Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 6 - Mechanism and Kinetics of Free Radical Chain Polymerization

January 29, 2001

Outline

- Mechanism of Radical Chain Polymerization
  - Fundamental steps (initiation, propagation, termination)
  - Kinetic chain length and molecular weight
- Chain Transfer
- Energetic Characteristics
  - Activation energies and frequency factors
  - Rate of polymerization
  - Degree of polymerization
- Autoacceleration

General Comments on Chain Reactions

- Polymerization is possible only if **ΔG < 0** for the transformation of monomer to polymer. This will depend only upon the initial and final states, not the nature of the intermediate (free radical, anion, cation).

- Substituents on a vinyl group will influence reactivity through **inductive, resonance,and steric effects**.

- Susceptibility to a particular chain mechanism depends on the degree of **stabilization of the propagating center**.

- **Radicals are "free" species**, but anionic and cationic end groups have counterions that influence reactivity.

- **High polymer is formed immediately** in a chain reaction. Increasing the reaction time simply increases the amount of high polymer produced.

Effect of Substituents on Chain Mechanism

Monomer	**Radical**	Anionic	Cationic	Hetero.
Ethylene	+	-	+	+
Propylene	-	-	-	+
1-Butene	-	-	-	+
Isobutene	-	-	+	-
1,3-Butadiene	+	+	-	+
Isoprene	+	+	-	+
Styrene	+	+	+	+
Vinyl chloride	+	-	-	+
Acrylonitrile	+	+	-	+
Methacrylate esters	+	+	-	+

- Almost all substituents allow resonance delocalization.
- Electron-withdrawing substituents lead to anionic mechanism.
- Electron-donating substituents lead to cationic mechanism.
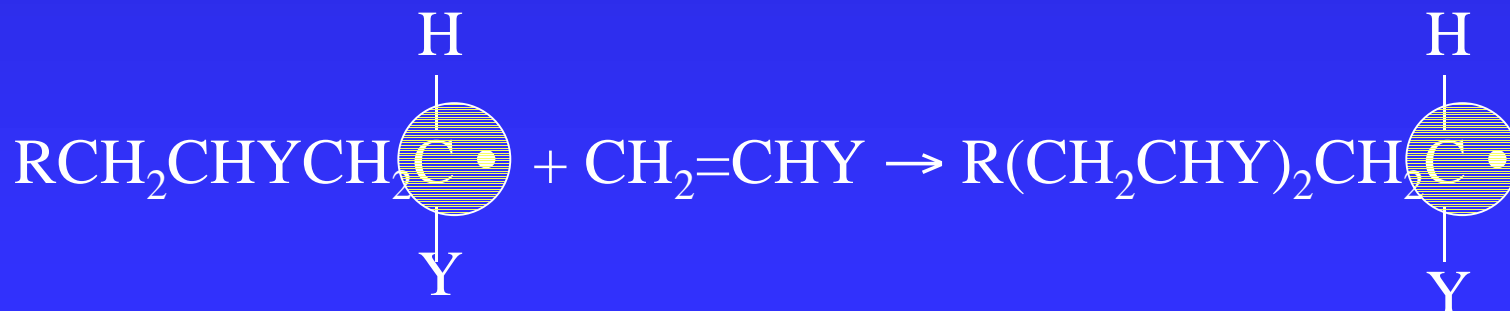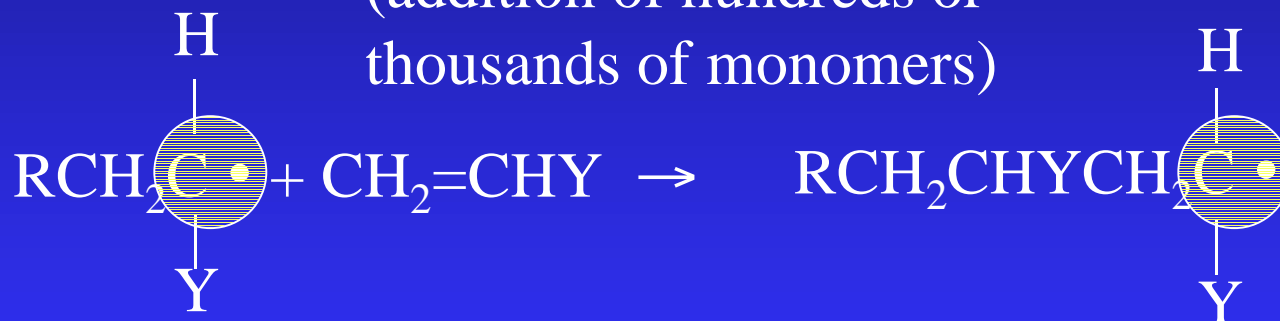
Mechanism of Radical Chain Polymerization

Initiation: (thermal or photochemical bond cleavage)

slow $\quad I \xrightarrow{k_d} 2R \bullet$
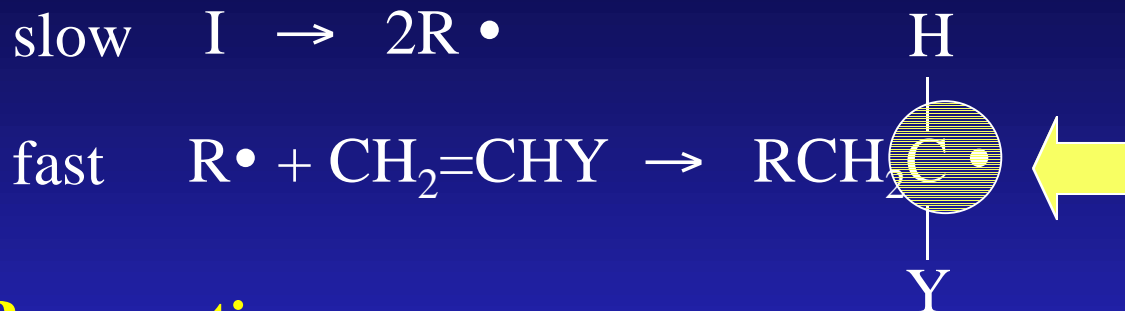
fast $\quad R\bullet + CH_2=CHY \rightarrow RCH_2\overset{\displaystyle H}{\underset{\displaystyle Y}{C}}\bullet$ ⬅ always the same identity and reactivity for head-to-tail reaction

Propagation: (addition of hundreds or thousands of monomers)

$RCH_2\overset{\displaystyle H}{\underset{\displaystyle Y}{C}}\bullet + CH_2=CHY \rightarrow RCH_2CHYCH_2\overset{\displaystyle H}{\underset{\displaystyle Y}{C}}\bullet$

$RCH_2CHYCH_2\overset{\displaystyle H}{\underset{\displaystyle Y}{C}}\bullet + CH_2=CHY \rightarrow R(CH_2CHY)_2CH_2\overset{\displaystyle H}{\underset{\displaystyle Y}{C}}\bullet$
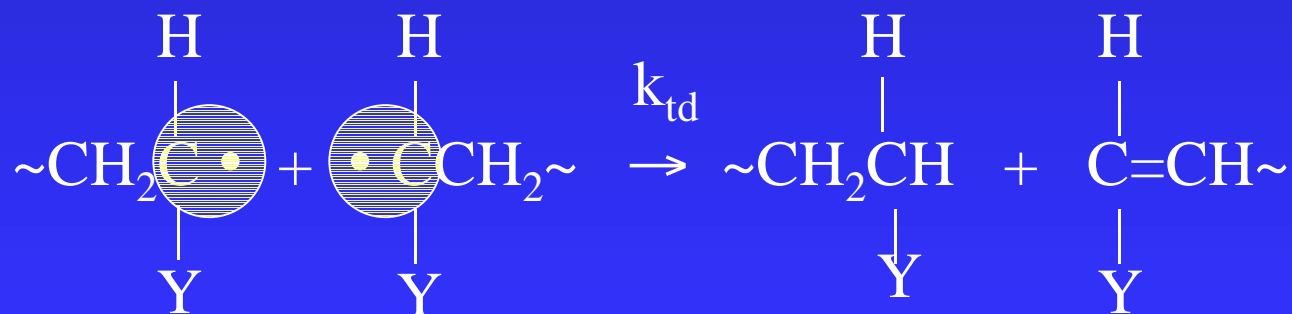
Mechanism of Radical Chain Polymerization

Termination: (Reactions are similar for radical and cationic.)
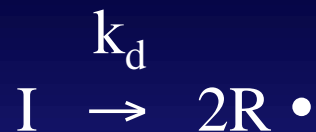
Coupling (molecular weight is effectively doubled)

$$\sim CH_2\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}}\cdot \ + \ \cdot \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}}CH_2\sim \ \xrightarrow{k_{tc}} \ \sim CH_2\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}}\text{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}}CH_2\sim$$
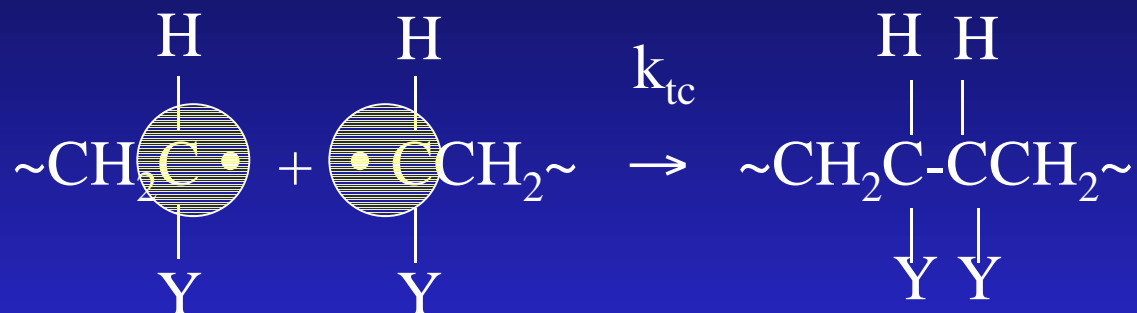
Disproportionation (molecular weight is unchanged)

$$\sim CH_2\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}}\cdot \ + \ \cdot \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}}CH_2\sim \ \xrightarrow{k_{td}} \ \sim CH_2\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Y}{|}}{C}}H \ + \ \overset{\overset{\displaystyle H}{|}}{C}=CH\sim$$

Most anionic reactions have no inherent termination step.

Mechanism of Radical Chain Polymerization

Initiation:

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

$$-\frac{d[I]}{dt} = R_i = k_d[I]$$

Azonitriles:

$$M_n \bullet + RN{=}NR \rightarrow M_nR + N_2 + R \bullet$$

Peroxides:

$$M_n \bullet + RO{-}OR \rightarrow M_nOR + RO \bullet$$

Propagation:

$$M_n \bullet + M \xrightarrow{k_p} M_{n+1} \bullet \qquad k_p \sim 10^2 - 10^4 \text{ liter/mole sec}$$

$$-\frac{d[M]}{dt} = R_p = k_p[M\bullet][M]$$

Termination:

$$M_n \bullet + M_m \bullet \xrightarrow{k_t} \text{dead polymer}$$
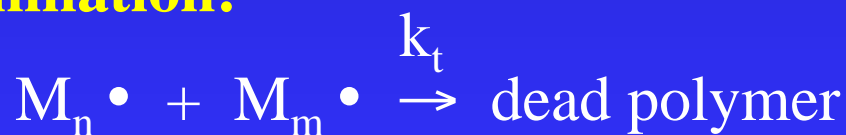
$$[M \bullet] \sim 10^{-7} - 10^{-9} \text{ mole/liter}$$

$$k_t \sim 10^6 - 10^8 \text{ liter/mole sec}$$

$$k_t = k_{tc} + k_{td}$$

$$R_t = 2k_t[M\bullet]^2$$

Note: $[M+]$, $[M-] \sim 10^{-2} - 10^{-3}$ mole/liter

Magnitudes of Reaction Parameters

TABLE 3-10 Reaction Parameters in Radical Chain Polymerization

Quantity	Units	General Range of Values	Methacrylamide Photopolymerization[a]
R_i	moles/liter-sec	10^{-8}–10^{-10}	8.75×10^{-9}
k_d	sec^{-1}	10^{-4}–10^{-6}	—
[I]	moles/liter	10^{-2}–10^{-4}	3.97×10^{-2}
$[M\cdot]_s$	moles/liter	10^{-7}–10^{-9}	2.30×10^{-8}
$(R_p)_s$	moles/liter-sec	10^{-4}–10^{-6}	3.65×10^{-6}
[M]	moles/liter	10–10^{-1}	0.20
k_p	liters/mole-sec	10^2–10^4	7.96×10^2
R_t	moles/liter-sec	10^{-8}–10^{-10}	8.73×10^{-9}
k_t	liters/mole-sec	10^6–10^8	8.25×10^6
τ_s	sec	10^{-1}–10	2.62
k_p/k_t	none	10^{-4}–10^{-6}	9.64×10^{-5}
$k_p/k_t^{1/2}$	(liters/mole-sec)$^{1/2}$	1–10^{-2}	2.77×10^{-1}

[a]Values are taken directly or recalculated from Dainton and Sisley [1963].

G. Odian, Principles of Polymerization, 3rd Ed., 1991, p 274.

Rate of Polymerization

Define the rate of polymerization based upon monomer loss.

$$-\frac{d[M]}{dt} = \cancel{R_i} + R_p$$

$$\sim 0$$

$$-\frac{d[M]}{dt} = R_p = k_p[M\bullet][M]$$

Assume that k_p and k_t are independent of size of radical.

Steady-state assumption: The net rate of production of free radicals is zero so that the initiation and termination rates are equal. This is usually true after about 1 minute reaction.

$$R_i = R_t = 2k_t[M\bullet]^2$$

$$[M\bullet] = \left(\frac{R_i}{2k_t}\right)^{1/2}$$

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2}$$

Rate of Initiation

Unimolecular decomposition:

$$[I] = [I_o] \exp(-k_d t)$$

$$-\frac{d[I]}{dt} = R_d = k_d[I]$$

$$\ln \frac{[I]_o}{[I]} = k_d t$$

Half life:

$$t_{1/2} = \frac{1}{k_d} \ln \frac{[I]_o}{[I]_o/2} = \frac{0.693}{k_d}$$

In actual reactions, not all initiator decompositions are effective in initiating polymerization. An efficiency factor f is introduced to account for this. ⇒

$$R_d = 2fk_d[I]$$

$$R_i = R_d$$

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2}$$

$$R_p = k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{1/2}$$

Kinetic Chain Length

ν = average number of monomer molecules consumed for each radical that initiates a polymer chain

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t}$$

$$\nu = \frac{k_p[M][M\bullet]}{2k_t[M\bullet]^2} = \frac{k_p[M]}{2k_t[M\bullet]}$$

$$R_p = k_p[M\bullet][M]$$ $\Longrightarrow$ $$\nu = \frac{k_p^{\,2}[M]^2}{2k_t R_p}$$

For initiation by thermal homolysis:

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

Typically, the initiator efficiency f is about 0.5.

Relationship Between Kinetic Chain Length and Molecular Weight

Coupling:

This is the most common mode for styrene, methyl acrylate, and acrylonitrile.

$$\overline{X}_n = 2\nu$$

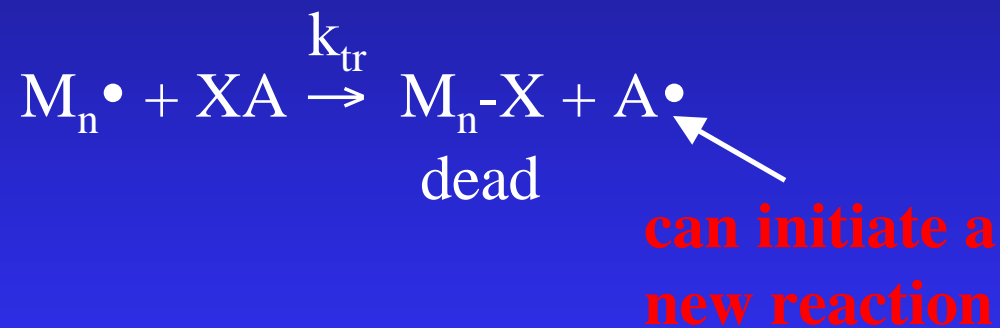(true only if there is no chain transfer)

Disproportionation:

Methyl methacrylate (MMA) has a combination of coupling and disproportionation. At 70 °C, MMA termination is almost 100% by disproportionation.

$$\overline{X}_n = \nu$$

(true only if there is no chain transfer)

Chain Transfer

Chain transfer is a **chain breaking** reaction leading to a decrease in the size of the propagating polymer chain. The **active center is transferred** from the growing chain to a different species (chain transfer agent, initiator, monomer, or polymer). The new species may initiate polymerization or may truncate it.

$$M_n\bullet + XA \xrightarrow{\text{k}_{tr}} M_n\text{-}X + A\bullet$$

dead

can initiate a new reaction

$$A\bullet + M \xrightarrow{\text{k}_a} M\bullet$$

$$R_{tr} = k_{tr}[M\bullet][XA]$$

Effect of Chain Transfer on Molecular Weight

Use the **kinetic chain length** approach to obtain the ratio of the polymerization rate to the sum of all termination rates:

$$\overline{X}_n = \frac{R_p}{\left(\dfrac{R_t}{2}\right) + k_{trM}[M\bullet][M] + k_{trS}[M\bullet][S] + k_{trI}[M\bullet][I]}$$

Define **chain transfer constants**:

$$C_M \equiv \frac{k_{trM}}{k_p} \qquad C_S \equiv \frac{k_{trS}}{k_p} \qquad C_I \equiv \frac{k_{trI}}{k_p}$$

$$\frac{1}{\overline{X}_n} = \frac{2R_p}{R_i} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]}$$

$$\frac{1}{\overline{X}_n} = \frac{k_t R_p}{k_p^{\,2}[M]^2} + C_M + C_S\frac{[S]}{[M]} + C_I\frac{k_t R_p^{\,2}}{k_p^{\,2} f k_d [M]^3}$$

Chain Transfer to Polymer

Consider a terminal free radical of polyethylene:

6   5   4 ⟵   Size of side chain after backbiting

$$\sim CH_2CH_2CH_2CH_2 \qquad \overset{\bullet}{C}H_2$$

$$CH_2 \qquad CH_2$$

$$CH_2$$

Short branches decrease crystallinity and are 20 - 50 times more prevalent than long branches. A typical polyethylene has 5 n-butyl branches and 1 - 2 each of ethyl, n-amyl, and n-hexyl branches per 1000 carbons.

Long branches, formed by normal chain transfer to polymer, **affect melt flow** properties.

Transfer to Chain Transfer Agent

$$\frac{1}{\overline{X}_n} = \left(\frac{1}{\overline{X}_n}\right)_o + C_S \frac{[S]}{[M]} \qquad \left(\frac{1}{\overline{X}_n}\right)_o = \frac{k_t R_p}{k_p^{\ 2}[M]^2} + C_M + C_I \frac{k_t R_p^{\ 2}}{k_p^{\ 2} f k_d [M]^3}$$

- Strong C-H bonds of aliphatics lead to small C_S.
- Acids, carbonyls, ethers, amines, and alcohols have higher C_S values than aliphatics due to stabilization by O, N, C=O.
- Weak S-S bonds lead to large C_S.
- Carbon-halogen bonds are very weak, with excellent radical stabilization.
- **Thiols** have the highest C_S due to the weak S-H bond.

Energetic Characteristics:
Activation Energies and Frequency Factors

Assume that all rate constants (k_d, k_p, k_t) are Arrhenius-like.

$$k = A\exp(-\frac{E}{RT})$$

A = frequency factor
E = activation energy

TABLE 3-12 Thermal Decomposition of Initiators[a,b,c]

Initiator	$k_d \times 10^5$	T (°C)	E_d
2,2'-Azobisisobutyronitrile	0.845	60	123.4
Acetyl peroxide	2.39	70	136.0
Benzoyl peroxide	5.50	85	124.3
Cumyl peroxide	1.56	115	170.3
t-Butyl peroxide	3.00	130	146.9
t-Butyl hydroperoxide	0.429	155	170.7

[a]All data are for decompositions in benzene solution.
[b]Data from Brandrup and Immergut [1989].
[c]The units of k_d are sec^{-1}; the units of E_d are kJ/mole.

G. Odian, Principles of Polymerization, 3rd Ed., 1991, p 277.

Energetic Characteristics:
Activation Energies and Frequency Factors

TABLE 3-11 Kinetic Parameters in Radical Chain Polymerization[a,b,c,d]

Monomer	$k_p \times 10^{-3}$	E_p	$A_p \times 10^{-7}$	$k_t \times 10^{-7}$	E_t	$A_t \times 10^{-9}$
Vinyl chloride (50°C)	11.0	16	0.33	210	17.6	600
Tetrafluoroethylene (83°C)	9.10	17.4	—	—	—	—
Vinyl acetate	2.30	18	3.2	2.9	21.9	3.7
Acrylonitrile	1.96	16.2	—	7.8	15.5	—
Methyl acrylate	2.09	29.7	10	0.95	22.2	15
Methyl methacrylate	0.515	26.4	0.087	2.55	11.9	0.11
2-Vinylpyridine	0.186	33	—	3.3	21	—
Styrene	0.165	26	0.45	6.0	8.0	0.058
Ethylene	0.242	18.4	—	54.0	1.3	—
1,3-Butadiene	0.100	24.3	12	—	—	—

[a] k_p and k_t values are for 60°C unless otherwise noted. The units of k_p and k_t are liters/mole-sec.
[b] E_p values are in kJ/mole of polymerizing monomer; E_t values are in kJ/mole of propagating radicals.
[c] A_p and A_t values are in liters/mole-sec.
[d] Data are from Brandrup and Immergut [1989], Eastmond [1976a, 1976b, 1976c], and Walling [1957].

G. Odian, *Principles of Polymerization*, 3rd. Ed., 1991, p 275.

Methyl methacrylate is sterically hindered, leading to low A_p.

Energetics: Rate of Polymerization

$$R_p = k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{1/2}$$

$$\Rightarrow \quad k_p\left(\frac{k_d}{k_t}\right)^{1/2}$$

This is the key.

$$\ln\left\{k_p\left(\frac{k_d}{k_t}\right)^{1/2}\right\} = \ln\left\{A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right\} = \frac{-\left\{E_p + \dfrac{E_d}{2} - \dfrac{E_t}{2}\right\}}{RT}$$

$$E_R \equiv E_p + \frac{E_d}{2} - \frac{E_t}{2}$$

composite activation energy, usually ~80-90 kJ/mole

$$\ln R_p = \ln\left\{A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right\} + \ln\left\{(f[I])^{1/2}[M]\right\} - \frac{E_R}{RT}$$

Energetics: Degree of Polymerization

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

$\Longrightarrow$

$$\frac{k_p}{(k_dk_t)^{1/2}}$$

This is the key.

$$\ln\left\{\frac{k_p}{(k_dk_t)^{1/2}}\right\} = \ln\left\{\frac{A_p}{(A_dA_t)^{1/2}}\right\} - \frac{E_p - \dfrac{E_d}{2} - \dfrac{E_t}{2}}{RT}$$

$$E_{\overline{X}_n} \equiv E_p - \frac{E_d}{2} - \frac{E_t}{2}$$
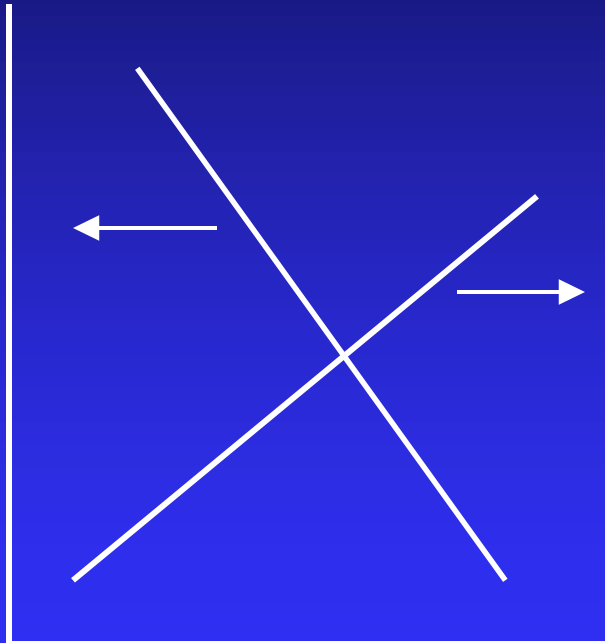
composite or overall activation energy

$$\overline{X}_n = 2\nu$$

coupling

$$\ln \overline{X}_n = \ln\left\{\frac{A_p}{(A_dA_t)^{1/2}}\right\} + \ln\left\{\frac{[M]}{(f[I])^{1/2}}\right\} - \frac{E_{\overline{X}_n}}{RT}$$

Temperature Dependence of Rate of Polymerization and Degree of Polymerization

Autoacceleration (Trommsdorff effect)

$$R_p = k_p[M]\left(\frac{fk_d[I]}{k_t}\right)^{1/2}$$

Normally, R_p decreases with time because [M] and [I] drop with extent of conversion.

TABLE 3-16   Effect of Conversion on the Polymerization of Methyl Methacrylate (22.5°C)[a]

% Conversion	Rate (%/hr)	τ (sec)	k_p	$k_t \times 10^{-5}$	$(k_p/k_t^{1/2}) \times 10^2$
0	3.5	0.89	384	442	5.78
10	2.7	1.14	234	273	4.58
20	6.0	2.21	267	72.6	8.81
30	15.4	5.0	303	14.2	25.5
40	23.4	6.3	368	8.93	38.9
50	24.5	9.4	258	4.03	40.6
60	20.0	26.7	74	0.498	33.2
70	13.1	79.3	16	0.0564	21.3
80	2.8	216	1	0.0076	3.59

[a]Data from Hayden and Melville [1960].

G. Odian, Principles of Polymerization, 3rd Ed., 1991, p 289.