Radical Chain Polymerization: Course Outline

- Mechanism
- Rate of polymerization
- Molecular weight and molecular weight distribution
- Chain transfer and control of molecular weight

Step Polymerization vs. Chain Polymerization

Step Polymerization

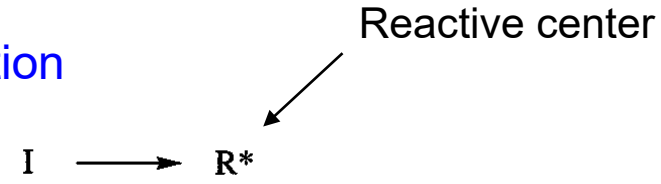
- Reaction occurs between any of the different sized species present in the reaction system
- Monomer disappears fast
- Molecular weight increases relatively slowly with conversion

Chain Polymerization

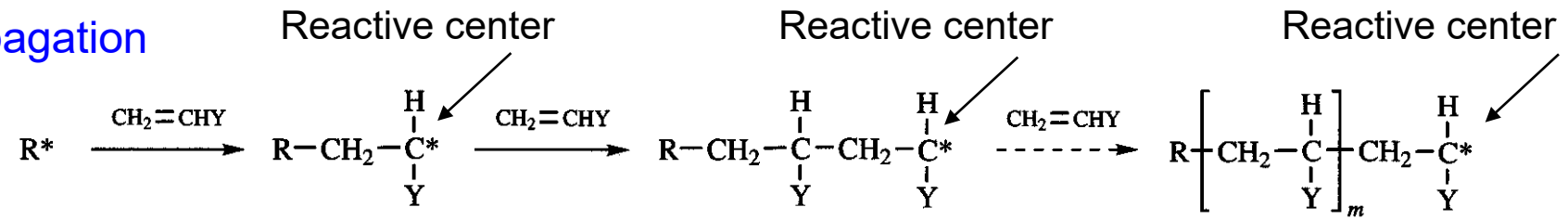
- Monomer only reacts with the reactive center
- Chain growth is very rapid, high molecular weight polymer is formed immediately
- Monomer concentration decreases throughout the polymerization, while the number of high molecular weight polymer molecules increases
- The molecular weight of the polymer is relatively independent on monomer conversion

General Mechanism of Chain Polymerization

1. Initiation



2. Propagation



3. Termination

The active species can be a:

Free radical	→ Radical chain polymerization
Anion	→ Anionic polymerization
Cation	→ Cationic polymerization

The choice of polymerization method does not only depend on the **structure of the monomer**, but also on the desired **molecular weight, molecular weight distribution**, etc.

General Considerations of Polymerizability

Polymerizability of vinyl monomers: $n\ CH_2{=}CHY \longrightarrow -[CH_2\text{-}CHY]_n-$

1. Thermodynamic feasibility: $\Delta G < 0$

   For a wide range of monomers, $\Delta G < 0$

2. Kinetic feasibility:

   Does the reaction proceed at a reasonable rate under a particular set of conditions?

   This depends on:

   (i) Type of propagating center (+, -, or •)

   (ii) Substituent effects (i.e. the nature of Y)
   - Inductive effects
   - Resonance effects

General Considerations of Polymerizability

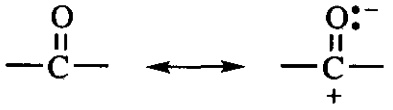
The ability to carry out a thermodynamically feasible polymerization depends on its kinetic feasibility

TABLE 3-1 Types of Chain Polymerization Undergone by Various Unsaturated Monomers

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

[a]Includes anionic coordination initiation (Chap. 8).

The carbonyl bond is not prone to radical polymerization due to its polarized nature



Electrical Effects: Inductive and Resonance Effects

Inductive and resonance effects are difficult to separate and often occur together

The inductive effect (I) describes the polarization of one bond caused by the polarization of an adjacent bond

Inductive effect

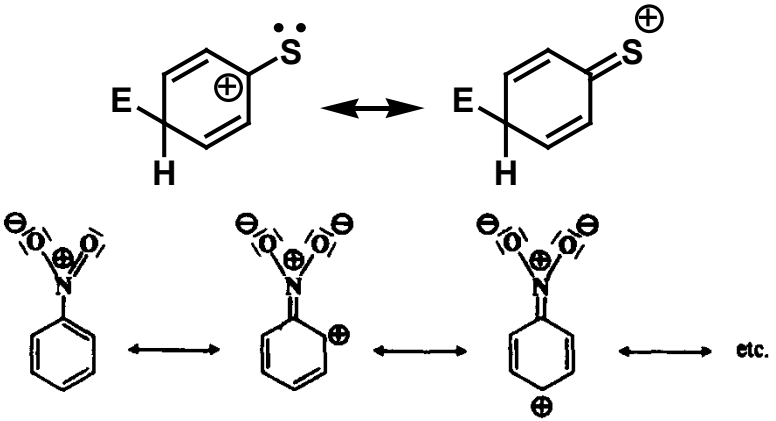
- Polarization of one bond due to polarization of an adjacent bond
- Operates through σ bonds
- Electronegativity

TABLE 1.3 Field effects of various groups relative to hydrogen

The groups are listed approximately in order of decreasing strength for both −I and +I groups

+I	−I (electron withdrawing)		
O^-	NR_3^+	COOH	OR
COO^-	SR_2^+	F	COR
CR_3	NH_3^+	Cl	SH
CHR_2	NO_2	Br	SR
CH_2R	SO_2R	I	OH
CH_3	CN	OAr	C≡Cr
D	SO_2Ar	COOR	Ar
			$CH{=}CR_2$

The **resonance effect (M)** of a substituent **S** refers to the possibility that the presence of **S** may increase or decrease the resonance stabilization



Resonance structures are different (hypothetical) structures of the same molecule/ion that only differ in the positions of the electrons. The „real" electron density is the average of these structures

TABLE 9.1 Some groups with + *M* and − *M* effects, not listed in order of strength of effect *Ar appears in both lists because it is capable of both kinds of effect*

+ *M* groups		−*M* groups	
O^-	SR	NO_2	CHO
S^-	SH	CN	COR
NR_2	Br	COOH	SO_2R
NHR	I	COOR	SO_2OR
NH_2	Cl	$CONH_2$	NO
NHCOR	F	CONHR	Ar
OR	R	$CONR_2$	
OH	Ar		
OCOR			

Resonance effect

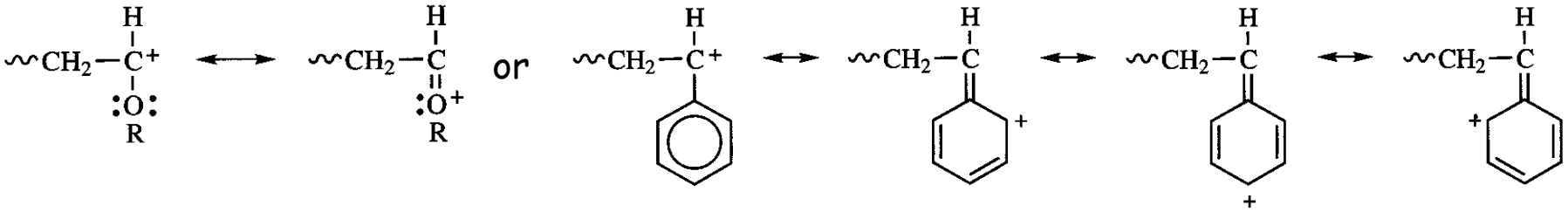
- Molecule can be represented by more than 1 canonical form
- Operates through π bonds
- Unshared electron pair on an atom connected to an unsaturated system

NOTE 1.: Many groups are –I and +M and for these it is not always possible to predict which effect will predominate

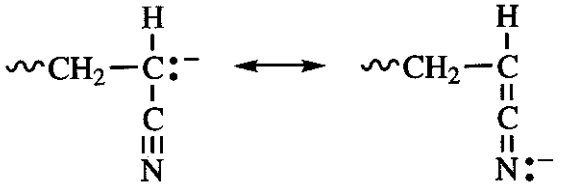
NOTE 2.: Conclusion of this and the previous slide: The structure of the monomer can stabilize or destabilize the active species and therefore governs the methods by which it can be polymerized

Whether a vinyl monomer polymerizes by radical, anionic or cationic initiators depends on the inductive and resonance characteristics of its substituents

- Electron donating substituents facilitate cationic polymerization:
  - Increased electron density at the double bond facilitates reactions with cationic species
  - Propagating species is stabilized by resonance, see e.g.:

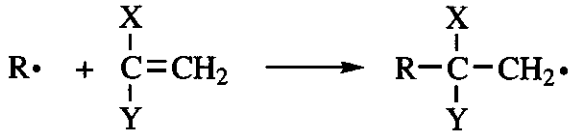


- Electron withdrawing substituents facilitate anionic polymerization:
  - Attack of anionic species is facilitated
  - Propagating species is stabilized by resonance, see e.g.:



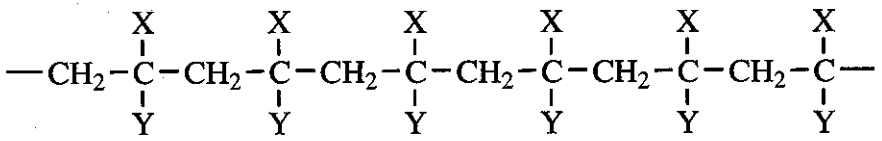
- Radical species are neutral and do not have stringent requirements for attacking the π-bond or for the stabilization of the propagating radical species. Resonance stabilization occurs with almost all substituents

Structural Arrangement of Monomer Units



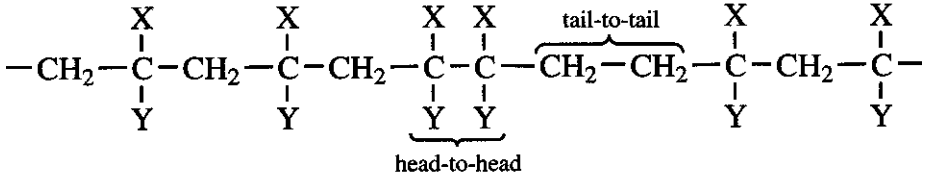
I

II



III

Head-to-tail (H-T)
or 1,3-placement



IV

Head-to-head placement (H-H)
or 1,2-placement

H-T placement is favored on both steric and resonance grounds

Radical Chain Polymerization: Course Outline

- Mechanism
- Rate of polymerization
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- Chain transfer and control of molecular weight

Radical Chain Polymerization

Industrially important:
In the US in 2001 40 billion pounds of polymer out of a total of 110 billion pounds were produced by radical chain polymerization

Specific examples of commercial polymers:

- Polyethylene
- Polystyrene
- Poly(vinyl chloride)
- Poly(methyl methacrylate)

Radical Chain Polymerization

1. Initiation

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

$$R\bullet + M \xrightarrow{k_i} M_1\bullet$$

R• = initiator radical / primary radical
M_1 • = chain-initiating species
k_d = rate constant for initiator decomposition
k_i = rate constant for the initiation step

2. Propagation

$$M_1\bullet + M \xrightarrow{k_p} M_2\bullet$$

$$M_2\bullet + M \xrightarrow{k_p} M_3\bullet$$

$$M_3\bullet + M \xrightarrow{k_p} M_4\bullet$$

etc., etc.

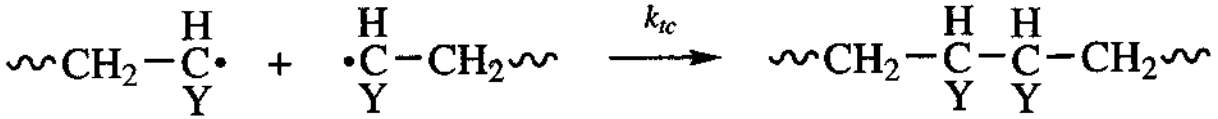
k_p = rate constant for propagation
(10^2-10^4 $L.mol^{-1}.s^{-1}$)

or in general terms

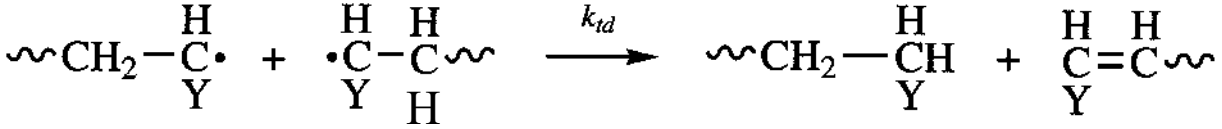
$$M_n\bullet + M \xrightarrow{k_p} M_{n+1}\bullet$$

[concept of equal reactivity of functional groups]

3. Termination



Combination (coupling)



Disproportionation

$$M_n\bullet + M_m\bullet \xrightarrow{k_{tc}} M_{n+m}$$

$$M_n\bullet + M_m\bullet \xrightarrow{k_{td}} M_n + M_m$$

or:

$$M_n\bullet + M_m\bullet \xrightarrow{k_t} \text{dead polymer}$$

k_{tc} = rate constant for termination by coupling

k_{td} = rate constant for termination by disproportionation

with: $k_t = ak_{tc} + (1-a)k_{td}$

- k_t = rate constant for termination (10^6-10^8 L.mol^{-1}.s^{-1})
- a and (1-a) the fractions of termination by coupling and disproportionation, respectively

Rate of Polymerization

Assumption: k_p and k_t independent of the size of the radical (concept of equal reactivity of functional groups)

$$\frac{-d[\mathrm{M}]}{dt} = R_i + R_p \quad \Longrightarrow \quad \frac{-d[\mathrm{M}]}{dt} = R_p \qquad R_p = k_p[\mathrm{M}\bullet][\mathrm{M}] \quad (1)$$

The number of monomer molecules reacting in the initiation step can be neglected compared to the polymerization step

Steady-state assumption:

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

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

Initiation of Radical Chain Polymerization

I. Thermal
II. Redox
III. Photochemical
IV. Ionizing radiation
V. Pure thermal initiation

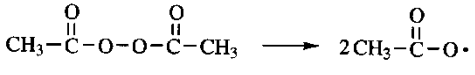
To be useful as a source of radicals, an initiator should be readily available, stable under ambient or refrigerated conditions and possess a practical rate of radical generation at reasonable temperatures (< 150 °C).

Thermal Initiation

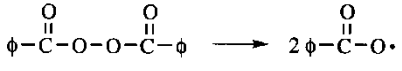
- Thermal homolytic dissociation:
  - Dissociation energy 100-170 kJ/mol
  - O-O, S-S, N-O compounds

- Examples:

Acyl peroxides

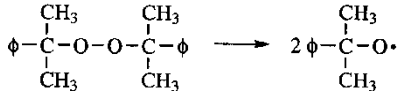


Acetyl peroxide

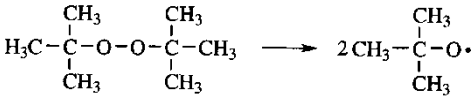


Benzoyl peroxide

Alkyl peroxides

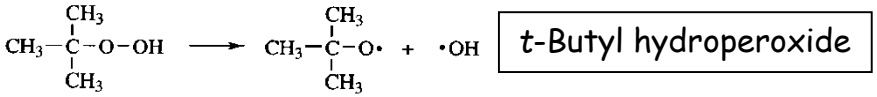


Cumyl peroxide

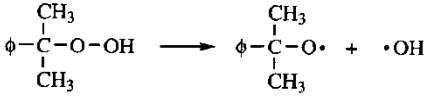


t-Butyl peroxide

Hydroperoxides

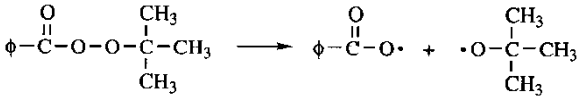


t-Butyl hydroperoxide



Cumyl hydroperoxide

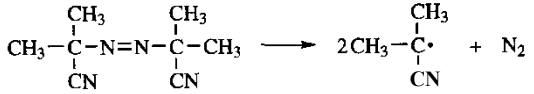
Peresters



t-Butyl perbenzoate

Azo compounds

(C-N bond dissociation energy is high, but homolysis is driven by the formation of the highly stable N_2 molecule)



2,2'-Azobisisobutyronitrile (AIBN)

Various initiators are used at different temperatures, e.g.:

- AIBN at 50 – 70 °C
- Acetyl peroxide at 70 – 90 °C
- Benzoyl peroxide at 80 – 95 °C

k_d is typically 10^{-4} – 10^{-9} s^{-1}, depending on initiator and temperature

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

$$[\mathrm{I}] = [\mathrm{I}]_0 e^{-k_d t} \quad \text{or} \quad \ln\frac{[\mathrm{I}]_0}{[\mathrm{I}]} = k_d t$$

$$t_{1/2} = \frac{0.693}{k_d}$$

TABLE 3-2 Half-Lives of Initiators[a,b]

	Half-Life at					
Initiator	50°C	70°C	85°C	100°C	130°C	175°C
Azobisisobutyronitrile	74 h	4.8 h	—	7.2 min	—	—
Benzoyl peroxide	—	7.3 h	1.4 h	20 min	—	—
Acetyl peroxide	158 h	8.1 h	1.1 h	—	—	—
t-Butyl peracetate	—	—	88 h	13 h	18 min	—
Cumyl peroxide	—	—	—	—	1.7 h	—
t-Butyl peroxide	—	—	—	218 h	6.4 h	—
t-Butyl hydroperoxide	—	—	—	338 h	—	4.81 h

[a] Data from Brandrup and Immergut [1989], Brandrup et al. [1999], and Huyser [1970]
[b] Half-life ($t_{1/2}$) values are for benzene or toluene solutions of the initiators.

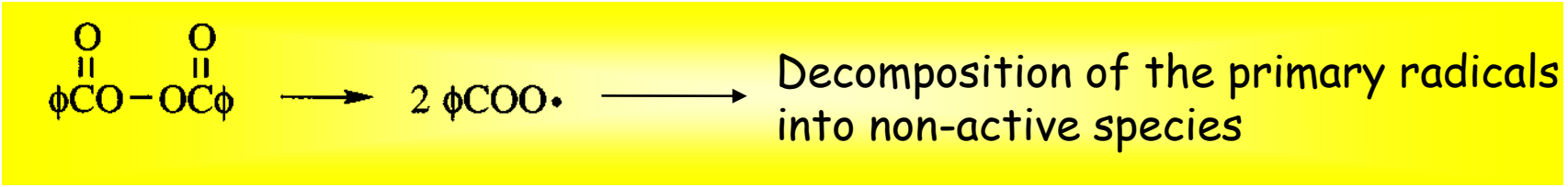
Initiator Efficiency

Initiator efficiency (f) = fraction of radicals formed in the primary step of initiator decomposition, which are successful in initiating polymerization

Initiator is wasted due to:

1) Induced decomposition of initiator (= chain transfer to initiator)

2) Side reactions of radicals formed in the primary decomposition step

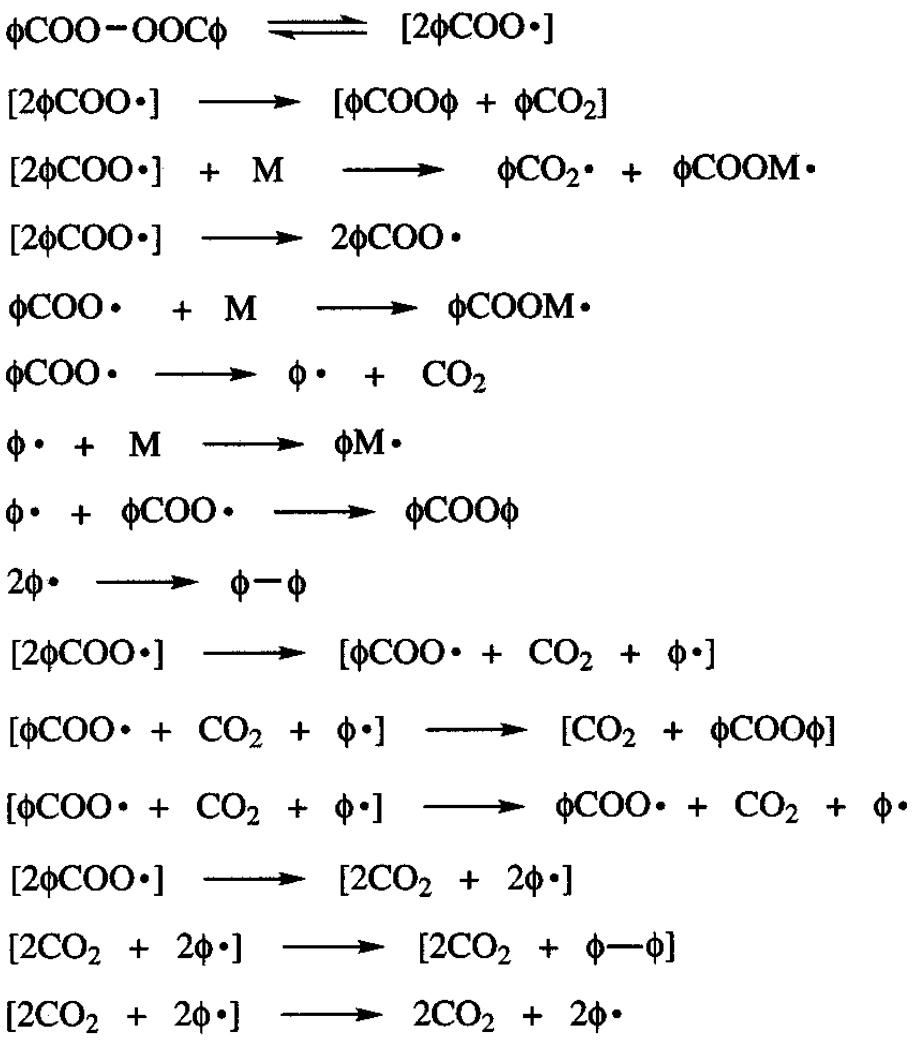


Often (1) is neglected when values of f are discussed

f: ~ 0.3-0.8

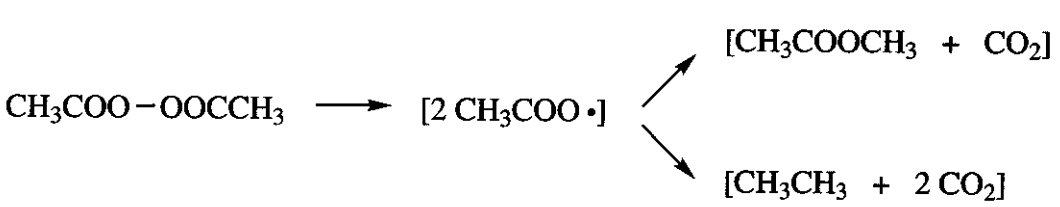
The Cage Effect

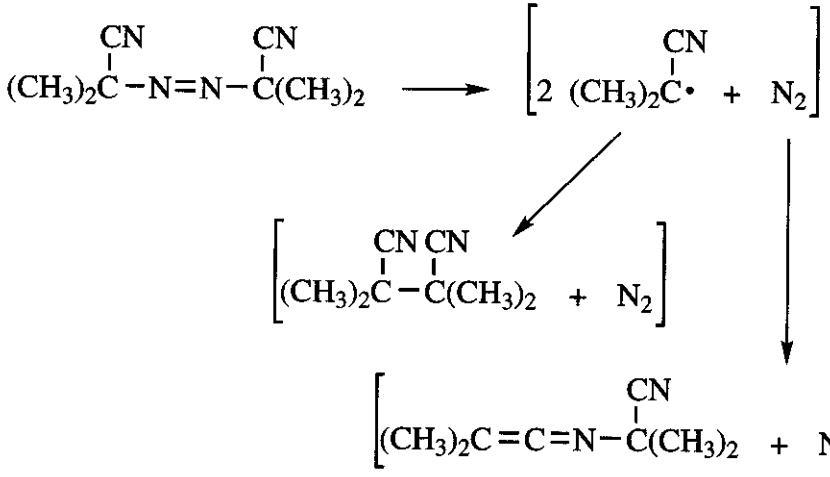
The cage effect describes lowering of f due to reactions of radicals entrapped in a solvent cage

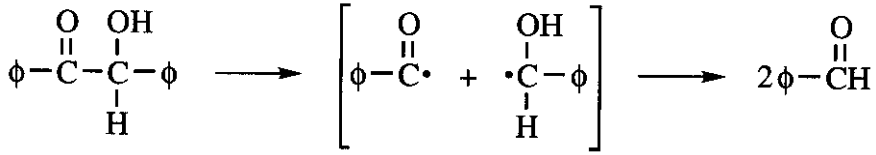


(the brackets indicate the presence of a solvent cage)

Other examples:



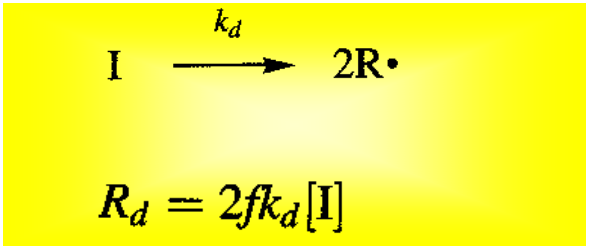




- Once a radical diffuses out of the solvent cage, reaction with monomer is the preferred reaction. This is due to the much greater monomer concentrations (10^{-1} – 10 M) compared to the radical concentrations (typically 10^{-7} – 10^{-9} M).
- f decreases as the viscosity of the medium increases (different solvent, higher conversion)

Kinetics of Thermally Initiated Radical Polymerization

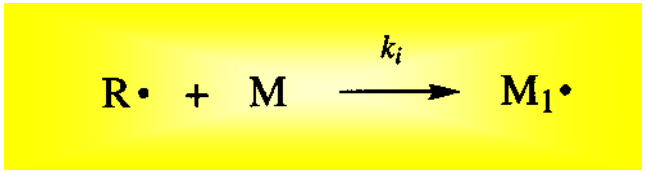
Step I



Initiator decomposition

[I] : concentration of the initiator
f : initiator efficiency (= fraction of radicals produced that initiates polymer chains)

Step II



Initiation of propagation

In most polymerizations, step II is much faster than step I; homolysis of the initiator is the rate determining step.

Rate of initiation (R_i) is given by: $R_i = 2fk_d[I]$

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

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

Deviations:

- At very high initiator concentrations the order of dependence of R_p on [I] may be less that $\frac{1}{2}$ due to a decrease in f with increasing initiator concentration

- If the termination mode changes from normal bimolecular termination to primary termination, which involves propagating radicals ($M_n\bullet$) reacting with primary radicals ($R\bullet$):

$$M_n\cdot + R\cdot \xrightarrow{k_{tp}} M_n - R$$

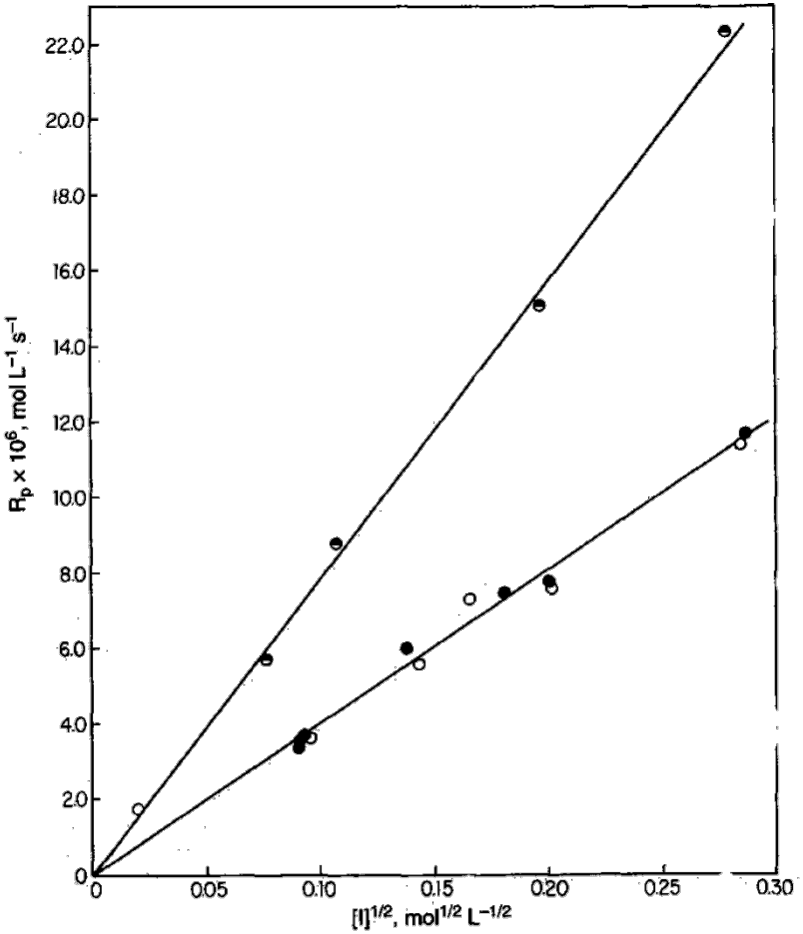


Fig. 3-1 Square root dependence of the polymerization rate R_p on the initiator concentration [I]. ● = Methyl methacrylate, benzoyl peroxide, 50°C. After Schulz and Blaschke [1942] (by permission of Akademische Verlagsgesellschaft, Geest and Portig K.-G., Leipzig). ○,● = Vinyl benzoate, azobisisobutyronitrile, 60°C. After Santee et al. [1964] and Vrancken and Smets [1959] (by permission of Huthig and Wepf Verlag, Basel and Wiley-VCH, Weinheim).

This can happen when primary radicals are produced at too high a concentration and/or in the presence of too low a monomer concentration. In this case:

$$R_p = \frac{k_p k_i[\mathrm{M}]^2}{k_{tp}}$$

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

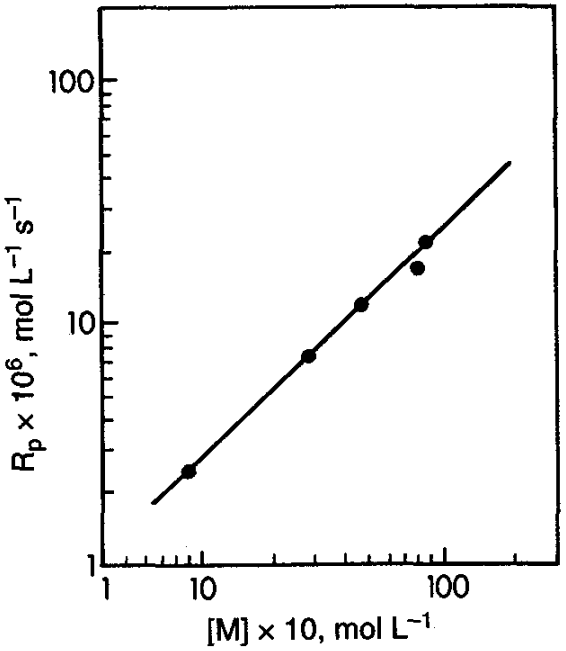


Fig. 3-2 First-order dependence of the polymerization rate R_p of methyl methacrylate on the monomer concentration [M]. The initiator is the *t*-butyl perbenzoate-diphenylthiourea redox system. After Sugimura and Minoura [1966] (by permission of Wiley-Interscience, New York).

- First order dependence of the polymerization rate on [M] is often observed
- Deviations may be due to the dependence of the initiation rate on [M] (to derive the above equation of R_p it was assumed that R_i is independent of [M])

Autoacceleration

Autoacceleration / Gel effect / Trommsdorff effect / Norrish-Smith effect

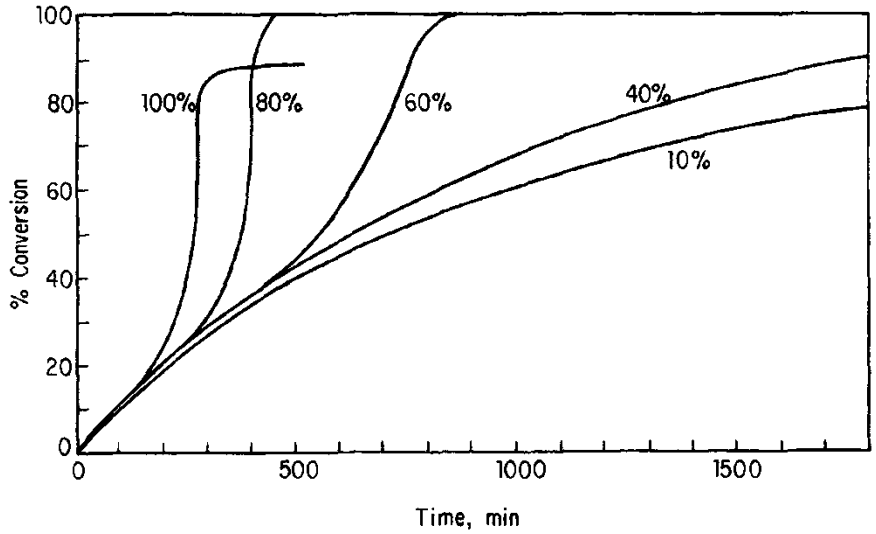


Fig. 3-15 Autoacceleration in benzoyl peroxide–initiated polymerization of methyl methacrylate in benzene at 50°C. The different plots represent various concentrations of monomer in solvent. After Schulz and Haborth [1948] (by permission of Huthig and Wepf Verlag, Basel).

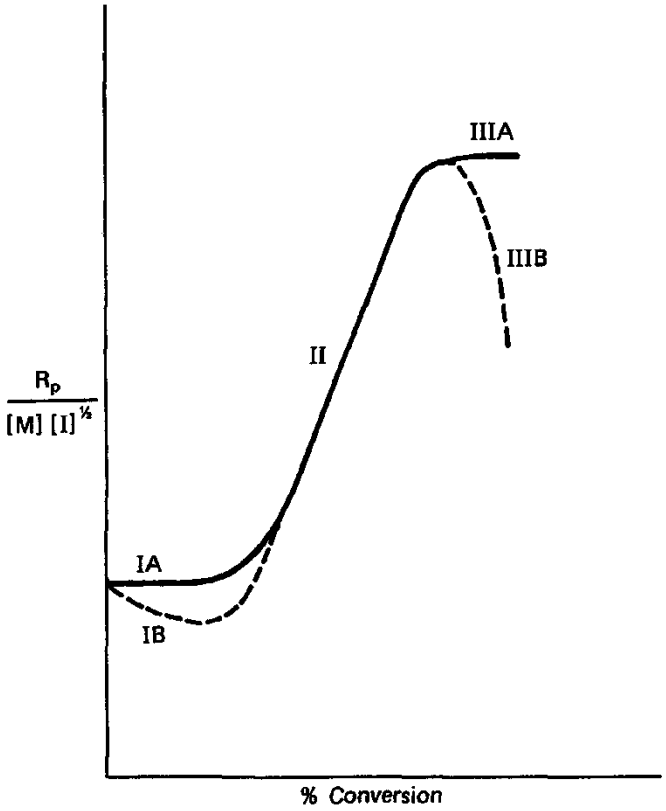


Fig. 3-16 Effect of conversion on polymerization rate.

$$R_p = k_p[\mathrm{M}]\left(\frac{fk_d[\mathrm{I}]}{k_t}\right)^{1/2} \Rightarrow \frac{R_p}{[M]\sqrt{[I]}} \sim \frac{k_p\sqrt{f\,k_d}}{k_t} \sim \frac{1}{k_t}$$

Termination of polymerization is diffusion-controlled

1. Translational diffusion of two propagating radicals:

$$M_n\bullet + M_m\bullet \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M_n\bullet\text{- - -}M_m\bullet]$$

XXXVIII

2. Rearrangement of the two chains to allow for reaction between the radical ends (segmental diffusion):

$$[M_n\bullet\text{- - -}M_m\bullet] \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [M_n\bullet / M_m\bullet]$$

XXXVIII **XXXIX**

3. Chemical reaction of two radical ends:

$$[M_n\bullet / M_m\bullet] \xrightarrow{k_c} \text{dead polymer}$$

XXXIX

Steady-state assumption for [**XXXVIII**] and [**XXXIX**] and with $k_c \gg k_4$ gives:

$$R_t = \frac{k_1 k_3 [M\bullet]^2}{k_2 + k_3}$$

Two limiting cases:

i. $k_3 \gg k_2$ (slow translational diffusion)

$$R_t = k_1 [M\bullet]^2$$

ii. $k_2 \gg k_3$ (slow segmental diffusion)

$$R_t = \frac{k_1 k_3 [M\bullet]^2}{k_2}$$

- Segmental diffusion increases with increasing conversion
- Translational diffusion decreases with increasing conversion

Propagation also becomes hindered at high conversions, but the effect is smaller compared to termination. Propagation involves reaction of one small molecule with one polymer radical; termination involves reaction of two polymer radicals

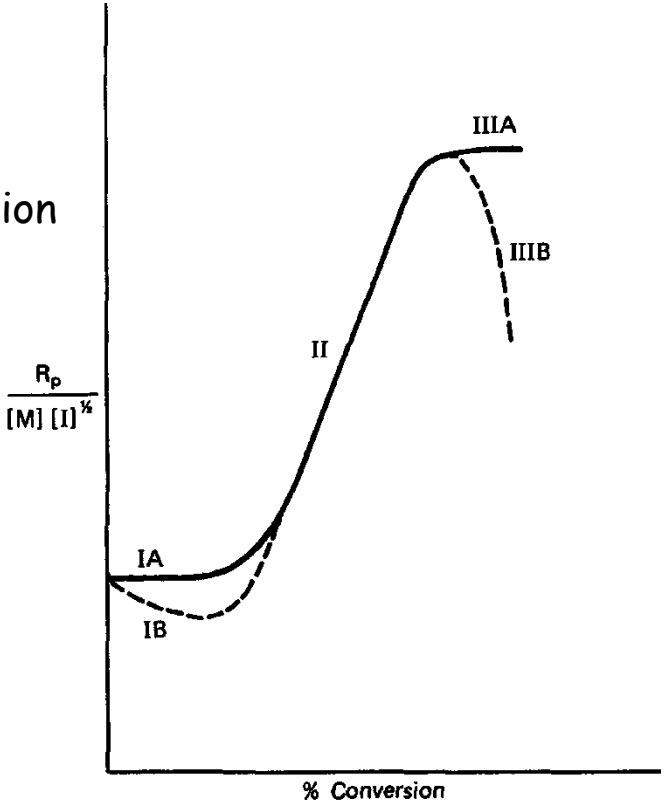


Fig. 3-16 Effect of conversion on polymerization rate.

TABLE 3-17 Effect of Conversion on the Polymerization of Methyl Methacrylate (22.5°C)[a]

% Conversion	Rate (%/h)	τ (s)	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].

At very high conversion (typically > 50%) k_p becomes sufficiently affected that $R_p/[M][I]^{1/2}$ begins to level off or decrease („glass or vitrification effect")

Molecular Weight

Kinetic chain length: the average number of monomer molecules polymerized per each radical, which initiates a polymer chain

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

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

$$R_i = 2fk_d[\mathrm{I}]$$

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

[M] and [I] are not very useful to control polymer molecular weight

Number-average degree of polymerization:

$\overline{X}_n = 2\nu$ for termination by coupling

$\overline{X}_n = \nu$ for termination by disproportionation

Number-average molecular weight of the polymer: $\overline{M}_n = M_o\overline{X}_n$

The average number of initiator fragments per polymer molecule, defined as the total initiator fragments divided by the total number of polymer molecules is given by:

$$b = \frac{an + (1-a)n}{an/2 + (1-a)n} = \frac{2}{2-a} \qquad (0 \le a \le 1)$$

Here: n = number of propagating chains

The fractions of coupling (a) and disproportionation (1-a) are given by:

$$a = \frac{2b-2}{b}$$

$$1-a = \frac{2-b}{b}$$

The general relationship between the degree of polymerization and the kinetic chain length is:

$$\overline{X}_n = b\nu = \frac{2\nu}{(2-a)}$$

Most polymer radicals terminate predominantly or entirely by coupling

Molecular Weight Distribution

Molecular weight distribution (MWD) in radical chain polymerization is complex. This is due to the fact that the molecular weight of the polymer varies with the overall percent conversion due to changes in the monomer and initiator concentration and the propagation and termination rate constants. MWD can be calculated, however, at low conversion where the kinetic parameters are approximately constant and the polymer molecular weight does not change with conversion

Two scenarios, depending on the mode of termination:

1. Termination via disproportionation:

$$\overline{X}_n = \frac{1}{(1-p)} \qquad \overline{X}_w = \frac{(1+p)}{(1-p)} \qquad \frac{\overline{X}_w}{\overline{X}_n} = (1+p)$$

2. Termination by coupling:

$$\overline{X}_n = \frac{2}{1-p} \qquad \overline{X}_w = \frac{2+p}{1-p} \qquad \frac{\overline{X}_w}{\overline{X}_n} = \frac{2+p}{2}$$

At high conversions, MWD is usually much broader, with X_w/X_n ~ 2-5

Chain Transfer and Control of Molecular Weight

Chain transfer reactions involve premature termination of growing polymer chains by transfer of a hydrogen or other atom or species to it from some compound present in the system (monomer, initiator, solvent). (chain transfer to initiator = induced initiator decomposition)

$$M_n\bullet + XA \xrightarrow{k_{tr}} M_n{-}X + A\bullet \qquad R_{tr} = k_{tr}[M\bullet][XA]$$

chain transfer

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

reinitiation

Effect of chain transfer of R_p and X_n

TABLE 3-3 Effect of Chain Transfer on R_p and $\overline{X}_n$

Case	Relative Rate Constants for Transfer, Propagation, and Reinitiation		Type of Effect	Effect on R_p	Effect on $\overline{X}_n$
1	$k_p \gg k_{tr}$	$k_a \simeq k_p$	Normal chain transfer	None	Decrease
2	$k_p \ll k_{tr}$	$k_a \simeq k_p$	Telomerization	None	Large decrease
3	$k_p \gg k_{tr}$	$k_a < k_p$	Retardation	Decrease	Decrease
4	$k_p \ll k_{tr}$	$k_a < k_p$	Degradative chain transfer	Large decrease	Large decrease

Taking into account chain transfer reactions, the degree of polymerization must be redefined as the rate of polymerization divided by the sum of the rates of all chain breaking reactions (i.e. normal termination modes plus chain transfer reactions):

$$\overline{X}_n = \frac{R_p}{(2-a)(R_t/2) + k_{tr,\mathrm{M}}[\mathrm{M}\bullet][\mathrm{M}] + k_{tr,\mathrm{S}}[\mathrm{M}\bullet][\mathrm{S}] + k_{tr,\mathrm{I}}[\mathrm{M}\bullet][\mathrm{I}]}$$

This equation assumes initiation by thermal homolysis of the initiator

If disproportionation does not occur (a = 1) and defining the following chain transfer constants:

$$C_\mathrm{M} = \frac{k_{tr,\mathrm{M}}}{k_p} \quad C_\mathrm{S} = \frac{k_{tr,\mathrm{S}}}{k_p} \quad C_\mathrm{I} = \frac{k_{tr,\mathrm{I}}}{k_p}$$

The expression becomes:

$$\frac{1}{\overline{X}_n} = \frac{R_i}{2R_p} + C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} + C_\mathrm{I}\frac{[\mathrm{I}]}{[\mathrm{M}]}$$

$$\frac{1}{\overline{X}_n} = \frac{k_t R_p}{k_p^2[\mathrm{M}]^2} + C_\mathrm{M} + C_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} + C_\mathrm{I}\frac{k_t R_p^2}{k_p^2 f k_d[\mathrm{M}]^3}$$

The Mayo equation

If disproportionation is also important, the Mayo equation becomes:

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

$\Rightarrow$ Controlled chain transfer may be employed to control molecular weight

Transfer to Monomer and Initiator

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

How to determine C_M and C_I ?

When chain transfer agent is absent, this simplifies to:

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

$$\frac{1}{\overline{X}_n} = \frac{k_t R_p}{k_p^2[M]^2} + C_M + C_I\frac{[I]}{[M]}$$

- The intercept of the linear portion yields C_M
- The slope of the linear portion is given by $k_t/(k_p^2[M]^2)$
- When chain transfer to initiator is absent a plot of $1/X_n$ versus R_p will be linear over the whole range

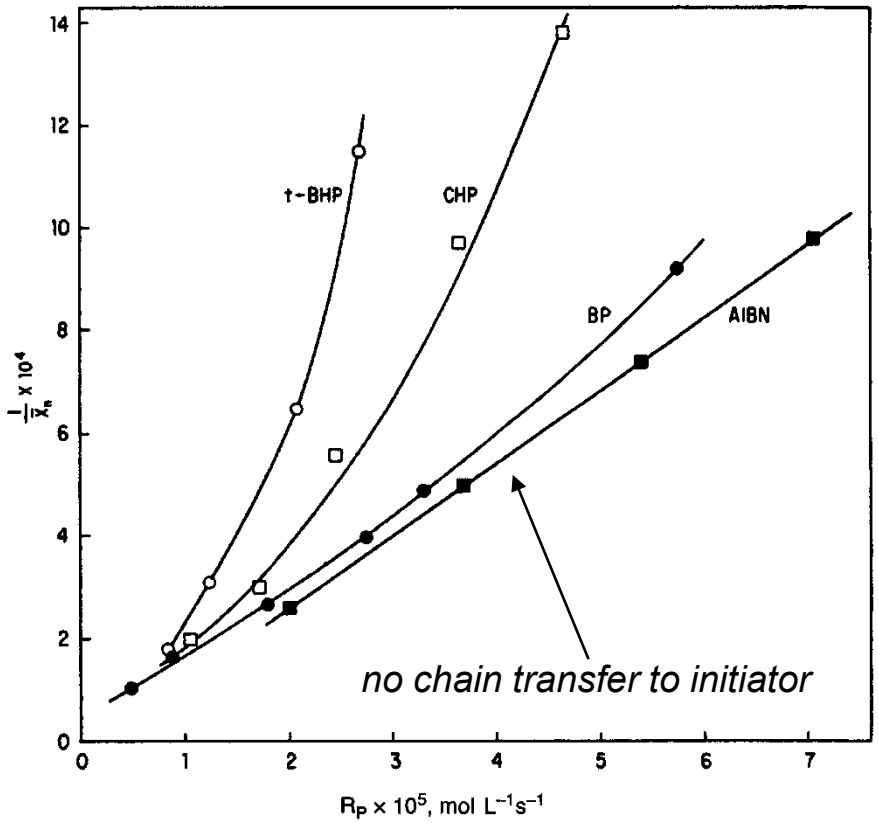


Fig. 3-5 Dependence of the degree of polymerization of styrene on the polymerization rate. The effect of chain transfer to initiator is shown for *t*-butyl hydroperoxide (○), cumyl hydroperoxide (□). benzoyl peroxide (●), and azobisisobutyronitrile (■) at 60°C. After Baysal and Tobolsky [1952] (by permission of Wiley-Interscience, New York).

$$\frac{1}{\bar{X}_n} = \frac{k_t R_p}{k_p^2[\mathrm{M}]^2} + C_\mathrm{M} + C_\mathrm{I}\frac{k_t R_p^2}{k_p^2 f k_d[\mathrm{M}]^3} \qquad \frac{1}{\bar{X}_n} = \frac{k_t R_p}{k_p^2[\mathrm{M}]^2} + C_\mathrm{M} + C_\mathrm{I}\frac{[\mathrm{I}]}{[\mathrm{M}]}$$

can be rearranged to:

$$\left[\frac{1}{\bar{X}_n} - C_\mathrm{M}\right]\frac{1}{R_p} = \frac{k_t}{k_p^2[\mathrm{M}]^2} + \frac{C_\mathrm{I} k_t R_p}{k_p^2 f k_d[\mathrm{M}]^3}$$

$[X_n^{-1} - C_M]R_p^{-1}$ versus R_p yields a straight line with slope $(C_I k_t)/(k_p^2 f k_d[M]^3)$

When chain transfer to monomer is negligible: $$\left[\frac{1}{\bar{X}_n} - \frac{k_t R_p}{k_p^2[\mathrm{M}]^2}\right] = C_\mathrm{I}\frac{[\mathrm{I}]}{[\mathrm{M}]}$$

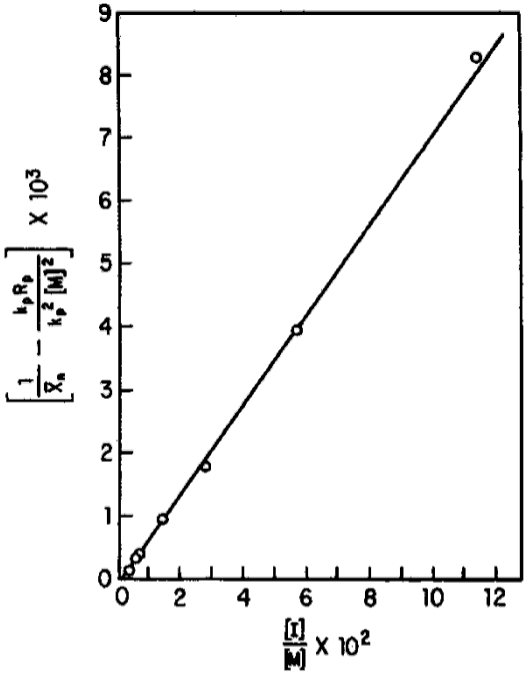
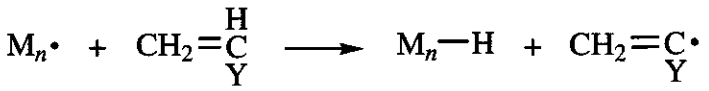


Fig. 3-6 Determination of initiator chain-transfer constants in the *t*-butyl hydroperoxide initiated polymerization of styrene in benzene solution at 70°C. After Walling and Heaton [1965] (by permission of American Chemical Society, Washington, DC.

Monomer chain transfer constants (C_M) are generally small because the reaction involves breaking the strong vinyl C-H bond:



The largest monomer transfer constants are observed when the propagating radicals have very high reactivities, e.g. ethylene, vinyl acetate and vinyl chloride

TABLE 3-4 Monomer Chain-Transfer Constants[a]

Monomer	$C_M \times 10^4$
Acrylamide	0.6, 0.12[b]
Acrylonitrile	0.26–0.3
Ethylene	0.4–4.2
Methyl acrylate	0.036–0.325
Methyl methacrylate	0.07–0.10
Styrene	0.60–0.92[c]
Vinyl acetate	1.75–2.8
Vinyl chloride	10.8–12.8

[a] All C_M are for 60°C except where otherwise noted.
[b] Value at 25°C.
[c] Data from Braks and Huang [1978]; all other data from Brandrup et al. [1999].

Initiator chain transfer constants (C_I)

TABLE 3-5 Initiator Chain-Transfer Constants[a,b]

Initiator	C_I for Polymerization of		
	Styrene	Methyl Methacrylate	Acrylamide
2,2-Azobisisobutyronitrile[c]	0.091–0.14	0	—
t-Butyl peroxide	0.0003–0.00086	—	—
Lauroyl peroxide (70°C)	0.024	—	—
Benzoyl peroxide	0.048–0.10	0–0.02	—
t-Butyl hydroperoxide	0.035	—	—
Cumyl hydroperoxide	0.063	0.33	—
Persulfate (40°C)	—	—	0.0028

[a] Data from Brandrup et al. [1999].
[b] All C_I values are for 60°C except where otherwise noted.
[c] Ayrey and Haynes [1974]; Braks and Huang [1978].

- Effect of growing polymer radical reactivity
- The acyl peroxides have higher transfer constants than the alkyl peroxides due to the weaker O-O bond of the former

Transfer to Chain-Transfer Agent

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

$$\frac{1}{\overline{X}_n} = \frac{1}{\overline{X}_{n0}} + C_S\frac{[S]}{[M]}$$

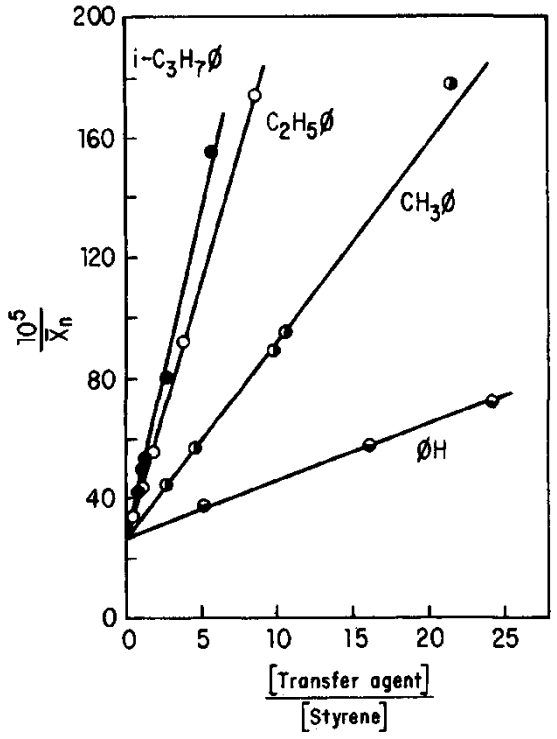


Fig. 3-8 Effect of various chain-transfer agents on the degree of polymerization of styrene at 100°C. After Gregg and Mayo [1948] (by permission of American Chemical Society, Washington, DC).

Structure – Reactivity Relationships

TABLE 3-6 Transfer Constants for Chain-Transfer Agents[a,b]

	$C_S \times 10^4$ for Polymerization of	
Transfer Agent	Styrene	Vinyl Acetate
Benzene	0.023	1.2
Cyclohexane	0.031	7.0
Heptane	0.42	17.0 (50°C)
Toluene	0.125	21.6
Ethylbenzene	0.67	55.2
Isopropylbenzene	0.82	89.9
t-Butylbenzene	0.06	3.6
n-Butyl chloride	0.04	10
n-Butyl bromide	0.06	50
2-Chlorobutane	1.2	—
Acetone	4.1	11.7
Acetic acid	2.0 (40°C)	1.1
n-Butyl alcohol	1.6	20
Ethyl ether	5.6	45.3
Chloroform	3.4	150
n-Butyl iodide	1.85	800
Butylamine	7.0	—
Triethylamine	7.1	370
Di-*n*-butyl sulfide	22	260
Di-*n*-butyl disulfide	24	10,000
Carbon tetrachloride	110	10,700
Carbon tetrabromide	22,000	28,700 (70°C)
1-Butanethiol	210,000	480,000

[a] Data from Brandrup et al. [1999] and Eastmond [1976a,b,c].
[b] All values are for 60°C unless otherwise noted.

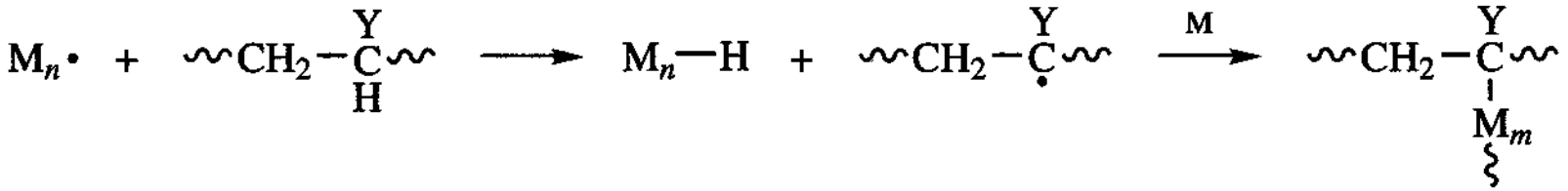
Chain transfer agents:

- Effect of monomer (compare styrene and vinyl acetate)
- Effect of chain transfer agent (compare benzene and toluene)
- Polar effects (see next slide)

Generally, the order of reactivity of a series of transfer agents remains the same irrespective of the monomer when the transfer agents are relatively neutral in polarity

Chain Transfer to Polymer

- At low conversions (conditions used to determine C_I, C_M and C_S) chain transfer to polymer is negligible
- Transfer to polymer, however, cannot be neglected at complete or high conversions. Transfer to polymer leads to the formation of branches



C_P, the chain transfer constant to polymer, is difficult to determine and the values available for a particular polymer often vary considerably. Typically C_P is ~ 10^{-4} for polymers such as PS or PMMA

Flory: $$\rho = -C_P\left[1 + \left(\frac{1}{p}\right)\ln(1-p)\right]$$

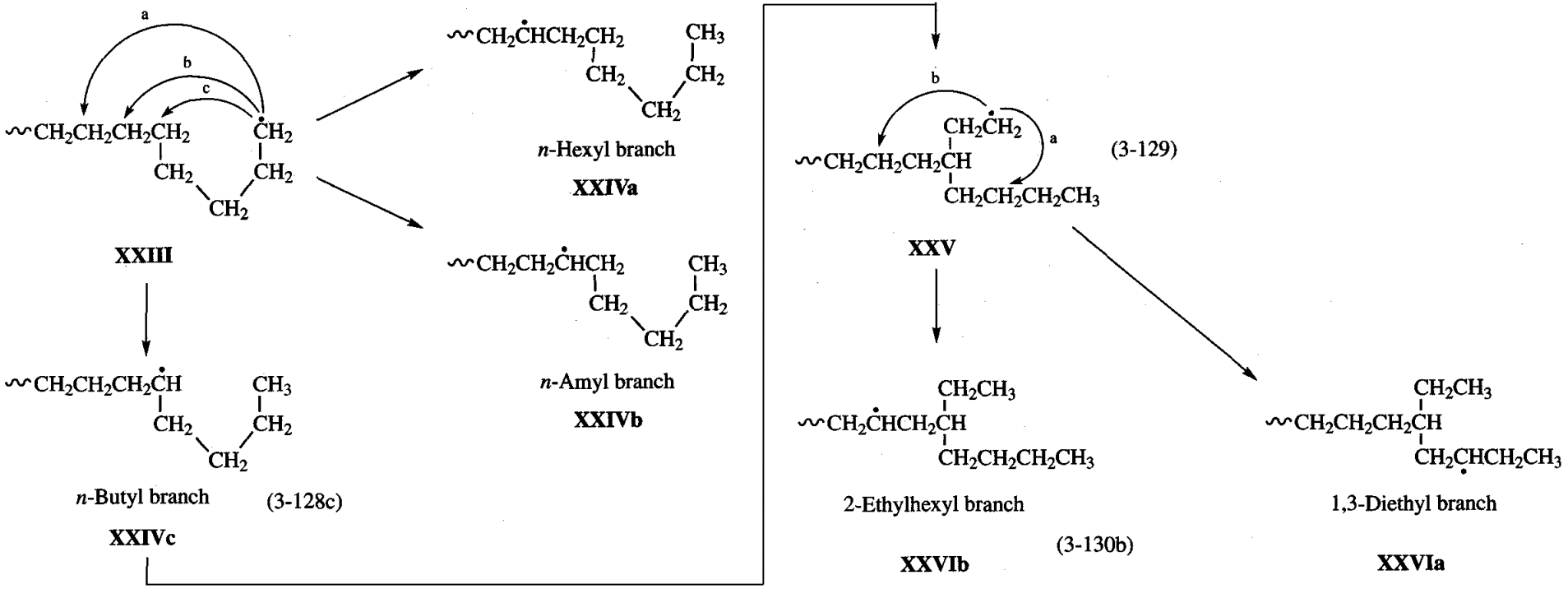
ρ = number of branches per monomer molecule polymerized

Branching is more significant for polymers such as poly(vinyl chloride), poly(vinyl acetate) (C_P ~ 2-5 x 10^{-4}) and polyethylene, which have very reactive propagating radicals

Branching in polyethylene can be as high as 15-30 branches per 500 monomer units:

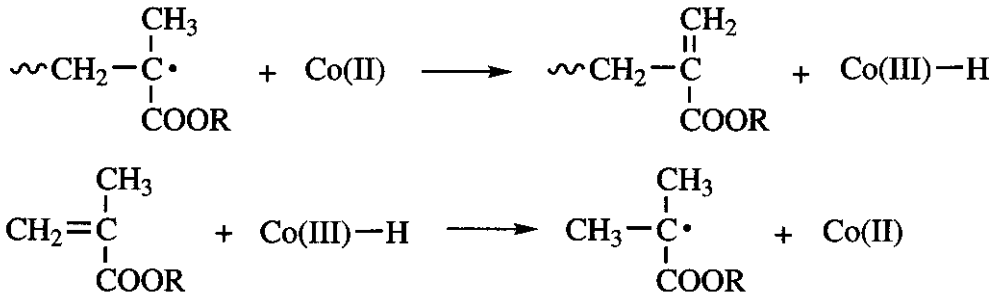
1. Long branches: due to „normal" chain transfer to polymer; affect viscosity
2. Short branches: less than 7 C-atoms (20-50 times long branches); polymer crystallinity

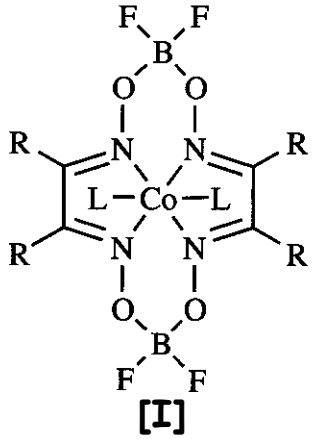
Formation of short branches: backbiting intramolecular transfer reaction (has also been verified for poly(vinyl acetate) and polyacrylates):



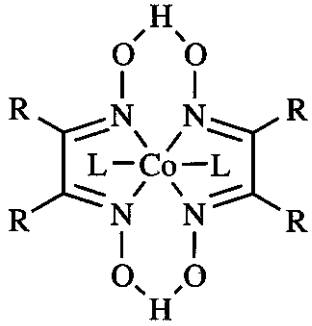
Catalytic Chain Transfer (CCT)

Transfer of an H-atom from a propagating chain to monomer:





[I]



- Chain transfer to monomer results in a polymer molecule with a saturated end group by transfer of an H atom or other atom from monomer to propagating chain
- CCT involves transfer of an H atom in the opposite direction (from propagating chain to monomer) and results in a polymer with an unsaturated end group

Catalytic chain transfer agents are much more active in chain transfer than most active conventional chain-transfer agents: C_C (**I**) = 3.2 x 10^4 vs. 10-20 for conventional agents such as 1-butanethiol

Advantages of CCT agents:

1. low-molecular weight polymers can be produced without the need for large amounts of conventional chain-transfer agents, high initiator : monomer ratios or high temperatures (the CCT agents are used catalytically in contrast to the common chain transfer agents, which are consumed upon reaction)
2. Polymers with unsaturated end groups are produced

$\Rightarrow$ Coating applications: high solid contents and low viscosity