ethylene; MA, methyl acrylate; MAN, methacrylonitrile; MMA, methyl methacrylate; St, styrene.

- Common assumption that \( k_p \) is independent of chain length is not completely correct. \( k_p \) for the first few propagation steps can be largely different from overall \( k_p \) (penultimate unit effect).

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
### Table 3: Kinetic parameters for propagation in selected radical polymerizations in bulk monomer

<table>
<thead>
<tr>
<th>Monomer</th>
<th>( k_p (60^\circ\text{C}) ) ( (\text{M}^{-1}\text{s}^{-1}) )</th>
<th>( A^p ) ( (\text{M}^{-1}\text{s}^{-1} \times 10^8) )</th>
<th>( E_p^p ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha)-H</td>
<td>28000</td>
<td>16.6</td>
<td>17.7</td>
</tr>
<tr>
<td>MA</td>
<td>31000</td>
<td>15.8</td>
<td>17.3</td>
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<tr>
<td>BA</td>
<td>39000</td>
<td>17.9</td>
<td>17.0</td>
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<td>8300</td>
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<td>20.7</td>
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<td>340</td>
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<td>32.5</td>
</tr>
<tr>
<td>St</td>
<td>200</td>
<td>80.5</td>
<td>35.7</td>
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<th>( \alpha)-Methyl</th>
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<tr>
<td>MAA</td>
<td>1200</td>
<td>-</td>
<td>-</td>
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<tr>
<td>MAA(MeOH)(^d)</td>
<td>1000</td>
<td>0.60</td>
<td>17.7</td>
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<tr>
<td>MAA(H(_2)O)(^e)</td>
<td>6700</td>
<td>1.72</td>
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<td>MMA</td>
<td>820</td>
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<tr>
<td>EMA</td>
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<td>4.06</td>
<td>23.4</td>
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<tr>
<td>nBMA</td>
<td>970</td>
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<td>22.9</td>
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<td>( \beta)BMA</td>
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<tr>
<td>HEMA</td>
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<td>21.9</td>
</tr>
<tr>
<td>GMA</td>
<td>1600</td>
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<tr>
<td>MAN</td>
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<td>2.69</td>
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<table>
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<th>( \alpha)-Other</th>
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<td>44</td>
<td>25</td>
<td>0.20</td>
<td>24.9</td>
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<tr>
<td>45</td>
<td>30</td>
<td>1.25</td>
<td>29.5</td>
</tr>
</tbody>
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---

- Lower \( k_p \) values are associated with more stable propagating radicals.
- Methacrylic monomers with protic substituents (e.g., methacrylic acid, 2-hydroxyethyl methacrylate) are associated with higher \( k_p \), possibly due to monomer/polymer association via HB.
- Larger size of \( \alpha\)-substituents results in lower \( k_p \) values.

---

Abbreviations: R, butadiene; RA, butyl acrylate; RMA, iso-butyl methacrylate; nRMA, n-buty. methacrylate; DA, dodecyl acrylate; DMA, dioleyl methacrylate; EMA, 2-ethylhexyl methacrylate; GMA, glycidyl methacrylate; HEMA, 2-hydroxyethyl methacrylate; MA, methyl acrylate; MAA, methacrylic acid; MAN, methacronylinitile; MMA, methyl methacrylate; St, styrene; VAc, vinyl acetate.

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Chain transfer

\[
\begin{align*}
\text{initiator, monomer, polymer, solvent, impurity, added CT agent}
\end{align*}
\]

- CT always reduces \( X_n \)
- CT results in branching or potentially cross-linking (e.g., LDPE)
- CT always becomes significant if polymerization is taken to high conversion even if \( C_{tr} \) is small, because:

\[
\frac{\text{rate of transfer to polymer}}{\text{rate of propagation}} = \frac{k_{tr,p}[P^\bullet][P_{seg}]}{k_p[P^\bullet][M]} = C_p \frac{[P_{seg}]}{[M]} \rightarrow \text{ratio diverges as reaction approaches 100% conversion}
\]

- CT agents with large \( C_{tr} \) (e.g., thiols) are often used in industrial polymerizations to control (limit or reduce) the MW and MW distribution of polymers, leading to the control over polymerization rate, exothermicity and viscosity.

\[
\frac{1}{X_n} = \frac{1}{X_{n_0}} + C_{trT} \frac{[T]}{[M]}
\]

(Mayo equation)

\[ C_{tr} = 1 \]: ratio of the rates at which CT agent and monomer are consumed is constant, so \([T]/[M]\) and therefore \( X_n \) remain constant throughout polymerization.

\[ C_{tr} \ll \text{ or } \gg 1 \]: \( X_n \) fluctuates → Add M or CT agent to maintain \([T]/[M]\).

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Termination of RP occurs via radical combination or disproportionation (depending on steric of the chain).

Radical centers must come into proximity for termination step, so self-reaction of propagating radicals is a diffusion-controlled process. Thus, no single rate constant for termination in RP.

Termination process determines the MW and MW distribution of the polymer.

Rate of termination

\[ R_t = -2k_t[P\bullet]^2 \]

\( k_t = k_{tC} + k_{tD}; \text{ generally } k_{tC} >> k_{tD} \)

Steady-state approximation

\[ -\frac{d[P\bullet]}{dt} = R_i - R_t = 2k_df[l_2] - 2k_t[P\bullet]^2 = 0 \quad \rightarrow \quad [P\bullet] = \left(\frac{k_df}{k_t}\right)^{1/2} [l_2]^{1/2} \]

Rate of polymerization

\[ R_p = k_p[P\bullet][M] = k_p\left(\frac{k_df}{k_t}\right)^{1/2} [l_2]^{1/2} [M] \]

This is instantaneous rate; [l] and [M] would decrease during polymerization, so \( R_p \) naturally slows with time

Process time

\[ t_p = \frac{[M]_0}{R_{p,i}} \]

Kinetic chain length

(i.e., average number of monomers polymerized by each initiating radical)

\[ \nu = \frac{\text{propagation rate}}{\text{initiation rate}} = \frac{k_p[P\bullet][M]}{2k_df[l_2]} = \frac{k_p[M]}{2(k_dfk_t)[l]^{1/2}} \]

Increasing \([l_2]\) increases \( R_p \) but produces shorter polymer!

Moade, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Termination Affects MW and MW distribution

Probability of a propagation event

\[ p = \frac{R_p}{R_p + R_t + R_{tr}} \]

If termination proceeds by disproportionation

\[
\overline{X}_n = \frac{1}{1-p} \quad \overline{X}_w = \frac{1+p}{1-p} \quad PDI = \frac{\overline{X}_w}{\overline{X}_n} = 1+p
\]

\( \overline{X}_n, \overline{X}_w \): number average and weight average degree of polymerization

\( PDI \): dispersity

For high-MW polymer \((p \rightarrow 1)\):

\( PDI \rightarrow 2 \)

If termination proceeds by combination

\[
\overline{X}_n = \frac{2}{1-p} \quad \overline{X}_w = \frac{2+p}{1-p} \quad PDI = \frac{\overline{X}_w}{\overline{X}_n} = \frac{2+p}{2}
\]

MW distribution is actually narrower if termination proceeds by combination.

For high-MW polymer \((p \rightarrow 1)\):

\( PDI \rightarrow 1.5 \)

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Polymerization Process

- Polymerization in solution or in a melt suffers from a dramatic increase in viscosity.
  - *Autoacceleration effect* (*Norrish–Trommsdorff effect*): increases in viscosity result in slow termination reactions, and rapid increase in overall rate of polymerization.
  - Problems in mixing and pumping of the reaction mass and heat transfer (e.g., adiabatic temp. increase at 100% conversion of monomer is 1810 °C for ethylene, 721 °C for acrylonitrile).

**Suspension polymerization**

- Reaction mixture (monomers and initiator) is divided into 50–1000 µm droplets (‘mini reactors’)
- Droplets are dispersed in immiscible fluid (e.g., water) and stabilized by added surfactant (i.e., amphiphilic polymers)
- Polymer particles can be isolated by filtration
- E.g.: PS (styrofoam), PVC, PMMA
Emulsion polymerization

- Monomers are dispersed in aq. medium to form 0.01–0.1 mm droplets stabilized by surfactant.
- Hydrophilic initiator radicals can't enter lipophilic micelles, so they preferentially propagate with monomers dissolved in water phase.

*If conc. of surfactant is above critical micelle conc., micelles (nm) are formed.*

- The resulting oligomeric radicals are lipophilic enough to enter the micelles. Radical propagation continues to form latex particles.

*If conc. of surfactant is below critical micelle conc., micelles (nm) aren't formed.*

- Oligomeric radicals grow until they become insoluble enough to undergo coil-to-globule transition.
- Hydrophobic globules are swollen with monomers and become latex particles.

Nesvadba, P. *Encyclopedia of Radicals in Chemistry, Biology and Materials*
Reversible Deactivation Radical Polymerization

- Living polymerization: a chain polymerization from which irreversible chain transfer and irreversible chain termination (deactivation) are absent.
  ⇒ 'Living' should NOT be used in radical polymerization (CT and termination are always present)!
- The term 'controlled' should only be used when the particular aspect of polymerization that is being controlled is specified.
  ⇒ 'Controlled' should not be used to indicate a system having a lower degree of livingness.
- IUPAC recommendation: 'reversible deactivation radical polymerization'

Criteria for living polymerization processes

1. Living polymerizations proceed until all monomer is consumed and may continue growth if further monomer is added.

2. MW increases linearly with conversion (In conventional RP, MW are initially high and decrease with conversion due to monomer depletion).

3. In a living polymerization, the concentration of active species remain constant.

4. Living polymerization provide narrow MW distributions (Theoretically, $P_D$ of 1.5 is the narrowest achievable in conventional RP with termination by combination. Good RDRP systems provide $P_D \sim 1.05-1.2$).

5. Block polymers can be prepared by sequential addition of monomers.

6. End groups are retained allowing end-functional polymers to be obtained in quant. yield.

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
How to Achieve Reversible Deactivation Radical Polymerization?

- $R_t \propto [P_n\cdot]^2$, while $R_p \propto [P_n\cdot] \rightarrow$ termination can be suppressed relative to propagation by reducing $[P_n\cdot]

$ \rightarrow$ Use of species that reversibly deactivate or terminate chains!

1) **Stable-radical-mediated polymerization (e.g., NMP)**

```
active chain                  dormant chain
P_n\cdot + X                  P_n\cdot \rightarrow X
```

Deactivation involves reversible coupling with persistent radicals

2) **Atom-transfer radical polymerization (ATRP)**

```
active chain                   dormant chain
P_n\cdot + X-Mt^{m+1}/L         P_n\cdot \rightarrow X + Mt^m/L
```

Deactivation involves reversible atom/group transfer catalyzed usually by TM complexes

3) **Degenerate-transfer radical polymerization (e.g., RAFT)**

```
active chain                   dormant chain
P_n\cdot + P_m\cdot \rightarrow Y P_n\cdot \rightarrow Y + P_m\cdot
```

Deactivation involves degenerative chain transfer

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Reversible Deactivation Radical Polymerization

Examples of polymer compositions accessible via RDRP

- Homopolymer
- Statistical copolymers
- Gradient copolymers
- Block copolymers
- Graft copolymers

Examples of polymer topologies accessible via RDRP

- Linear
- Star/Multi-armed
- Comb polymers
- Networks
- (Hyper)branched

Stable-radical-mediated polymerization

- The use of NMP for producing block and end-functional polyacrylates was first reported by Solomon (1985)
- The method only received attention after Georges (1993) demonstrated that NMP could be used to prepare PS with narrow dispersity.

Criteria for initiators

1. One of the radicals formed on initiator decomposition is persistent or long-lived and unable (or slow) to initiate polymerization
2. Primary radical termination (exclusively by combination) or transfer to initiator (exclusively by group transfer) should be the only significant mechanism for the interruption of chain growth.
3. The bond to the end group (X) must be thermally or photochemically labile.
4. $R_i \geq R_p$

Process 1—involves the use of conventional radical initiator in presence of persistent radical

- $I_2 = AIBN, BPO$ to generate $I$–$X$ in situ
- $PDI = 1 + \frac{1}{X_n} + \left(\frac{2 - c}{c}\right) \frac{k_d[X]}{k_{deact}}$
- $[X]$ is unknown and poorly controlled

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4. \( R_i \geq R_p \)

Process 2—involves the direct use of a species I–X

\[
\begin{align*}
\text{I–X} & \quad \xrightleftharpoons[k_{\text{act}}']{k_{\text{deact}}'} I^* + X \\
\text{P}_{1–X} & \quad \xrightleftharpoons[k_{\text{deact}}]{k_{\text{act}}} P_{1^*} + X
\end{align*}
\]

Examples of alkoxyamine initiators

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3. The bond to the end group (X) must be thermally or photochemically labile.
4. $R_i \geq R_p$

Process 3—involves the use of a species $X-X$ (e.g., dithiurams, disulfides)

\[
\begin{align*}
X-X & \quad \stackrel{k_{act}'}{\leftrightarrow} \quad X^* + X^* \\
\quad P_1-X & \quad \stackrel{k_{act}}{\leftrightarrow} \quad P_1^* + X
\end{align*}
\]
Macromolecular Architectures Accessible via NMP

Hawker (1996)—Synthesis of graft and dendrigraft copolymers via NMP

Moad, G. Radical Polymerization. 2016. DOI: 10.1016/B978-0-12-803581-8.01346-1
Atom Transfer Free Radical Polymerization

First ATRPs were reported by Sawamoto, Matyjaszewski and Percec (1995).
Typical ATRP active TM complexes have facile 1e redox chemistry and relatively low oxo-phlicity (late or mid-TMs: copper, ruthenium, iron).

Examples of initiators:
- R-O-C-Br
- H$_2$N-C-Cl
- Br
- CN

Examples of ligands:
- C$_4$H$_9$-N-C$_4$H$_9$
- N-N

Atom Transfer Free Radical Polymerization

![Chemical reaction diagram](attachment:image.png)

**Rate of polymerization**

\[ R_p = k_p K \frac{[RX][Mt^n]}{[Mt^{n+1}X]} [M] \]

- \( R_p \propto [Mt^{n+1}X]^{-1} \rightarrow \) reducing \([Mt^{n+1}X]\) by using ligands that provide limited solubility of deactivator \(Mt^{n+1}X\) or metal (0) compound could accelerate the polymerization.

**Dispersity**

\[ PDI = 1 + \frac{1}{X_n} + \left( \frac{2 - c}{c} \right) k_p \frac{[RX]}{k_{deact} [Mt^{n+1}X]} \]

- More uniform polymers are obtained at higher conversions, when [deactivator] is high and [initiator] is low.

**Note:** the amount of metal catalyst should be minimized (<100 ppm) for the applicability of this method in industry (catalytically regenerate activators *in situ*)

Reversible Addition-Fragmentation Chain Transfer

Initiation

Initiator $\rightarrow I^\cdot \rightarrow P_n^\cdot$

Pre-equilibrium

$P_n^\cdot + \text{SSS}_R^Z \rightleftharpoons P_n^\cdot \text{SSS}_R^Z \rightleftharpoons P_n^\cdot \text{SS}_{R^Z} + R^\cdot$

Reinitiation

$R^\cdot + M \rightarrow P_m^\cdot$

Main equilibrium

$P_n^\cdot + \text{SSS}_{P_m}^Z \rightleftharpoons P_n^\cdot \text{SSS}_{P_m}^Z \rightleftharpoons P_m^\cdot \text{SS}_{Z} + P_m^\cdot$

Termination

$\text{dead polymers}$

Reversible Addition-Fragmentation Chain Transfer

*Important stoichiometric ratios influence the reaction*

1. \([M]/[RAFT]\): as the amount of RAFT agent determines the number of polymer chains formed, \([M]/[RAFT]\) determines \(X_n(\text{calc.})\) and \(M_n\). A defined \([M]/[RAFT]\) ratio provides polymers with targeted MW.

\[
M_n = \frac{[M]_0 - [M]_t}{[RAFT]_0 + df[I]_0 (1 - e^{-kt})} \times M_M + M_{RAFT} \approx \frac{[M]_0 - [M]_t}{[RAFT]_0} \times M_M + M_{RAFT}
\]

\(\rightarrow \) (# chains (initiator derived) << # chains (RAFT derived))

2. \([RAFT]/[I]\): this ratio influences the functionality at both chain-ends of polymers and the 'livingness' of the system.

\[
L = \frac{[RAFT]_0}{[RAFT]_0 + 2f[I]_0 (1 - e^{-kt}) \left(1 - \frac{f_c}{2}\right)}
\]

3. \([M]/[I]\): this ratio influences the rate of polymerization

\[
R_p = k_p \left(\frac{k_d f e^{-kt}}{k_t}\right)^{1/2} [I]^{1/2} [M]
\]

Monomer Classes and RAFT Agent

'More activated' monomers (MAMs)—bearing vinyl group conjugated to a double bond/aromatic ring/carbonyl/nitrile

'Less activated' monomers (LAMs)—bearing vinyl group adjacent to electron-rich atoms

For successful RAFT: C=S bond is more reactive to radical addition than C=C bond of monomer

- $Z$: responsible for reactivity of C=S bond and governs the stability of intermediate radical
- $R$: has to form a radical stable enough to be formed and reactive enough so that it can add to monomer

Switchable RAFT

MAMs + H$^+$ → LAMs

Universal RAFT agents