Radical Polymerizations I

Chain Growth Basics

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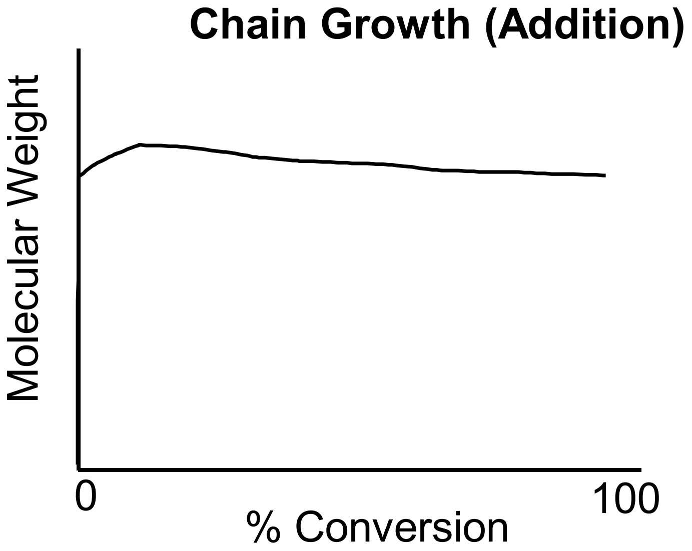
Chain Polymerizations

- Typical chain reaction
  - $I \rightarrow I^*$ Initiation
  - $I^* + M \rightarrow IM^*\ (=P_1^*)$
  - $P_n^* + M \rightarrow P_{n+1}^*$ Propagation
  - $P_n^* + P_m^* \rightarrow D_{n+m}$ Termination
  - $P_n^* + P_m^* \rightarrow D_n + D_n$
  - $P_n^* + A \rightarrow D_n + A^*$

- * = reactive species
  - Radical
  - Anion
  - Cation



Olefinic Mononmers

Monomers	**Type of Initiation**		
	Radical	**Cationic**	**Anionic**
Ethylene	+	-	+
1-Alkyl olefins (α-olefins)	-	-	-
1,1-Dialkyl olefins	-	+	-
1,3-Dienes	+	+	+
Styrene, α-methyl styrene	+	+	+
Halogenated olefins	+	-	-
Vinyl esters (CH_2=CHOCOR)	+	-	-
Acrylates, methacrylates	+	-	+
Acrylonitrile, methacrylonitrile	+	-	+
Acrylamide, methacrylamide	+	-	+
Vinyl ethers	-	+	-
N-Vinyl carbazole	+	+	-
N-Vinyl pyrrolidone	+	+	-
Aldehydes, ketones	-	+	+

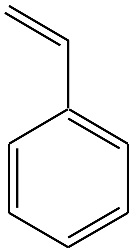
Initiators and Solvents

- Initiators
  - Peroxides
  - Azo compounds
  - Redox
  - Thermal
  - UV
  - γ-rays

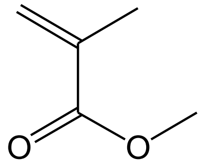
- Solvents
  - Danger of radical transfer to solvent
    - E.g. C_6H_6 is better than $C_6H_5CH_3$
  - Water is okay
  - Remove O_2
    - Formation of stable peroxide radicals
      - ~~~O-O• (relatively stable)

Some Typical Conditions

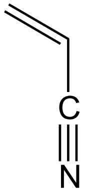
- Styrene
  - Bulk, under N_2
  - 125°C, 1-7 days, M_n~150,000



- Methyl methacrylate (MMA)
  - Solution, 0.5% AIBN
  - 1-2 days, 60°C, M_n~100,000



- Acrylonitrile
  - Emulsion, H_2O, N_2, surfactant
  - $K_2S_2O_8$/$NaHSO_3$ (redox)
  - 35°C, 24 hrs, M_n~50,000



Elementary Reactions …1

- Initiation
  - R• = primary radicals
  - $R_d = 2k_d[I] << R_i = k_i[R\bullet][M]$

$$I \xrightarrow{k_d} 2\,R\bullet$$

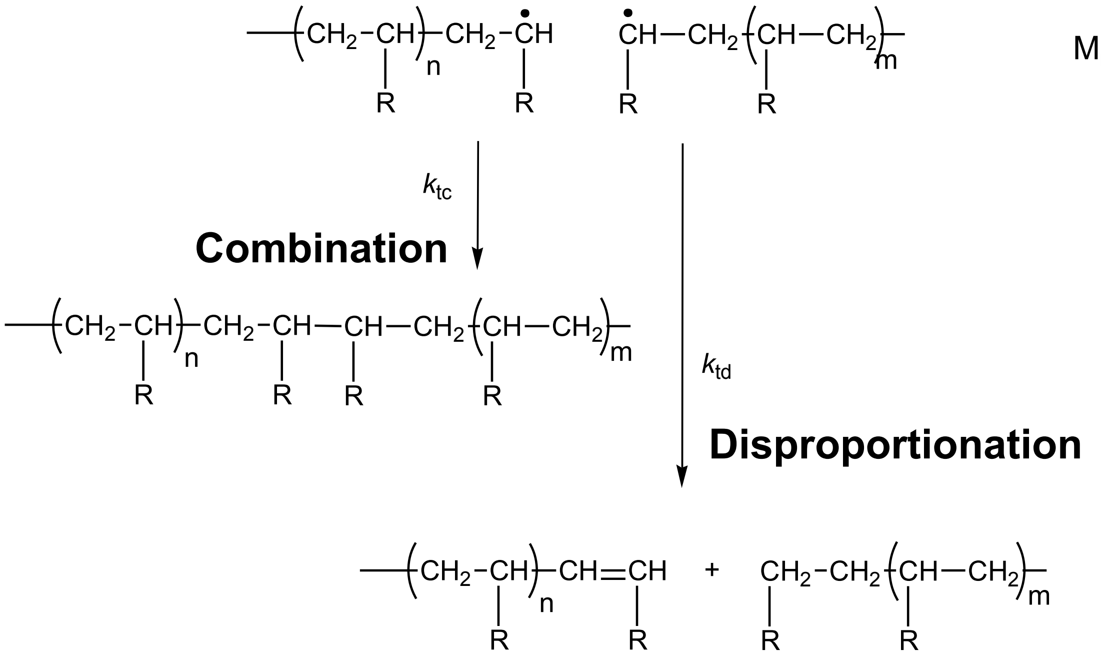
$$R\bullet + M \xrightarrow{k_i} M_1^\bullet \quad (R\text{-}M\bullet)$$

- Propagation
  - $R_p = k_p[R\bullet][M]$

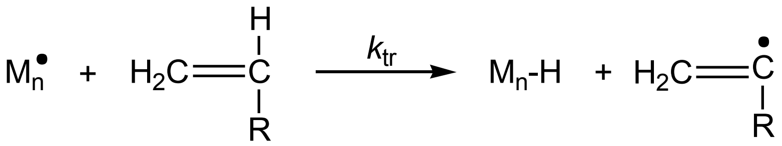
$$\left.\begin{array}{l} M_1^\bullet + M \xrightarrow{k_{p1}} M_2^\bullet \\ M_2^\bullet + M \xrightarrow{k_{p2}} M_3^\bullet \\ M_3^\bullet + M \xrightarrow{k_{p3}} M_4^\bullet \end{array}\right\} \quad M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet$$

Elementary Reactions …1

- Termination (radical–radical)



- Transfer
  - E.g. to monomer



$$M_n^{\bullet} + H_2C{=}\underset{R}{\overset{H}{C}} \xrightarrow{k_{tr}} M_n\text{-}H + H_2C{=}\underset{R}{\overset{\bullet}{C}}$$

  - Solvent
  - Polymer
  - Additives

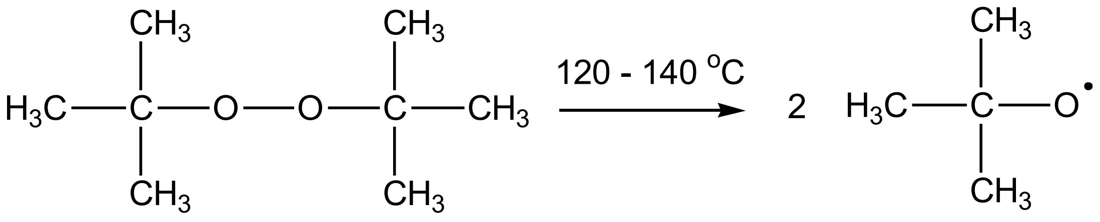
Initiation

- Rate of radical formation
  - $d[R]/dt = 2\, k_d\, [I]$
  - Typical values
    - $k_d \sim 10^{-6} – 10^{-4}\ s^{-1}$
    - $[I] \sim 0.01$ M (0.1%)
  - $d[R]/dt \sim 10^{-8} – 10^{-6}\ M\ s^{-1}$

- Temperature at which half lifetime = 10 hrs
  - Depends on initiator structure
  - $\tau_{1/2} = (\ln 2)/k_d$

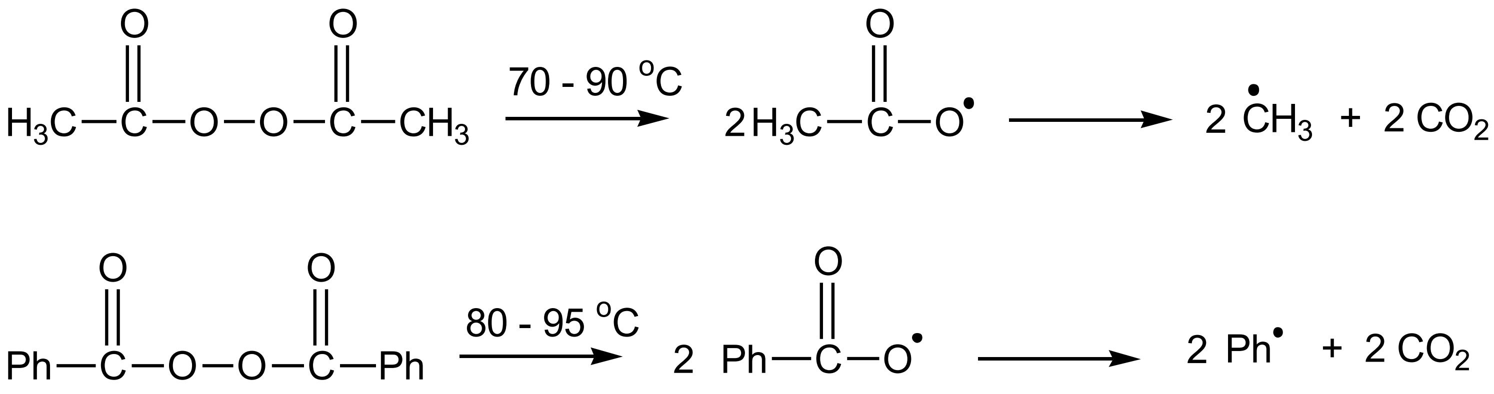
Thermal Initiators …1

- Peroxides
  - Dialkyl peroxides



$$(CH_3)_3C-O-O-C(CH_3)_3 \xrightarrow{120 - 140\ ^{o}C} 2\ (CH_3)_3C-O^{\bullet}$$

  - Diacyl peroxides

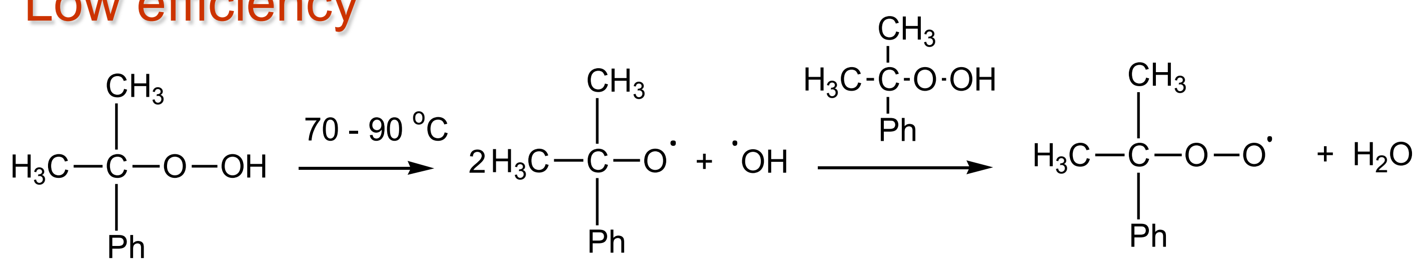


$$H_3C-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{70 - 90\ ^{o}C} 2\,H_3C-\overset{O}{\overset{\|}{C}}-O^{\bullet} \longrightarrow 2\ \dot{C}H_3 + 2\ CO_2$$

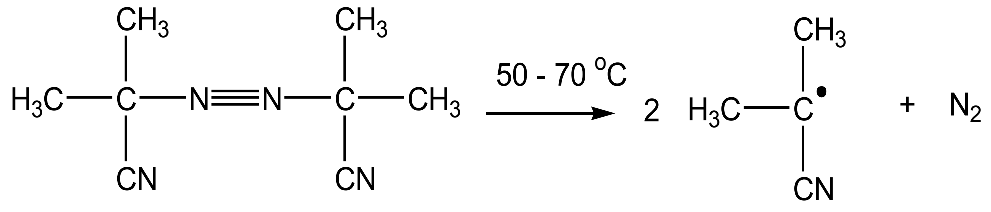
$$Ph-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{80 - 95\ ^{o}C} 2\ Ph-\overset{O}{\overset{\|}{C}}-O^{\bullet} \longrightarrow 2\ Ph^{\bullet} + 2\ CO_2$$

Thermal Initiators …2

- Hydroperoxides
  - Low efficiency



- Azo initiators
  - AIBN
    - Azobisisobutyronitrile



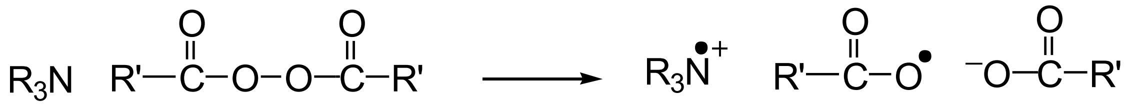
  - Others
    - R-N=N-R
    - R = Me (250°C), isopropyl (200°C), PhC(H)Me (110°C), Me_2(CN)C (60°C), Ph_2CH (30°C)

Redox Initiators

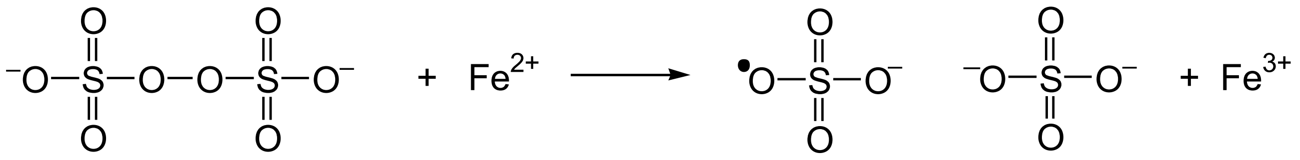
- Advantages
  - Lower temperatures
  - Good solubilities
  - High initiation efficiency
    - One mole radicals per mole initiator

$$HO{-}OH \quad + \quad Fe^{2+} \longrightarrow HO^{\bullet} \quad + OH^{-} \; + \; Fe^{3+}$$

$$RO{-}OH \quad + \quad Fe^{2+} \xrightarrow{15\text{ - }30^{o}C} RO^{\bullet} \quad + OH^{-} \; + \; Fe^{3+}$$



$$R_3N \quad R'{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}R' \longrightarrow R_3N^{\bullet +} \quad R'{-}\overset{O}{\overset{\|}{C}}{-}O^{\bullet} \quad {}^{-}O{-}\overset{O}{\overset{\|}{C}}{-}R'$$

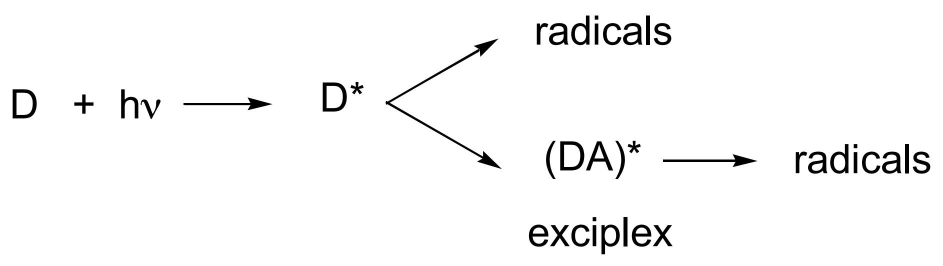


$${}^{-}O{-}\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}{-}O{-}O{-}\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}{-}O^{-} \quad + \quad Fe^{2+} \longrightarrow {}^{\bullet}O{-}\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}{-}O^{-} \quad {}^{-}O{-}\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}{-}O^{-} \quad + \quad Fe^{3+}$$

Photochemical Initiator

- Advantages
  - Spatially directed polymerization
  - Easy to turn on/off
  - Initiation rates can be controlled

- Absorb light > 300 – 350nm
  - Dye-sensitized



$$\mathrm{D} + h\nu \longrightarrow \mathrm{D}^*$$

$\mathrm{D}^* \longrightarrow$ radicals

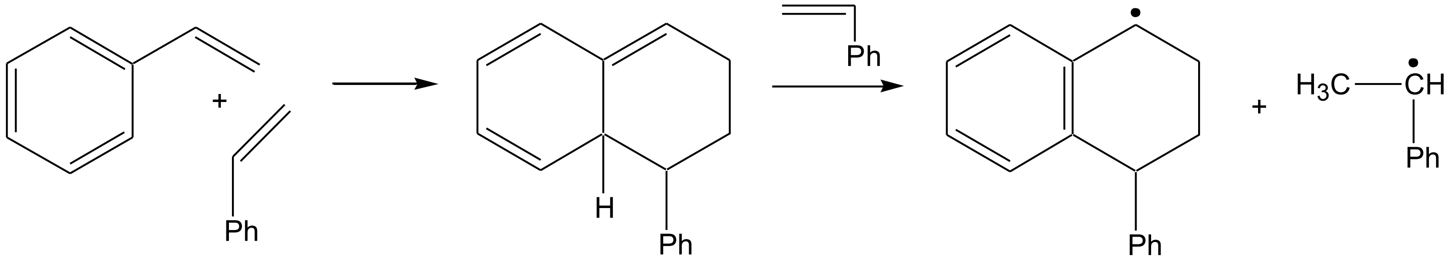
$\mathrm{D}^* \longrightarrow (\mathrm{DA})^* \longrightarrow$ radicals

exciplex

Radiation & Pure Thermal

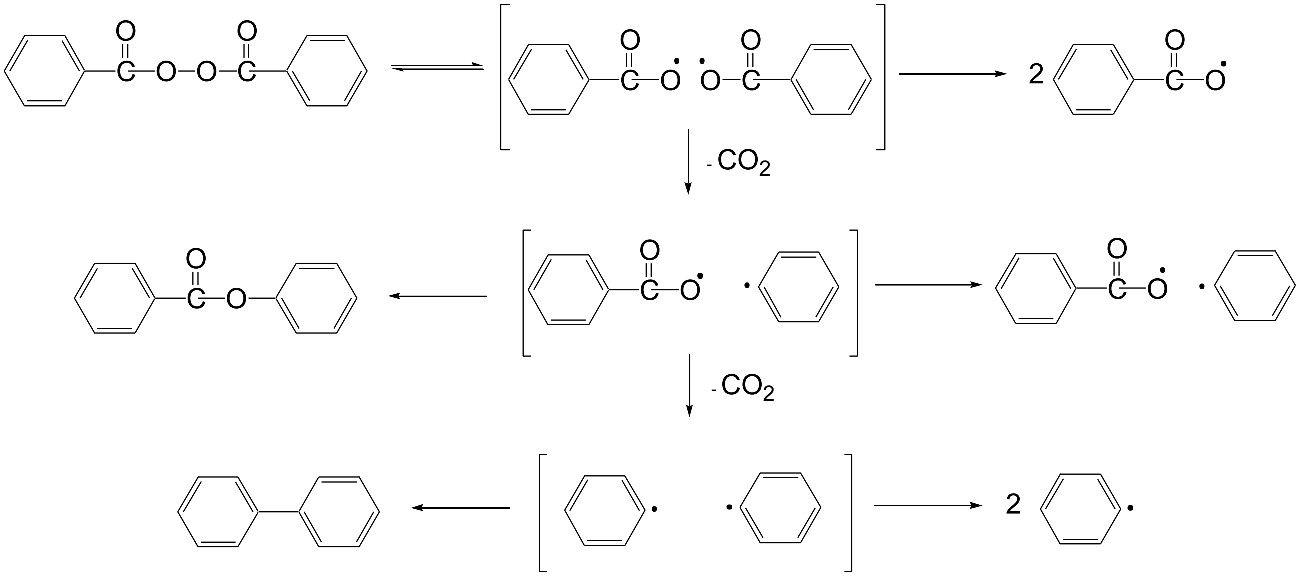
- Radiation
  - Neutrons, α-particles, β-rays, γ-rays, x-rays
  - Homolytic cleavage

- Pure thermal
  - Styrene



Initiation Efficiency

- Cage effect
  - *f* = initiator efficiency ~ 0.3 – 0.8
  - Dependent on conversion (viscosity)



- No cage effect for redox
  - One radical generated

Kinetics of Initiation

- Rate of initiation
  - Generation of radicals through thermal initiation
    - $R_d = 2\ f\ k_d\ [I]$
  - Rate of change in primary radical concentration
    - $d[R\bullet]/dt = 2\ f\ k_d\ [I] - k_i\ [R\bullet]\ [M] = 0$
      - Steady-state assumption
      - Assumes *f* is invariant
  - Rearranging for [R•]
    - $[R\bullet] = (2\ f\ k_d\ [I])/(k_i\ [M])$
  - Assume decomposition is slowest step:

$$\boxed{R_i = 2\ f\ k_d\ [I]}$$

Kinetics of Propagation

- Rate of propagation
  - $R_p = -d[M]/dt = k_p\,[M\bullet]\,[M]$
    - Assumes that monomer only consumed during propagation
  - $d[M\bullet]/dt = k_i\,[R\bullet]\,[M] - 2\,k_t\,[M\bullet]^2 = 0$
    - Assumes steady state for radical concentration
  - $2\,f\,k_d\,[I] - 2\,k_t\,[M\bullet]^2 = 0$
  - $[M\bullet] = (f\,k_d\,[I]\,/\,k_t)^{0.5}$

» $[M\bullet]$ = polymer radical conc.
» $[R\bullet]$ = primary radical conc.

$$\boxed{R_p = \frac{d\,[M]}{dt} = k_p\,[M]\sqrt{\frac{2\,f\,k_d\,[I]}{2\,k_t}}}$$

$$\boxed{R_p = \frac{d\,[M]}{dt} = k_p\,[M]\sqrt{\frac{R_i}{2\,k_t}}}$$

Rate of Polymerization

- Predictions:
  - 1st order in monomer
  - ½ order in initiator
- Plot of R_p vs. $[I]^{0.5}$
  - Linear
- Classical kinetics justified (?)

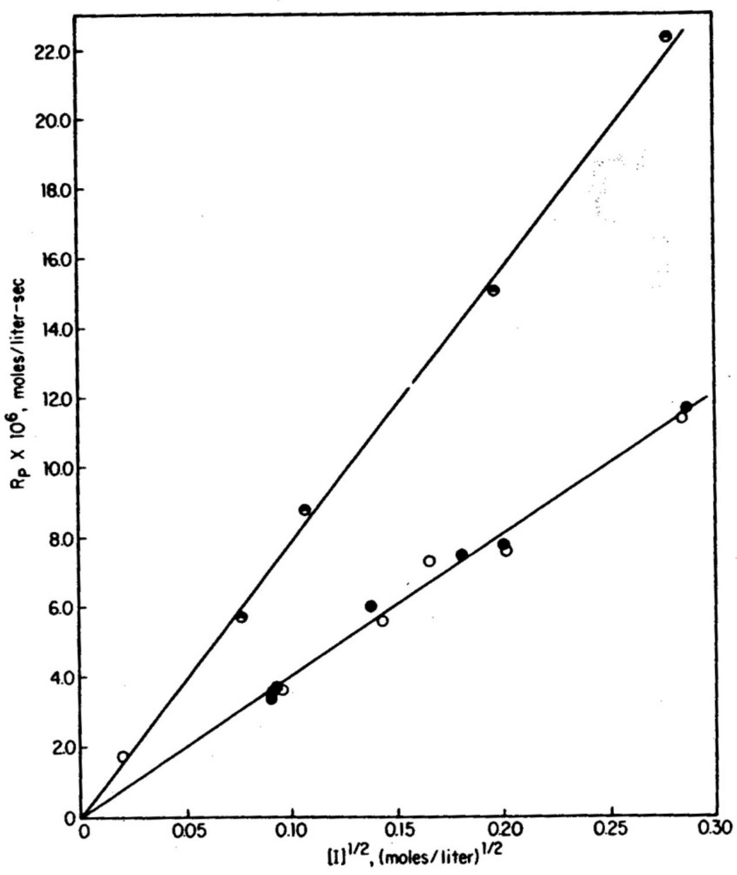


Fig. 3-3 Square-root dependence of the polymerization rate R_p on the initiator concentration [I]. ◐ = Methyl methacrylate, benzoyl peroxide, 50°C. After Schulz and Blaschke [1942] (by permission of Akademische Verlagsgesellschaft, Geest and Portig K.-G., Leipzig). ○, ● = Vinyl benzoate, azobisisobutyronitrile, 60°C. After Santee et al. [1964] and Vrancken and Smets [1959] (by permission of Huthig and Wepf Verlag, Basel).

G. Odian, *Principles of Polymerization*, 3rd edition, Wiley-Interscience, Hoboken, New Jersey.

Assumptions Made in Kinetic Analysis

- Propagation rate constant is constant
  - k_p is independent of chain length
- Termination rate constant is constant
  - k_t is independent of chain length
- Very long chains
  - Monomer only consumed in propagation
- One type of active site
  - Only head-to-tail addition
    - Otherwise (at least) 2 types of active sites
- Steady state
  - [M•] = constant (polymer)
  - [R•] = constant (primary)

Kinetics for Photoinitiation …1

- Rate of initiation
  - $R_i = 2\,\Phi\,I_a$
  - $I_a = I_0\,\varepsilon\,[A]\,b$
    - Φ = quantum yield for initiation
    - I_a = intensity of light absorbed
    - I_0 = intensity of incident light
    - ε = extinction coefficient of A
    - A = molecule absorbing light
    - b = total thickness of reaction flask
- If absorbance does not vary with thickness

$$R_p = k_p\,[M]\sqrt{\frac{R_i}{k_t}} = k_p\,[M]\sqrt{\frac{2\,\Phi\,I_a}{k_t}} = k_p\,[M]\sqrt{\frac{2\,\Phi\,\varepsilon\,I_0\,[A]\,b}{k_t}}$$

Kinetics for Photoinitiation …2

- If appreciable absorption
  - Beer-Lambert law
    - $I = I_0 \, (10^{-\varepsilon \, [A] \, b'})$
      - b' = distance into reaction flask
      - I = intensity at distance b' into flask
  - $I_a = I_0 - I$
  - Therefore: $R_p = k_p \, [M] \sqrt{\dfrac{2 \, \Phi \, I_0 \, (1 - 10^{-\varepsilon [A] b'})}{k_t}}$

Dead-End Polymerization

- Measures k_d
- Low [Initiator]
  - Initiator is consumed before polymerization is complete
    - p = extent of monomer conversion
    - p_∞ = limiting extent of monomer conversion

$$-\ln\left[1-\frac{\ln(1-p)}{\ln(1-p_\infty)}\right]=\frac{k_d t}{2}$$

  - Plot LHS vs. time gives k_d as slope

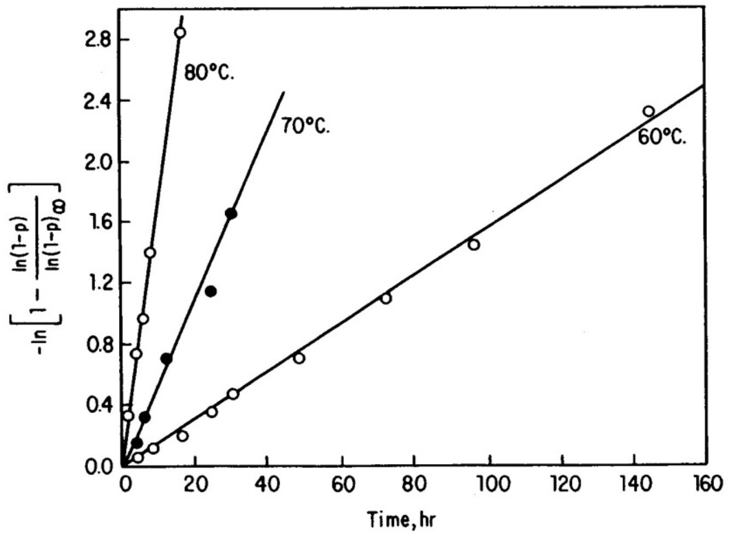


Fig. 3-6 Dead-end polymerization of isoprene initiated by azobisisobutyronitrile. After Gobran et al. [1960] (by permission of Wiley-Interscience, New York).

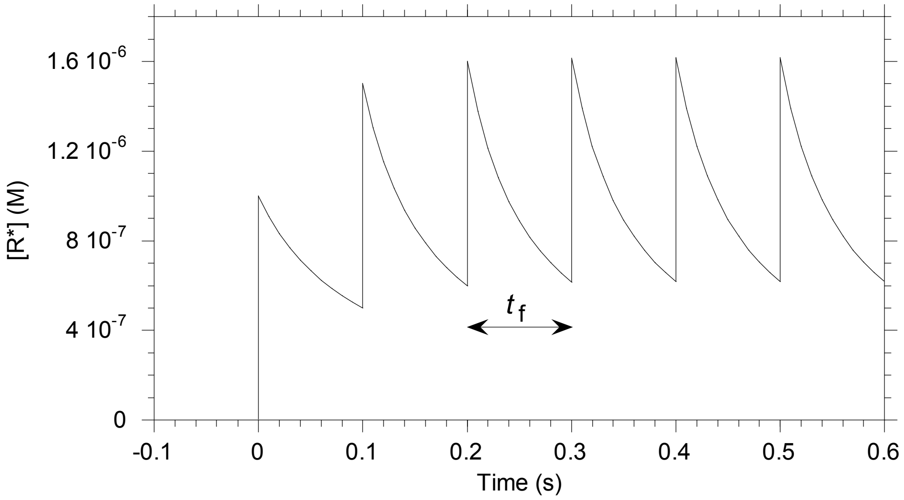
G. Odian, *Principles of Polymerization*, 3rd edition, Wiley-Interscience, Hoboken, New Jersey.

Non-Steady State Kinetics

- Steady state kinetics
  - Gives coupled form of (k_p^2/k_t)
- Non-steady state kinetics
  - Gives coupled form of (k_p/k_t)
- Combine both methods
  - Gives k_p and k_t individually
- Rotating sector method
  - Most common non-steady state method (until recently)
  - Determines average lifetime of a growing radical (τ_s)
  - Complex analysis yields (k_p/k_t)

Pulsed Laser Polymerization …1

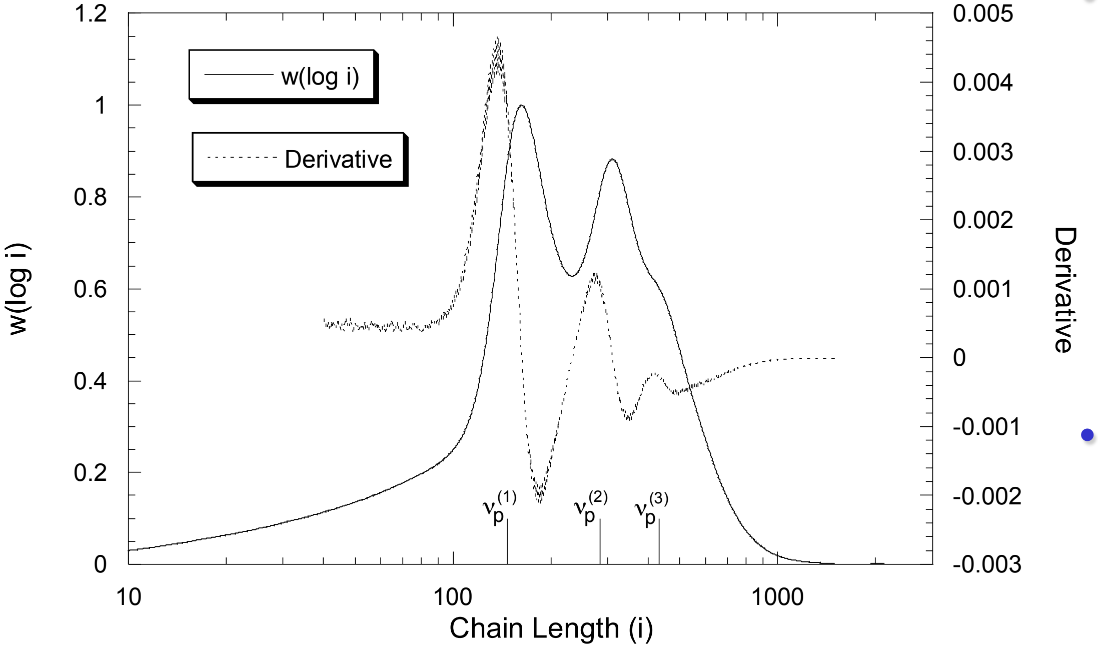
- Obtains k_p by itself
- Periodic initiation established by laser flashes
  - Initiation effectively instantaneous (10 ns)



- Propagation occurs between pulses
- Most termination occurs at time of laser pulses
  - Chains tend to start growth at laser pulse and terminate at a subsequent pulse

Pulsed Laser Polymerization …2

- Average time for a propagation event
  - Avg. time = $1/(k_p[M])$
- Number of propagation events in time t_f
  - $\nu_p = k_p [M] t_f$
- Measure ν_p from GPC, know t_f & [M] (low conversion)
  - Estimate k_p



- From PLP of MMA
  - From $\nu_p^{(1)}$
    - $k_p = 331\ M^{-1}s^{-1}$
  - From $\nu_p^{(2)}$
    - $k_p = 328\ M^{-1}s^{-1}$
  - From $\nu_p^{(3)}$
    - $k_p = 329\ M^{-1}s^{-1}$
- Lit. value
    - $k_p = 323\ M^{-1}s^{-1}$

Termination Rates

- Radical-radical termination
  - Fast; usually diffusion-controlled
  - k_t ~10^6 – 10^9 $M^{-1}s^{-1}$
    - low conversion & viscosity
  - k_t decreases with monomer conversion
    - From ~10^9 to 10^2 or less

- No method of unambiguously determining k_t
  - Viscosity dependent
  - Chain length dependent
    - $k_t(i,j)$ where i, j = radical chain lengths

How k_t Varies During Polymerization

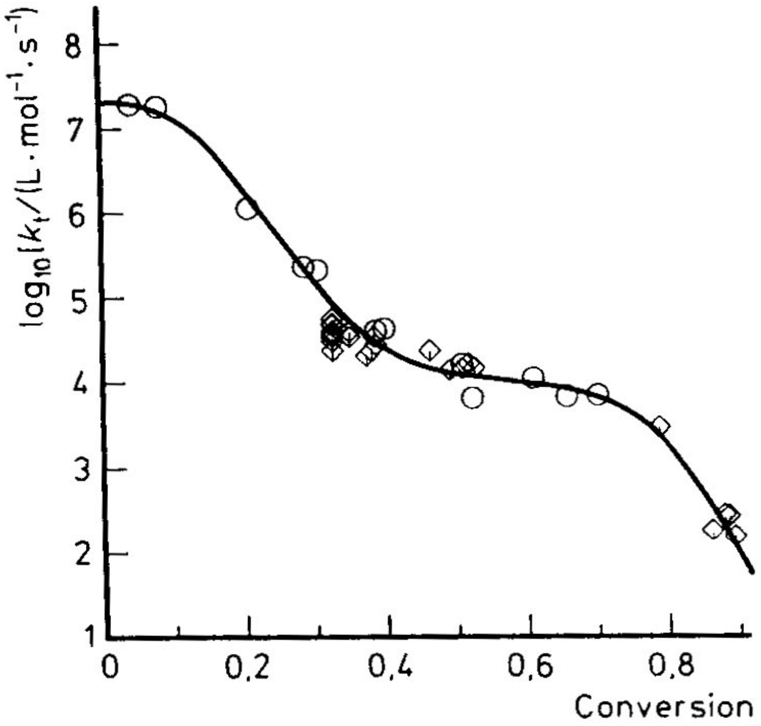


Fig. 6. Conversion dependence of k_t for the free-radical polymerization of methyl methacrylate. The experimental data are: (○) from ref. [8] (for 0°C) and (◇) from ref. [9] (for 50°C). The full line represents k_t from Eq. (11) with the rate coefficients and kinetic parameters given in the text

M. Buback *Macromol. Chem. Phys.* **1990**, *191*, 1575-1587.

Termination Chemistry

- Two mechanisms
  - Combination (or coupling)
  - Disproportionation

- Proportions of both depend on monomer

	%D	%C
– Acrylonitrile	~0	~100
– Styrene	~10	~90
– Vinyl acetate	~10	~90
– MMA	~60	~40

  - More H’s available ⇒ more disproportionation

Kinetic Chain Length

- Kinetic chain length = ν
  - Number of monomer molecules per radical
  - $\nu = R_p / R_i = R_p / R_t$ (steady state)

$$\nu = \frac{k_p[\mathrm{M}]}{2k_t[\mathrm{radical}]} = \frac{k_p{}^2[\mathrm{M}]^2}{2k_t R_p}$$

  - For thermolysis:

$$\nu = \frac{k_p[\mathrm{M}]}{2(fk_d k_t[\mathrm{I}])^{1/2}}$$

  - Increase R_p (through increase [radical])
    - Decrease in ν

Molecular Weights …1

- Average degrees of polymerization
  - Dependent on mode of termination
    - Disproportionation
    - Combination

- Define:
  - p = probability of propagation over termination or transfer

$$p = \frac{R_p}{R_p + R_{tr} + R_t}$$

Molecular Weights …2

- Disproportionation
  - X_n = number average degree of polymerization = ν

$$X_n = \frac{1}{1-p} \qquad X_w = \frac{1+p}{1-p}$$

$$\frac{X_w}{X_n} = 1+p$$

- Combination
  - $X_n = 2\nu$

$$X_n = \frac{2}{1-p} \qquad X_w = \frac{2+p}{1-p}$$

$$\frac{X_w}{X_n} = \frac{2+p}{2}$$

Chain Transfer …1

- Transfer may occur to:
  - Monomer (M)
  - Polymer (P)
  - Solvent (S)
  - Impurity
  - Chain transfer agent (A)

$$M_n^{\bullet} + XA \xrightarrow{k_{tr}} M_n\text{-}X + A^{\bullet}$$

$$A^{\bullet} + M \xrightarrow{k_a} M_1^{\bullet}$$

Case	**Relative Rates**		**Effect**	**R_p**	**X_n**
1	$k_p >> k_{tr}$	$k_a \sim k_p$	Normal	None	↓
2	$k_p << k_{tr}$	$k_a \sim k_p$	Oligomerization	None	Large ↓
3	$k_p >> k_{tr}$	$k_a < k_p$	Retardation	↓	↓
4	$k_p << k_{tr}$	$k_a < k_p$	Degradative Chain Transfer	Large ↓	Large ↓

Chain Transfer …2

- Transfer constants = *C*
  - Defined by the ratio of k_{tr}/k_p for a particular transfer agent

    E.g. monomer ($C_M=k_{tr,M}/k_p$), solvent ($C_S=k_{tr,S}/k_p$), etc.

- Redefine X_n:
  - Rate of polymerization divided by all chain-terminating processes

$$X_n = \frac{R_p}{R_t + R_{tr,M} + R_{tr,S} + \ldots.}$$

$$= \frac{k_p[M\cdot][M]}{k_{tc}[M\cdot]^2/2 + k_{tr,M}[M\cdot][M] + k_{tr,S}[M\cdot][S] + \ldots.}$$

  - Then rearrange ……

Chain Transfer …3

- After rearranging …

$$\frac{1}{X_n} = \frac{k_t[M\cdot]}{2k_p[M]}\left(\frac{k_p[M]}{k_p[M]}\right) + \frac{k_{tr,M}}{k_p} + \frac{k_{tr,S}[S]}{k_p[M]} + \ldots$$

$$\boxed{\frac{1}{X_n} = \frac{k_t R_p}{k_p{}^2[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{k_t R_p^2}{k_p{}^2 f k_d [M]^3}}$$

- For transfer to monomer
  - $C_S[S]/[M]$ & other terms vanish
  - Plot $1/X_n$ vs. R_p
    - Intercept yields C_M
    - Slope yields k_p^2/k_t

Chain Transfer …4

- Added transfer agent (A)
  - Dominates any transfer events
- Mayo equation:

$$\frac{1}{X_n} = \left(\frac{1}{X_n}\right)_0 + C_A \frac{[A]}{[M]}$$

  - $(1/X_n)_0$ = value of $(1/X_n)$ in absence of A
  - Plot $1/X_n$ vs. [A]/[M]
    - Slope = C_S

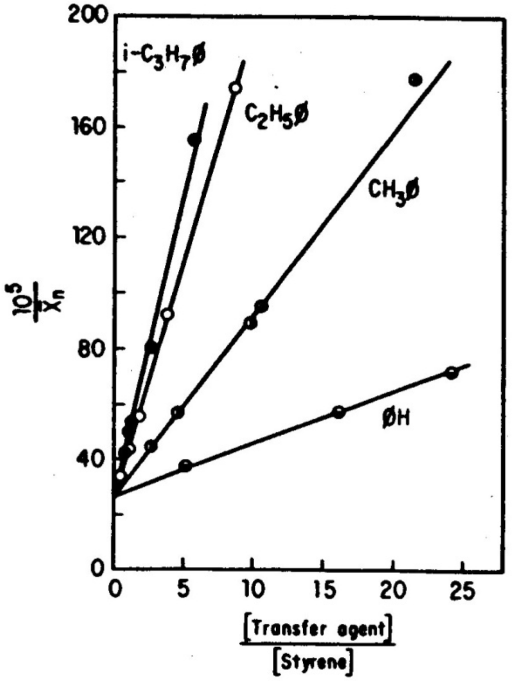


Fig. 3-10 The effect of various chain-transfer agents on the degree of polymerization of styrene at 100°C. After Gregg and Mayo [1948] (by permission of American Chemical Society, Washington, D.C.).

G. Odian, *Principles of Polymerization*, 3rd edition, Wiley-Interscience, Hoboken, New Jersey.

Transfer Agents & Constants

- Transfer agents and constants for styrene polymerization at 60°C

Transfer Agent	**C_A**
Benzene	1.0×10^{-6}
Toluene	1.05×10^{-5}
Butyl alcohol	6.0×10^{-6}
t- Butyl alcohol	6.7×10^{-4}
CBr_4	1.8
CCl_4	8.4×10^{-3}
$CHCl_3$	5×10^{-5}
1-Octanethiol	19
Triethylamine	1.4×10^{-4}
Water	0

  - Alkyl thiols often used to control molecular weight

Gel Effect - Autoacceleration

- Expect rate to decrease with time
  - Monomer is consumed
    - $R_p = k_p$ [M•] [M]
- But, rate usually increases
- Cause
  - Decrease in k_t
    - Diffusion-controlled process
  - R_p increases

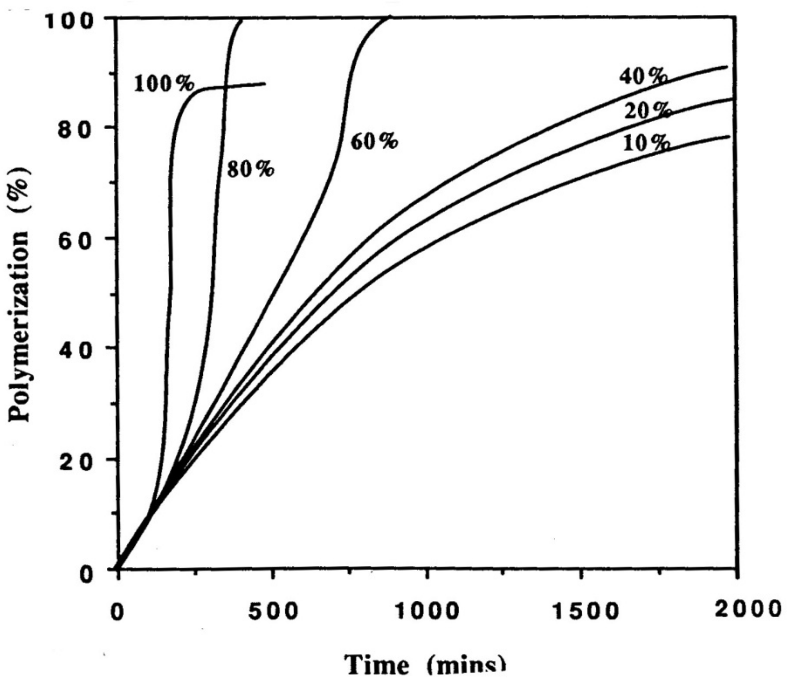
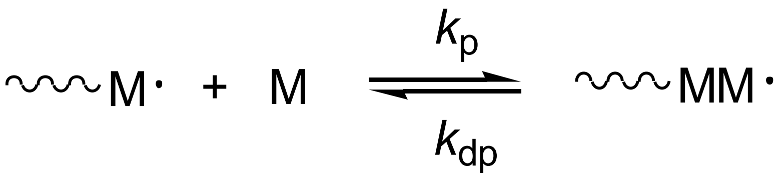


Figure 3.4 *Plot of conversion vs time, for the free radical polymerization of methyl methacrylate at 50°C using benzoyl peroxide at various concentrations in benzene. Redrawn from the data of G.V. Schulz and G. Harborth,* Macromol. Chem., **1** *106 (1967).*

$$R_p = \frac{d\,[M]}{dt} = k_p\,[M]\sqrt{\frac{R_i}{2\,k_t}}$$

Ceiling Temperature

- Propagation as an equilibrium



  - $\Delta G = \Delta G^o + RT \ln K$
    - $K = k_p/k_{dp} = [\sim\sim MM\bullet]/[\sim\sim M\bullet][M] = 1/[M]$

- At equilibrium ($\Delta G = 0$)
  - $\Delta H^o + T\Delta S^o = -RT \ln K$

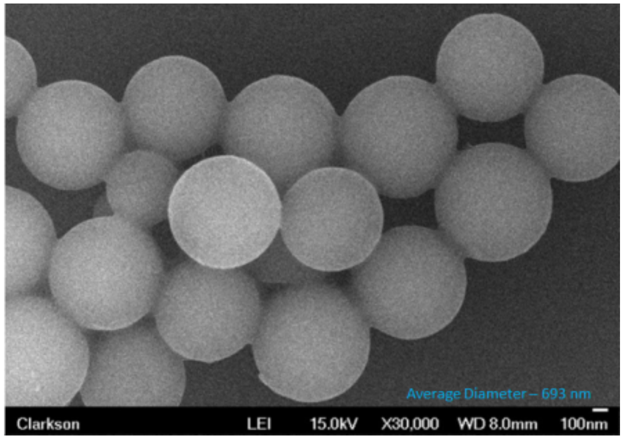
$$T_c = \frac{\Delta H^o}{\Delta S^o + R\ln[M]_c} \qquad \ln[M]_c = \frac{\Delta H^o}{RT_c} - \frac{\Delta S^o}{R}$$

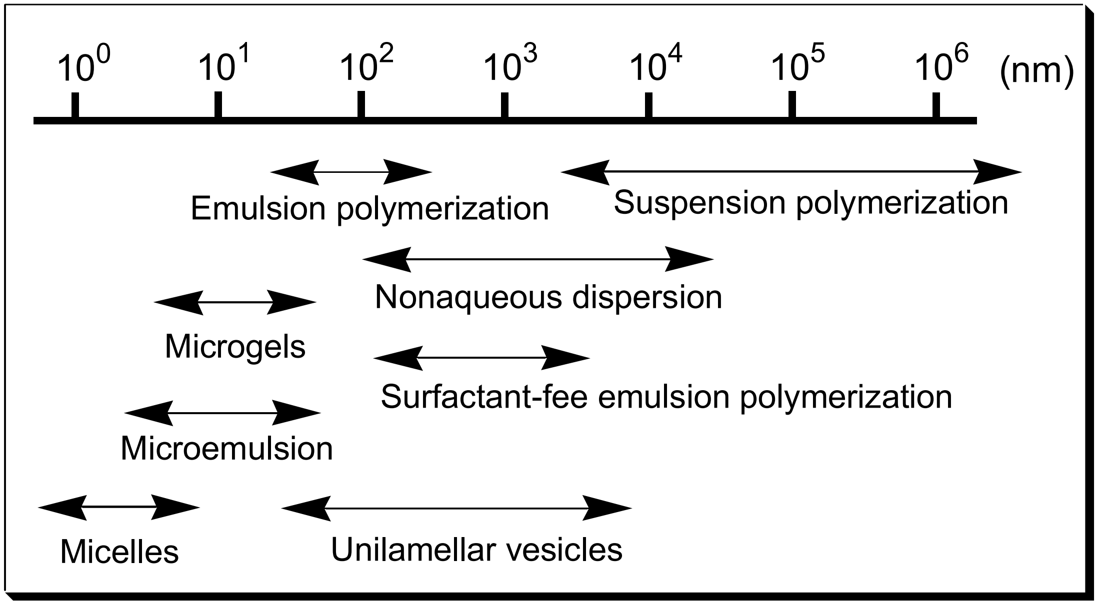
  - T_c = ceiling temperature
  - $[M]_c$ = equilibrium monomer conc.

- For α-methyl styrene
  - Neat, $T_c = 61^oC$
  - $T = 25^oC$, $[M]_c = 2.2$ M

Heterogeneous Radical Polymerizations

- Particle-forming polymerizations
  - Emulsion polymerizations
    - Mini-emulsion, micro-emulsion and emulsion
  - Dispersion polymerizations
  - Suspension polymerizations





10^0 10^1 10^2 10^3 10^4 10^5 10^6 (nm)

Emulsion polymerization

Suspension polymerization

Nonaqueous dispersion

Microgels

Surfactant-fee emulsion polymerization

Microemulsion

Micelles

Unilamellar vesicles

Heterogeneous Polymerization …1

- Advantages
  - Bulk – batch
    - Reduces effect of impurities
  - Bulk – continuous
    - Better temperature control
  - Solution
    - Temperature control
  - Suspension
    - Temperature control
    - Low viscosity
    - Isolation
    - Size control
  - Emulsion
    - Temperature control
    - Low viscosity
    - Latex product
    - High molecular weight & polymerization rate

Heterogeneous Polymerization …2

- Disadvantages
  - Bulk – batch
    - Temperature control difficult
    - High viscosity
    - Incomplete conversion possible
  - Bulk – continuous
    - Isolation
    - Agitation required
    - Recycling
  - Solution
    - Isolation
    - Chain transfer to solvent
    - Solvent removal
  - Suspension
    - Agitation required to maintain suspension
    - Washing, drying
    - Removal of suspending agents (stabilizers)
  - Emulsion
    - Sensitive to impurities
    - Removal of emulsifier maybe required
    - Cost

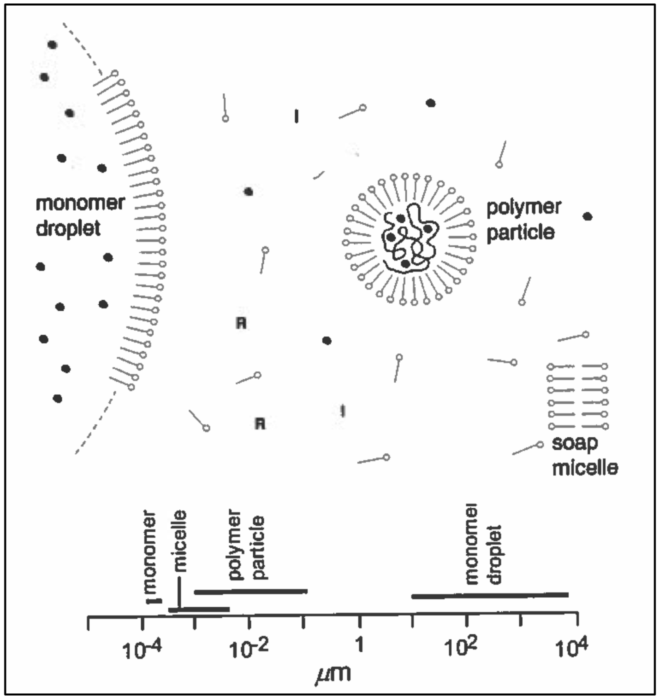
Suspension vs. Emulsion

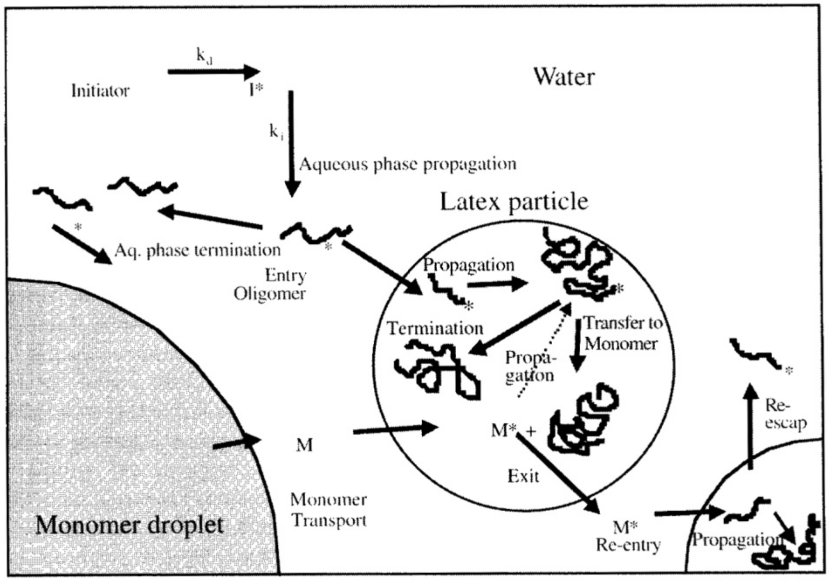
- Comparison of suspension and emulsion polymerizations

Suspension		Emulsion	
Monomer	35.7	Monomer	32.8
H_2O	64.2	H_2O	65.6
Poly(vinyl alcohol)	0.0143	$H(CH_2)_7CO_2^-NH_4^+$	1.64
Laurel peroxide	0.0714	$K_2S_2O_8$	0.0328
Size of monomer droplet (ϕ)	0.1-5 mm	Size of monomer droplet (ϕ)	10^{-4} mm (100nm)

Weight %

Emulsion Polymerizations





- Nucleation
  - Micellar
    - Radicals from H_2O into micelle
  - Homogeneous
    - Polymer radicals precipitate from H_2O

J. R. Fried, *Polymer Science & Technology*, 3rd edition, Pearson Education, Upper Saddle River, New Jersey.

Suspension Polymerization

- Monomer
  - Discontinuous suspension in a continuous phase (usually water)
- Initiators
  - Monomer-soluble
- Surfactants
  - Determine monomer droplet size
  - Control agglomeration
- Polymerizing droplets
  - Diameter of 50 – 500 micron
  - Heat removed easily
- Monomers
  - Styrene/divinyl benzene
  - Vinyl chloride, vinyl acetate
  - Methacrylic esters
  - Tetrafluoro ethylene
    - Homo- and co-polymers

Mini- & Micro-Emulsions, Precipitation

- Mini-emulsion polymerization
  - Similar to emulsions but droplet nucleation
- Micro-emulsion polymerization
  - An emulsion that is thermodynamically stable
  - Usually particles are 10-50 nm
- Precipitation polymerization

Dispersion Polymerizations

- Monomer
  - Homogeneous monomer phase in solvent (usually water)
  - Polymer is insoluble in solvent, therefore becomes heterogeneous
- Initiators
  - Monomer-soluble
- Surfactants
  - Stabilize polymer particles
  - Control agglomeration
- Polymerizing particles
  - Diameter of 1– 10 micron
  - Heat removed easily
- Monomers
  - Vinyl acetate
  - Methacrylates, acrylates
    - Homo- and co-polymers