Ch1. Introduction

1-1. Types of Polymers and Polymerization

a. Polymer Composition and Structure

- Condensation Polymer

: formed from polyfunctional monomers by condensation reactions with the elimination of small molecules

- Addition Polymer

: formed from monomers without the loss of small molecules

Ch1. Introduction

1-1. Types of Polymers and Polymerization

b. Polymerization Mechanism

- Step Polymer
  : formed by the addition of monomer or polymers (oligomers) to other monomers or polymers(oligomers)

- Chain Polymer
  : the polymer growth proceeds only between monomers and reactive site

Ch1. Introduction

1-2. Nomenclature of Polymers

a. Nomenclature Based on Source

Styrene -> Poly(styrene)

Vinyl chloride -> Poly(vinyl chloride)

6-Aminocaproic acid -> Poly(6-aminocaproic acid)

ε-Caprolactam -> Poly(ε-Caprolactam)

Ch1. Introduction

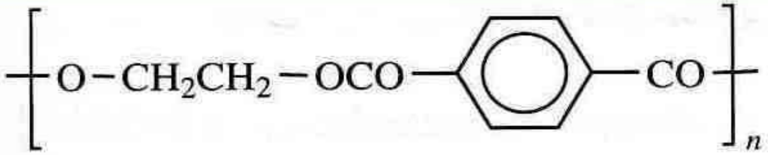
1-2. Nomenclature of Polymers

b. Nomenclature Based Structure

$$\left[\mathrm{HN}-(\mathrm{CH_2})_6-\mathrm{NHCO}-(\mathrm{CH_2})_8-\mathrm{CO} \right]_n$$

Poly(hexamethylene sebacamide)

IV



Poly(ethylene terephthalate)

V

$$\left[\mathrm{O}-\mathrm{CH_2CH_2CH_2}-\mathrm{OCONH}-\mathrm{CH_2CH_2}-\mathrm{NHCO} \right]_n$$

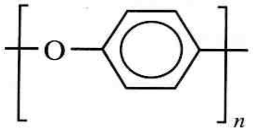
Poly(trimethylene ethyleneurethane)

VI

Ch1. Introduction

1-2. Nomenclature of Polymers

b. IUPEC Structure-Based Nomenclature System

$\left(CH_2CH_2\right)_n$ **XVII**	Polyethylene or polyethene Polymethylene
 $\left(\underset{\displaystyle CH_3}{\underset{\mid}{C}}HCH_2\right)_n$ **XVIII**	Polypropylene or polypropene Poly(1-methylethylene)
 $\left(\underset{\displaystyle \phi}{\underset{\mid}{C}}HCH_2\right)_n$ **XIX**	Polystyrene Poly(1-phenylethylene)
 $\left(\underset{\displaystyle COOCH_3}{\underset{\mid}{C}}HCH_2\right)_n$ **XX**	Poly(methyl acrylate) Poly[1-(methoxycarbonyl)ethylene]
$\left(OCH_2\right)_n$ **XXI**	Polyformaldehyde Poly(oxymethylene)
	Poly(phenylene oxide) Poly(oxy-1,4-phenylene)

Chapter 2. Step Polymerization

1. Two different bifunctional and/or polyfinctional monomers
   -> each monomer possesses only one type of functional group
2. A single monomer containing both types of functional group

2-1 Reactivity of functional groups

Rate of a step polymerization

$M_1 + M_1 \longrightarrow M_2$

$M_1 + M_2 \longrightarrow M_3$

$M_2 + M_2 \longrightarrow M_4$

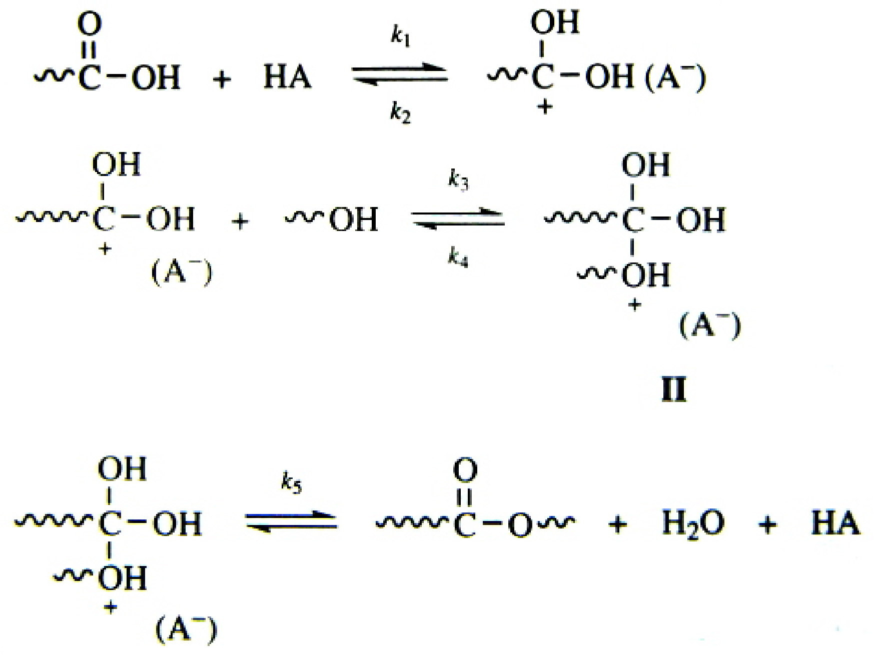
- Same reactivity for longer chains

i) Diffusion > combination rate
   then combination step is RDS
   rxn rate is independent of size

ii) Diffusion < combination
   the diffusion is RDS
   rxn rate $\propto$ size

Diffusion controlled rxn => very viscous system

2-2 Kinetics of Step Polymerization



$$R = \frac{-d[\mathrm{COOH}]}{dt} = k_3[\overset{+}{\mathrm{C}}(\mathrm{OH})_2][\mathrm{OH}]$$

$$K = \frac{k_1}{k_2} = \frac{[\overset{+}{\mathrm{C}}(\mathrm{OH})_2]}{[\mathrm{COOH}][\mathrm{HA}]}$$

$$\frac{-d[\mathrm{COOH}]}{dt} = k_3K[\mathrm{COOH}][\mathrm{OH}][\mathrm{HA}]$$

2-2a Self Catalyzed Polymerization

$$\frac{-d[\mathrm{COOH}]}{dt} = k[\mathrm{COOH}]^2[\mathrm{OH}]$$

$$\frac{-d[\mathrm{M}]}{dt} = k[\mathrm{M}]^3$$

$$\frac{-d[\mathrm{M}]}{[\mathrm{M}]^3} = k\,dt$$

$$2kt = \frac{1}{[\mathrm{M}]^2} - \frac{1}{[\mathrm{M}]_0^2}$$

$$[\mathrm{M}] = [\mathrm{M}]_0 - [\mathrm{M}]_0 p = [\mathrm{M}]_0(1-p)$$

$$\frac{1}{(1-p)^2} = 2[\mathrm{M}]_0^2 kt + 1$$

2-2a-3 Molecular Weight of Polymer

$$\overline{X}_n = \frac{N_0}{N} = \frac{[\mathrm{M}]_0}{[\mathrm{M}]}$$

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

$$\overline{M}_n = M_o\overline{X}_n + M_{eg} = \frac{M_o}{(1-p)} + M_{eg}$$

$$\overline{M}_n = M_o\overline{X}_n = \frac{M_o}{(1-p)}$$

$$\overline{X}_n^2 = 1 + 2[\mathrm{M}]_0^2 kt$$

2-2b External Catalysis of Polymerization

$$\frac{-d[\mathrm{M}]}{dt} = k'[\mathrm{M}]^2$$

$$k't = \frac{1}{[\mathrm{M}]} - \frac{1}{[\mathrm{M}]_0}$$

$$[\mathrm{M}]_0 k't = \frac{1}{(1-p)} - 1$$

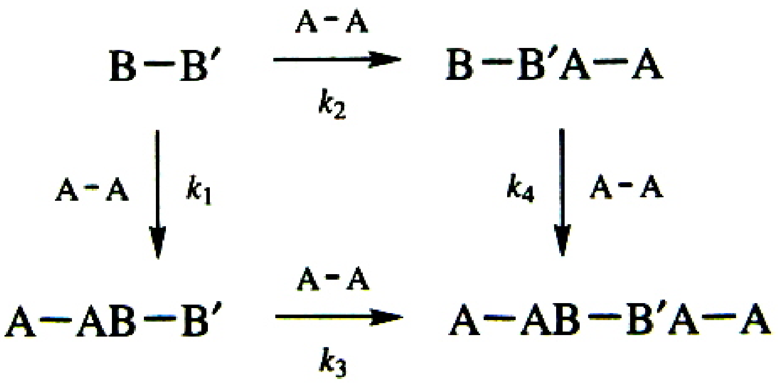
$$\overline{X}_n = 1 + [\mathrm{M}]_0 k't$$

Catalyzed vs uncatalyzed

$\frac{-d\mathrm{M}}{dt} = k[\mathrm{M}]^3 + k'[\mathrm{M}]^2$ If k′ >>> k -> 2nd order

2-2d-2 Kinetics

When the functional groups have different reactivities



$$\begin{tikzcd}
\mathrm{B{-}B'} \arrow[r, "\mathrm{A{-}A}", "k_2"'] \arrow[d, "\mathrm{A{-}A}"', "k_1"] & \mathrm{B{-}B'A{-}A} \arrow[d, "k_4"', "\mathrm{A{-}A}"] \\
\mathrm{A{-}AB{-}B'} \arrow[r, "\mathrm{A{-}A}", "k_3"'] & \mathrm{A{-}AB{-}B'A{-}A}
\end{tikzcd}$$

If $k_1 = k_4$ AB, AB′
$k_2 = k_3$ AB, AB′

If $k_1 \neq k_2$, $k_1 = k_4$ & $k_2 = k_3$

1. No neighboring group effect
2. No chain length effect

$$\frac{-d[\mathrm{B}]}{dt} = k_1[\mathrm{A}][\mathrm{B}]$$

$$\frac{-d[\mathrm{B'}]}{dt} = k_2[\mathrm{A}][\mathrm{B'}]$$

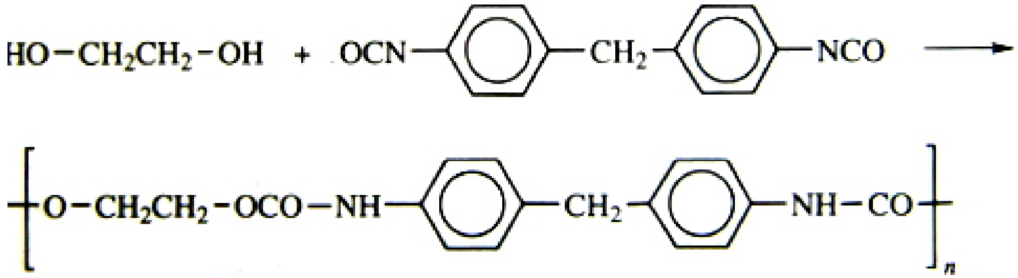
$$\frac{-d[\mathrm{A}]}{dt} = k_1[\mathrm{A}][\mathrm{B}] + k_2[\mathrm{A}][\mathrm{B'}]$$

$$[\mathrm{A}]_0 = 2[\mathrm{B}]_0 = 2[\mathrm{B'}]_0$$

$$[\mathrm{A}] = [\mathrm{B}] + [\mathrm{B'}]$$

$$\frac{-d[\mathrm{A}]}{dt} = (k_1 - k_2)[\mathrm{A}][\mathrm{B}] + k_2[\mathrm{A}]^2$$

2-3 Accessibility of Functional Groups



2-4 Equilibrium Considerations

2-4a Closed System

$$K = \frac{[\mathrm{COO}][\mathrm{H_2O}]}{[\mathrm{COOH}][\mathrm{OH}]} = \frac{(p_e[\mathrm{M}]_0)^2}{([\mathrm{M}]_0 - p_e[\mathrm{M}]_0)^2}$$

$$K = \frac{p_e^2}{(1 - p_e)^2}$$

$$p_e = \frac{K^{1/2}}{1 + K^{1/2}}$$

$$\overline{X}_n = 1 + K^{1/2}$$

Polyesterification	1 ~ 10
Polyamidation	100 ~ 1000

(K value)

2-4b Open, Driven System

$$K = \frac{[\mathrm{COO}][\mathrm{H_2O}]}{[\mathrm{COOH}][\mathrm{OH}]}$$

$$K = \frac{p[\mathrm{H_2O}]}{[\mathrm{M}]_0(1-p)^2}$$

$$K = \frac{p[\mathrm{H_2O}]\overline{X}_n^2}{[\mathrm{M}]_0}$$

$$[\mathrm{H_2O}] = \frac{K[\mathrm{M}]_0}{\overline{X}_n(\overline{X}_n - 1)}$$

2-4c Kinetics of Reversible Polymerization

P_e : extent of rxn at equilibrium = const.
P : extent of rxn at t => variable

2-5 Cyclization vs. Linear Polymerization

1. Thermodynamic stability of ring structure
   Stability : 3,4 < 5,6,8~13 < 6, n-alkane
2. Kinetic feasibility

2-6 Molecular Weight Control in Linear Polymerization

i) Quenching the reaction
=> Subsequent heat can change the Molecular Weight
ii) Stoichiometric Control
1. One of reactants are in slight excess
2. Addition of small amount of monofunctional molecule

2-6c Kinetics of Nonstoichiometric Polymerization

$$\frac{-d[\mathrm{A}]}{dt} = k[\mathrm{A}][\mathrm{B}]$$

$$[\mathrm{A}]_0 - [\mathrm{A}] = [\mathrm{B}]_0 - [\mathrm{B}]$$

$$\frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0} \ln \left[\frac{[\mathrm{A}]_0[\mathrm{B}]}{[\mathrm{B}]_0[\mathrm{A}]}\right] = kt$$

$$r = [\mathrm{A}]_0/[\mathrm{B}]$$

$$\ln \frac{[\mathrm{B}]}{[\mathrm{A}]} = -\ln\ r + [\mathrm{B}]_0(1-r)kt$$

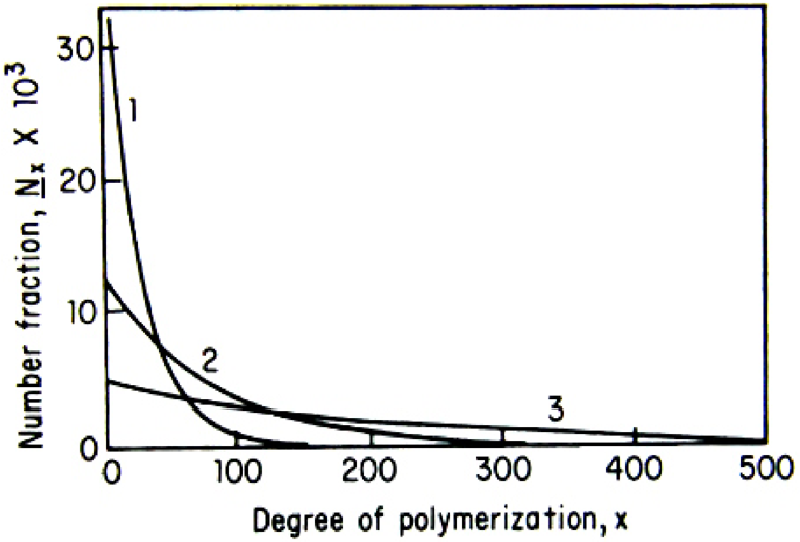
2-7 Molecular Weight Distribution in Linear Polymerization

Flory : A-B monomer system (A-A, B-B)
Polymers with x structural unit

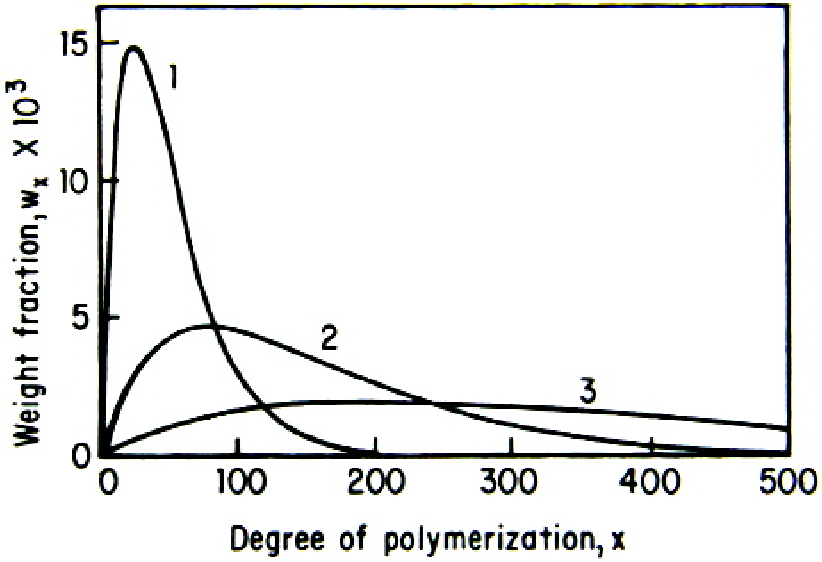
$$\underline{N}_x = p^{x-1}(1-p)$$
$$N_x = Np^{x-1}(1-p)$$
$$N_x = N_0(1-p)^2p^{x-1}$$
$$w_x = x(1-p)^2p^{x-1}$$

$$\overline{X}_n = \frac{\Sigma xN_x}{\Sigma N_x} = \Sigma x\underline{N}_x$$
$$\overline{X}_n = \Sigma xp^{x-1}(1-p)$$
$$\overline{X}_n = \frac{1}{(1-p)}$$

$$\overline{X}_w = \Sigma xw_x$$
$$\overline{X}_w = \Sigma x^2p^{x-1}(1-p)^2$$
$$\overline{X}_w = \frac{(1+p)}{(1-p)}$$



Number-fraction distrubution curve for linear polymerization



Weight-fraction distrubution curve for linear polymerization

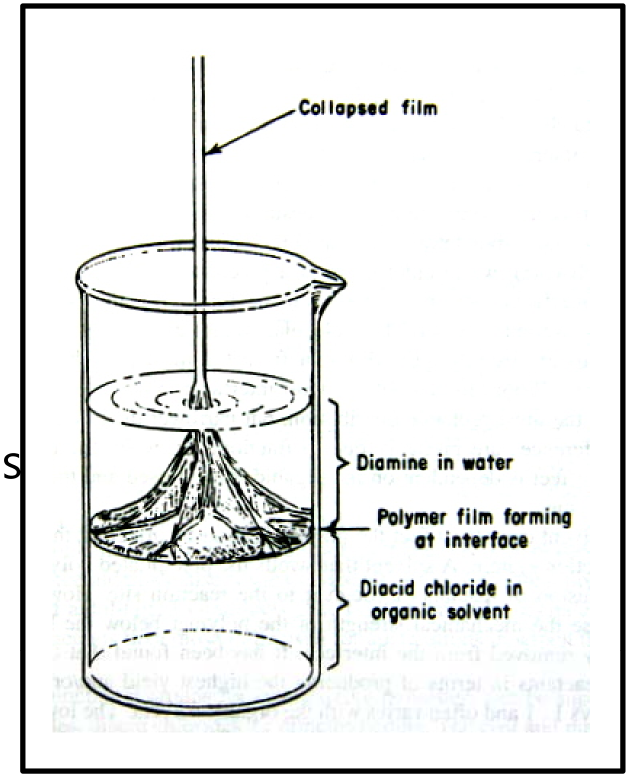
2-8 Process Conditions

To obtain polymers with High Molecular Weight

i) Minimize the side rxn
   -> cyclization
   -> polymerization at high conc.
ii) r = 1 High purity of reactants or stoichiometric balance
iii) Removal of byproduct

2-8c Interfacial Polymerization

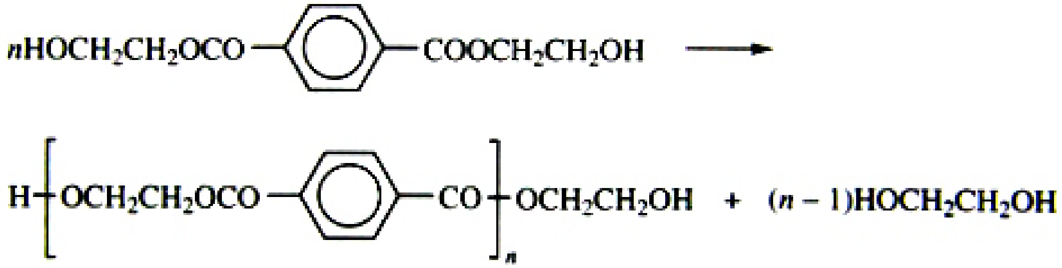
⇒ Schotten – Baumann reaction
i) Low temperature polymerization
ii) Diacyl chloride <-> -NH
iii) Diffusion controlled rxn
   rxn rate > diffusion rate
iv) Stoichiometry automatically exist
   High molecular weight is obtained regardless of the amount of monomers
v) Inorganic base is in the aqueous phase
vi) The choice of organic solvent
   Polymerization site is organic solvent



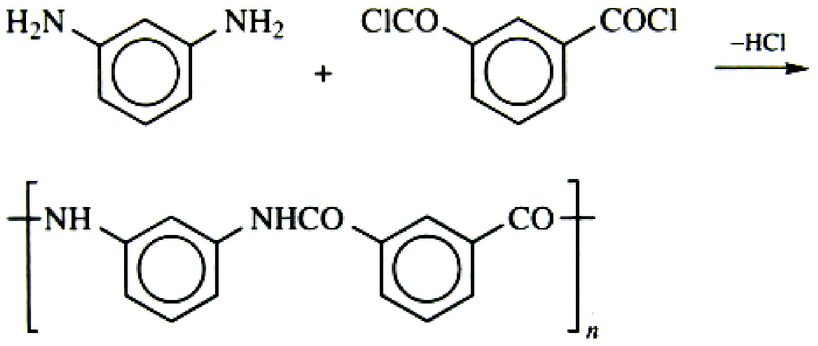
2-8d Polyesters

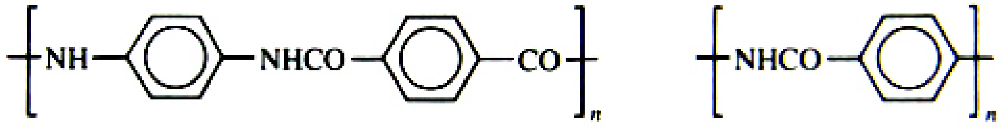
High temperature melt polymerization

Two stage ester exchange reaction



2-8f Polyamide





2-9 Multichain Polymerization

2-9a Branching

A-B with small amount of A-┬-A
A

2-9b Molecular Weight Distribution

$$\frac{\overline{X}_w}{\overline{X}_n} = 1 + \frac{frp}{(frp + 1 - rp)^2} \qquad \frac{\overline{X}_w}{\overline{X}_n} = 1 + \frac{1}{f}$$

2-10 Crosslinking

2-10a Carothers Equation $\overline{X}_n \rightarrow \infty$

$$f_{\text{avg}} = \frac{\Sigma N_i f_i}{\Sigma N_i}$$

$$\overline{X}_n = \frac{N_0}{N}$$

$$\overline{X}_n = \frac{2}{2 - p f_{\text{avg}}}$$

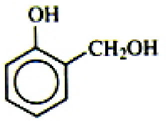
$$p = \frac{2}{f_{\text{avg}}} - \frac{2}{\overline{X}_n f_{\text{avg}}}$$

$$\boxed{p_c = \frac{2}{f_{\text{ave}}} \quad \text{Critical extent of rxn for gelation}}$$

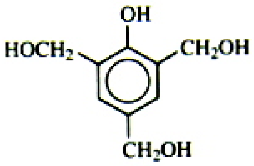
2-12b Phenolic Polymers

A. Resole

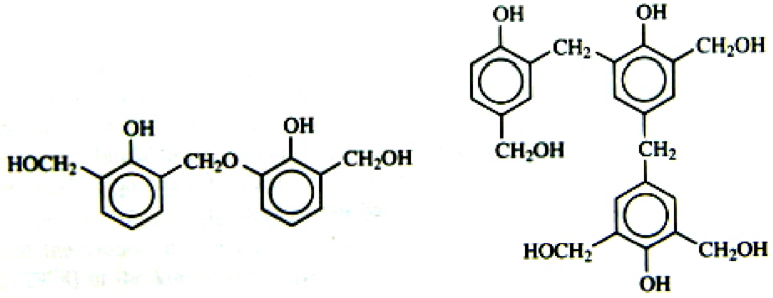
Phenol/formaldehyde = 1/1.2~1.3



XXIa

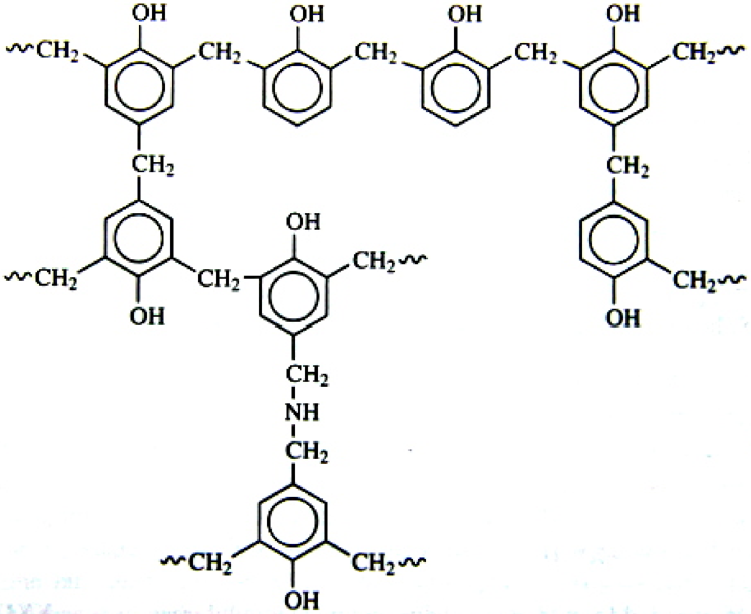


XXIb

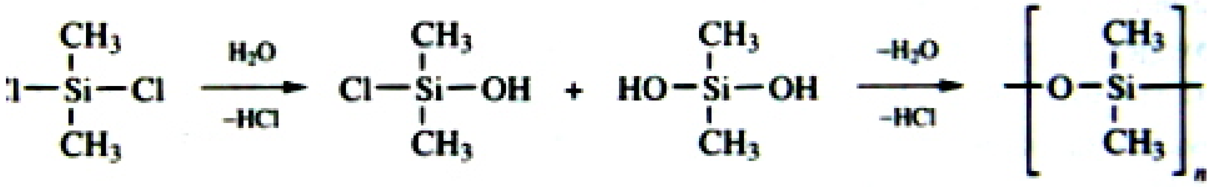


B. Novolac

Phenol/formaldehyde = 1/0.7~0.8



2-12f Silicon Polymers



2-16 Dendritic (Highly branced) Polymers

- Dendritic polymer => globular shape
- Less attractive force between the polymers
- High solubility & miscibility
- Lower hydrodynamic volume
- Large # of chain end
- Linear protein : bone, skin, nail, muscle
- Globular protein : catalytic, transport,
  regulatory hormonal, other functions

2-16a Random Hyperbranced Polymers

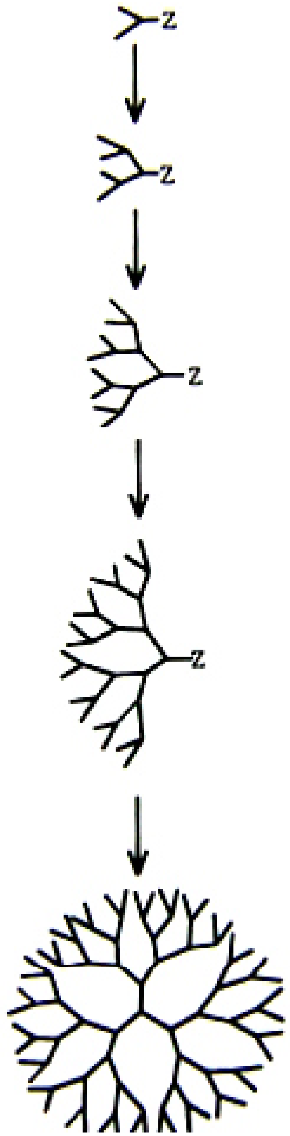
Polymerization of A-┬-B
B

2-16b Dendribmers

⇒Dendritic polymer with a more controlled structure

Two Synthetic Procedure

1. Divergent Synthesis
2. Convergent Synthesis



Convergent synthesis of dendrimers

Chapter 3. Radical Chain Polymerization

3-1 NATURE OF RADICAL CHAIN POLYMERIZATION

* Comparison of Chain and Step Polymerization
(monomer concentration vs time, Mw vs time)

* Chain Polymerization
- Radical Polymerization
- Ionic Polymerization (anionic, cationic, coordination)

* Effect of Substituent for Vinyl Monomers in Chain Polymerization
- electron donating group ; cationic polymerization possible
- electron withdrawing group ; anionic polymerization possible
- radical : neutral
  (both electron donating, withdrawing group stabilize the radical)

3-2 STRUCTURAL ARRANGEMENT OF MONOMER UNITS

* Two Possible Mode of Propagation
- Head-to-head
- Head-to-tail

→ Steric hinderence(kinetics), thermodynamics, temperature effect

3-3 RATE OF RADICAL CHAIN POLYMERIZATION

3-3a Sequence of Events

1. Initiation → Active Center (Radical) ; K_i
   (Initiators)

2. Propagation ; K_p

3. Termination ; K_t
   (Combination , Disproportionation)

3-3b Rate Expression

- Assumption : K_p, K_t → constant

- $R_p = K_p[M\cdot][M]$

- Steady-State Assumption : $[M\cdot]$ is constant
  $[M\cdot]$: Generated by initiation, Terminated by termination

- $[M\cdot] = \left(\frac{R_i}{2K_t}\right)^{\frac{1}{2}}$, $R_p = K_p[M]\left(\frac{R_i}{2K_t}\right)^{\frac{1}{2}}$

3-3c Experimental Determination of Rp ; rate of polymerization : $-\frac{d[M]}{dt}$

1. Physical Separation or Isolation of the Product
   - Precipitation using non-solvent
   - Distillation : Boiling point (removing monomers)

2. Chemical and Spectroscopic Approach
   - using NMR or IR

3. Dilatometry
   - Volume Change

4. Other Methods
   - Refractive Index
   - Heat of Polymerization

3-4 INITIATION

- Free Radical
  a. Homolytic Cleavage
  b. As an Intermediate in Chemical Reaction; Redox Initiation
  c. By Adding or Removing Electron from Molecules
  → Using Electrochemical Device or Ionizing Radiation

3-4a Thermal Decomposition of Initiators

1. Weaker Bond (E : kcal/mol)
→ C-C (70-80), C-H (~100), O-O (35), N-N (20), C-N (48)

2. The Initiator Decompose to form Stable Product such as N2 or CO2
(dialkylperoxy dicarbonate, alkylperoxy pivalate)

3. Radical formed are Stabilized

4. Polar Effect

* Initiator Halflife
→ The time for the concentration of initiator to decrease to one half of its original concentration

3-4a-3 Depencence of Propagation Rate on Initiator

$$R_p = K_p[M]\left(\frac{fK_d[I]}{K_t}\right)^{\frac{1}{2}}$$

3-4b Redox Initiation

→ Low Temperature Polymerization Possible (0°C ~ 50°C)

* Haber-Weiss Mechanism

* Pure Benzoyl Peroxide vs Benzoyl Peroxide with N,N-aniline

* Kinetics of Polymerization by Redox Initiation

3-4d Initiation by Ionizing Radiation

→ X-ray, γ-ray, e-beam, etc. (High Energy, Short Wavelength System)

3-4e Pure Thermal Initiation

* Electrochemical Initiation

→ Cage Effect

3-4g Initiation Efficiency, f

→ The fraction of radicals formed in the decomposition steps which are successful initiating polymerization

- $0<f\leq1$
- Quantitative Data for the Initiation Reactions
- Summary

3-4g-3 Experimental Determination of f

1. Direct Measurement (High Resolution NMR, for not very high Mw Polymer)

2. The use of Radical Scavenger or Spin Traps

3. Electron Spin Resonance (ESR) → Concentration of Radicals

4. Dead End Polymerization

3-5 MOLECULAR WEIGHT

3-5a Kinetic Chain Length

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

3-6 CHAIN TRANSFER

- Effect of Chain Transfer
- Transfer to Monomer and Initiator
- Transfer to Chain-Transfer Agent
- Chain Transfer to Polymer (LDPE and HDPE)
- Catalytic Chain Transfer

3-7 INHIBITION (Stop) AND RETARDATION (Slow)

(Figure 3-9)

- Inhibition
  ; DPPH (P233), $FeCl_3$, $CuCl_2$ (Organic Inhibitor, P263)
  ; Use in Distillation Process

- Retardation
  ; Slower rate, Termination → Conversion↓

* Kinetics of Inhibition

* Chloranil (2,3,5,6-tetrachlorobenzoquinone) ; Table 3-8

* Oxygen is most toxic for Radical Polymerization

3-7c Autoinhibition of Allylic Monomers

(Table 3-3 ; Case 4)

* Kinetics of Polymerization of Allylic Monomers
  ; Steady-State Assumption
  (P269, Table 3-10)

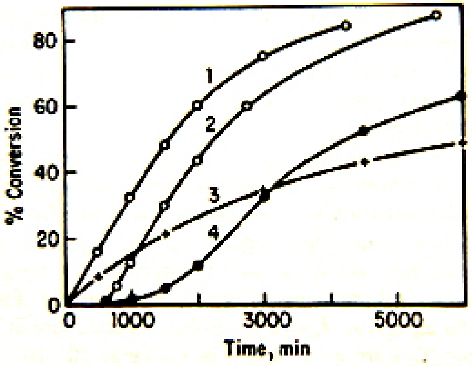


Fig. 3-9 Inhibition and retardation in the thermal, self-initiated polymerization of styrene at 100°C. Plot 1, no inhibitor; plot 2, 0.1% benzoquinone; plot 3, 0.5% nitrobenzene; plot 4, 0.2% nitrosobenzene. After Schulz [1947] (by permission of Verlag Chemie GmbH and Wiley-VCH, Weinheim).

TABLE 3-8 Inhibitor Constants[a]

Inhibitor	Monomer[b]	$z = k_z/k_p$
Nitrobenzene	Methyl acrylate	0.00464
	Styrene	0.326
	Vinyl acetate	11.2
1,3,5-Trinitrobenzene	Methyl acrylate	0.204
	Styrene	64.2
	Vinyl acetate	404
p-Benzoquinone	Acrylonitrile	0.91
	Methyl methacrylate	5.5 (44°C)
	Styrene	518
Chloranil	Methyl methacrylate (44°C)	0.26
	Styrene	2,040
DPPH	Methyl methacrylate (44°C)	2,000
$FeCl_3$	Acrylonitrile (60°C)	3.3
	Styrene (60°C)	536
$CuCl_2$	Acrylonitrile (60°C)	100
	Methyl methacrylate (60°C)	1,027
	Styrene	~11,000
Oxygen	Methyl methacrylate	33,000
	Styrene	14,600
Sulfur	Methyl methacrylate (44°C)	0.075
	Vinyl acetate (44°C)	470
Aniline	Methyl acrylate	0.0001
	Vinyl acetate	0.015
Phenol	Methyl acrylate	0.0002
	Vinyl acetate	0.012
p-Dihydroxybenzene	Vinyl acetate	0.7
1,2,3-Trihydroxybenzene	Vinyl acetate	5.0
2,4,6-Trimethylphenol	Vinyl acetate	0.5

[a] Data from Brandrup and Immergut [1975].

[b] All data are for 50°C except where otherwise noted.

3-9 ENERGETIC CHARACTERISTICS

* Thermodynamics of Polymerization

- Entropy Change

- Enthalpy Change
  (P275, Table 3-15)

- Enthalpy Difference
  a. Steric Effect

  b. Resonance Stabilization

  c. Difference in H-Bonding or Dipole Interactions

* Polymerization-Depolymerization
- K_p, K_{dp}

- Table 3-16

- Ceiling Temperature

- Floor Temperature

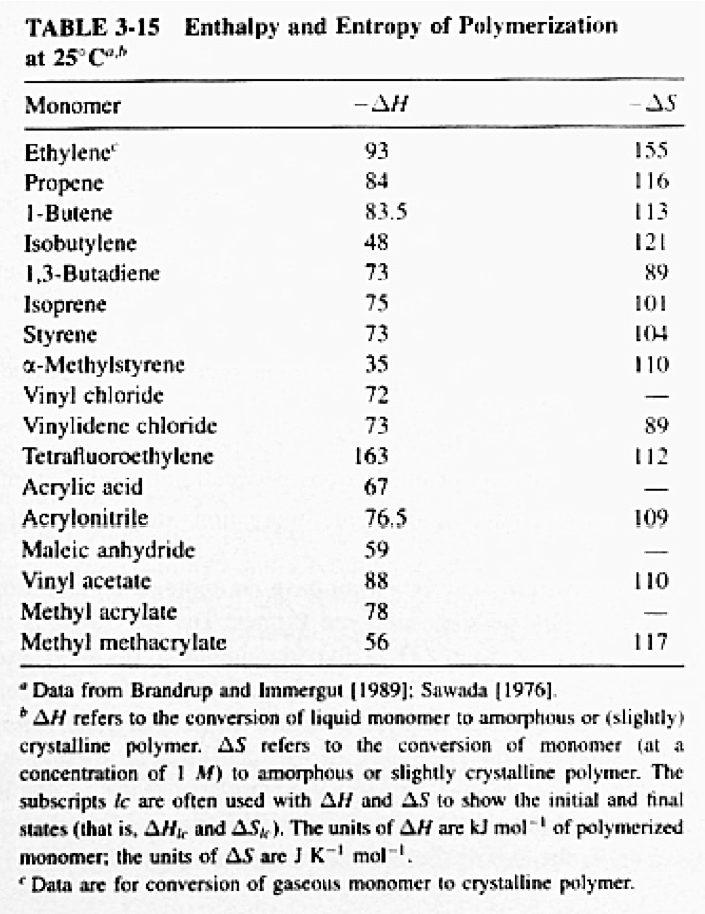


TABLE 3-15 Enthalpy and Entropy of Polymerization at 25°C[a,b]

Monomer	$-\Delta H$	$-\Delta S$
Ethylene[c]	93	155
Propene	84	116
1-Butene	83.5	113
Isobutylene	48	121
1,3-Butadiene	73	89
Isoprene	75	101
Styrene	73	104
α-Methylstyrene	35	110
Vinyl chloride	72	—
Vinylidene chloride	73	89
Tetrafluoroethylene	163	112
Acrylic acid	67	—
Acrylonitrile	76.5	109
Maleic anhydride	59	—
Vinyl acetate	88	110
Methyl acrylate	78	—
Methyl methacrylate	56	117

[a] Data from Brandrup and Immergut [1989]; Sawada [1976].

[b] ΔH refers to the conversion of liquid monomer to amorphous or (slightly) crystalline polymer. ΔS refers to the conversion of monomer (at a concentration of 1 *M*) to amorphous or slightly crystalline polymer. The subscripts *lc* are often used with ΔH and ΔS to show the initial and final states (that is, ΔH_{lc} and ΔS_{lc}). The units of ΔH are kJ mol^{-1} of polymerized monomer; the units of ΔS are J K^{-1} mol^{-1}.

[c] Data are for conversion of gaseous monomer to crystalline polymer.

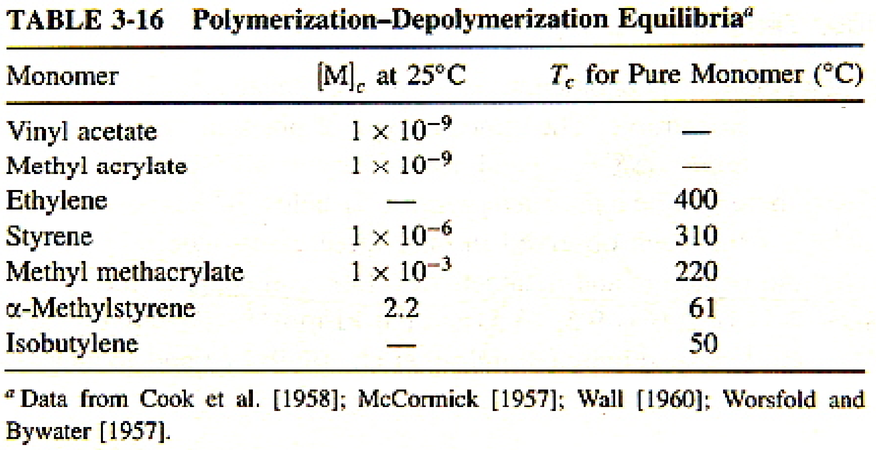


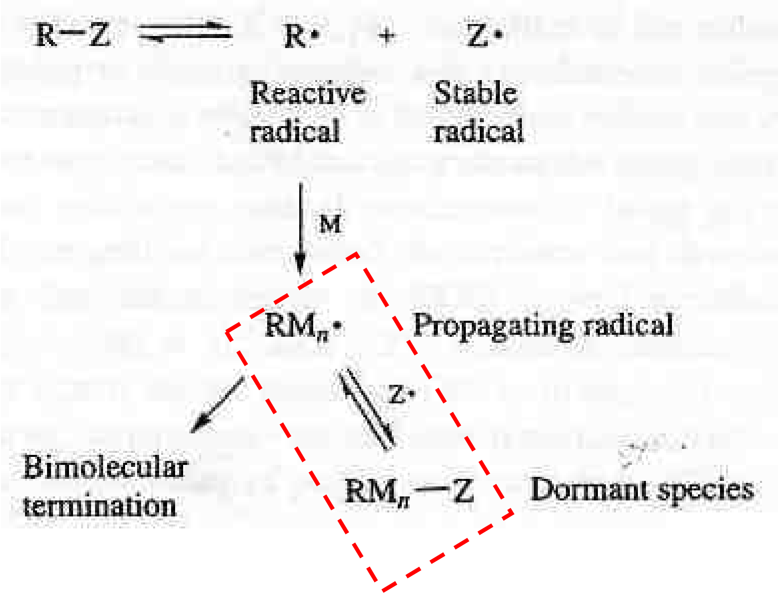
TABLE 3-16 Polymerization–Depolymerization Equilibria[a]

Monomer	$[M]_c$ at 25°C	T_c for Pure Monomer (°C)
Vinyl acetate	1×10^{-9}	—
Methyl acrylate	1×10^{-9}	—
Ethylene	—	400
Styrene	1×10^{-6}	310
Methyl methacrylate	1×10^{-3}	220
α-Methylstyrene	2.2	61
Isobutylene	—	50

[a] Data from Cook et al. [1958]; McCormick [1957]; Wall [1960]; Worsfold and Bywater [1957].

- Controlled/Living Radical polymerization

  - chain polymerization without chain-breaking reactions.
  - by minimizing normal bimolecular termination and prolonging the lifetime of propagating polymer chains.



Controlled/Living Radical Polymerization(CRP), Pseudo-living, quasi-living, immortal, truly living, etc.

Introduction

- Advantage of Living Radical Polymerization

- Controlled molecular weight
  ; time(conversion) or stoichiometry
- Low molecular weight distribution (low PDI)
  ; less than 1.3
- It is easy to synthesize block copolymers
- Well defined star, graft, comb, hyperbranched polymer can be synthesized

Introduction

- Conditions

- All the initiator decomposes at once or in a very short time
- Equilibrium constant between the propagating radical and dormant species must be low but not too low.
- The concentration of stable radicals increases to at least 4 orders of magnitude greater than the concentration of propagating radicals.
- Avoid high conversion.

Introduction

- Criteria for Living Polymerization

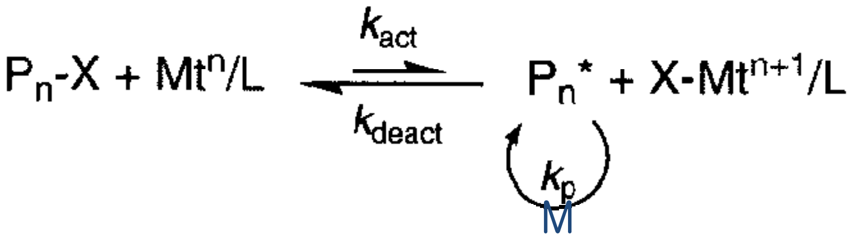
1. polymerization proceeds until all monomer has been consumed. Further addition of monomer results in continued polymerization
2. The number average molecular weight is a linear function of conversion
3. The number of polymer chains is constant and independent of conversion
4. The molecular weight can be controlled by the stoichiometry of the reaction
5. Narrow molecular weight can be prepared in quantitative yields.

– Quirk R.P. –

Introduction

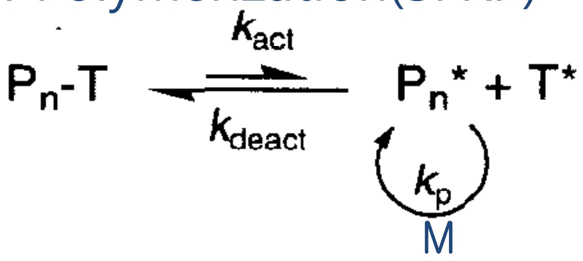
Controlled/Living Radical Polymerization

Atom Transfer Radical Polymerization(ATRP)



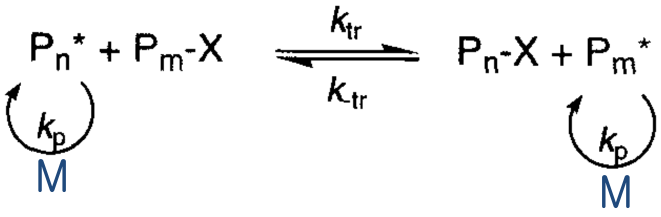
$$P_n\text{-}X + Mt^n/L \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^* + X\text{-}Mt^{n+1}/L$$

Stable Free Radical Polymerization(SFRP)



$$P_n\text{-}T \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^* + T^*$$

Reversible Addition Fragmentation Transfer(RAFT)



$$P_n^* + P_m\text{-}X \underset{k_{tr}}{\overset{k_{tr}}{\rightleftharpoons}} P_n\text{-}X + P_m^*$$

ATRP

- Atom Transfer Radical Polymerization (ATRP)

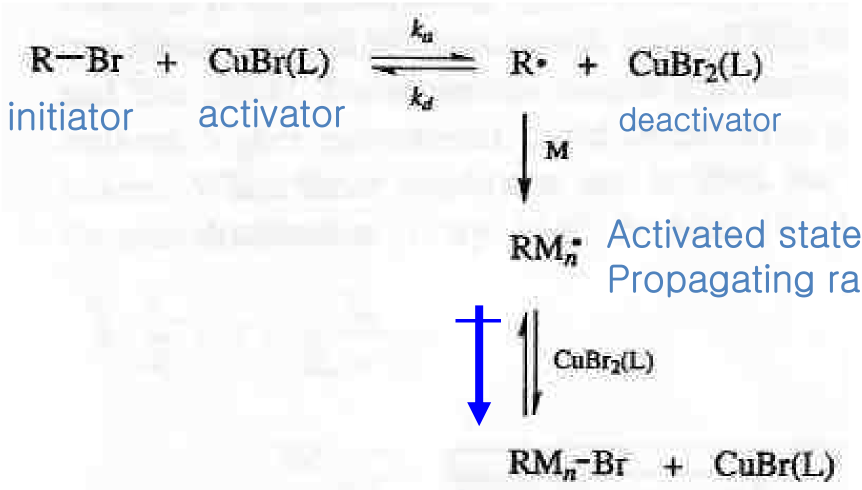
- Prevention bimolecular termination by reversible termination with halogen atom.

- Initiator(organic halide), transition metal catalysts(with two oxidation states), ligand, and monomer, (and solvent).

- Dormant state (deactivated propagating chain) is dominant.
  - low equilibrium constant $K \sim 10^{-7}$

Mechanism of ATRP

Mechanism of ATRP



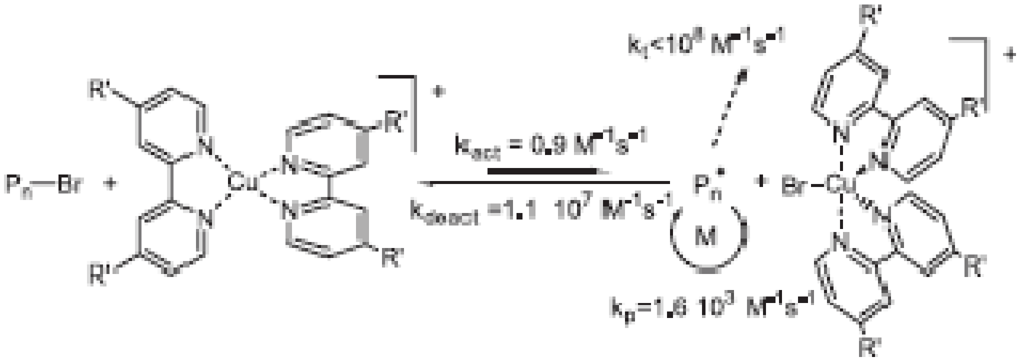
initiator

activator

deactivator

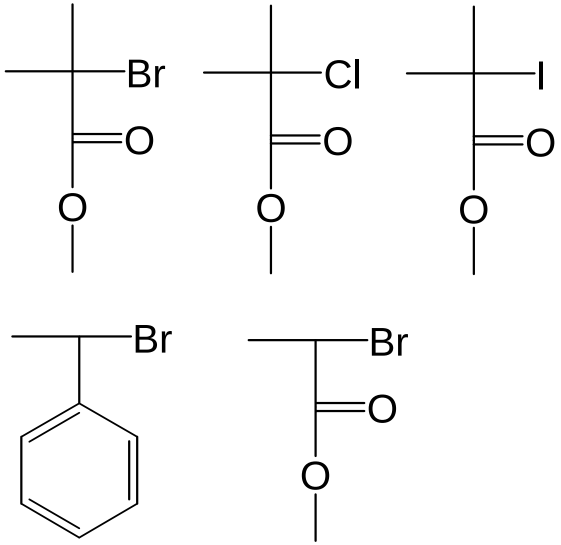
Activated state
Propagating radical

Dormant state

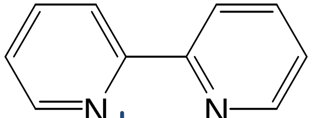


Components of ATRP

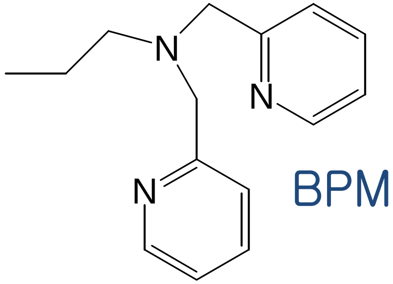
Initiators



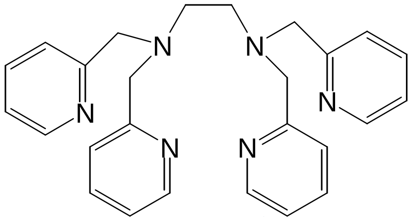
Ligands



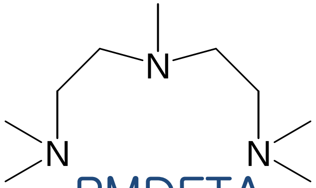
bpy



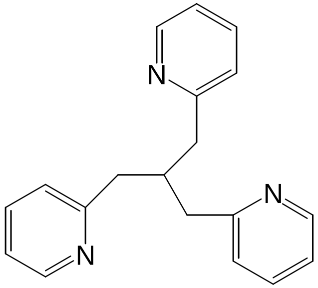
BPMPrA



TPEDA



PMDETA



TPMA

Transition Metals

Cu, Co, Fe, ets ; Various middle and late transition metals (group 6–11).

Reactivity study of ATRP

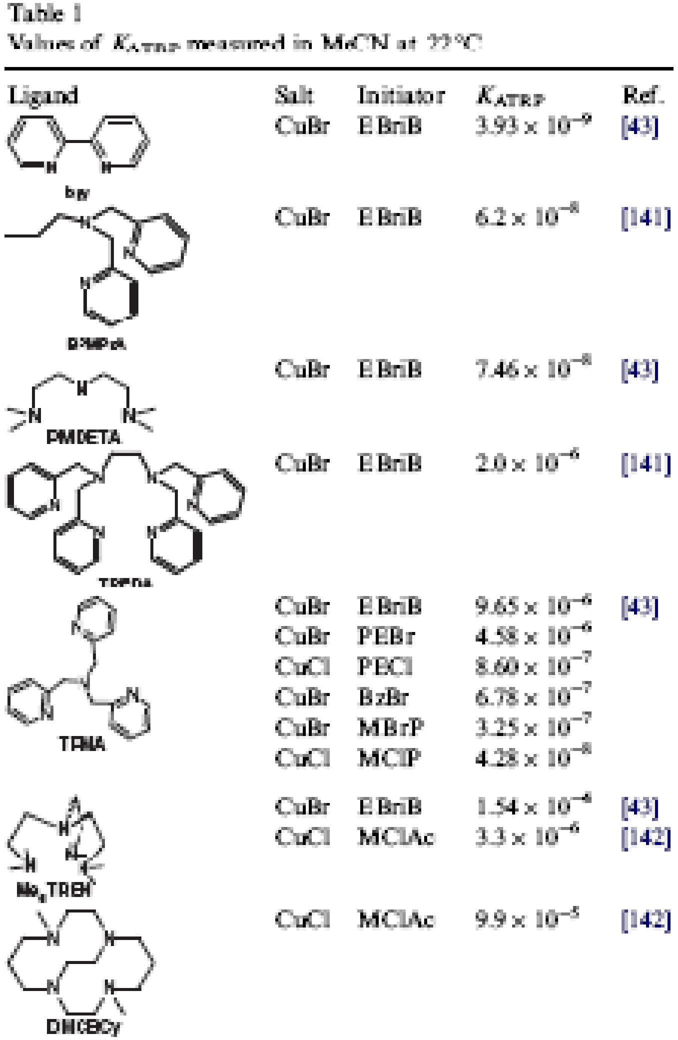
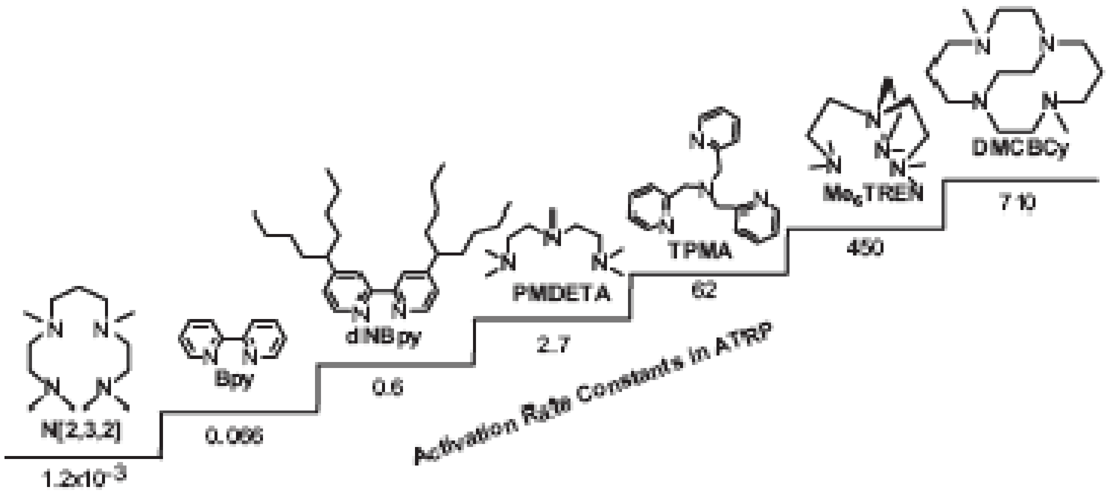
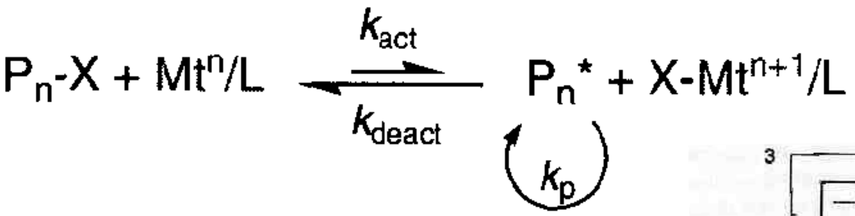


Table 1
Values of K_{ATRP} measured in MeCN at 22 °C

Ligand	Salt	Initiator	K_{ATRP}	Ref.
bpy	CuBr	EBriB	3.93×10^{-9}	[43]
BPMPrA	CuBr	EBriB	6.2×10^{-8}	[141]
PMDETA	CuBr	EBriB	7.46×10^{-8}	[43]
TPEDA	CuBr	EBriB	2.0×10^{-6}	[141]
TPMA	CuBr	EBriB	9.65×10^{-6}	[43]
	CuBr	PEBr	4.58×10^{-6}	
	CuCl	PECl	8.60×10^{-7}	
	CuBr	BzBr	6.78×10^{-7}	
	CuBr	MBrP	3.25×10^{-7}	
	CuCl	MClP	4.28×10^{-8}	
Me$_6$TREN	CuBr	EBriB	1.54×10^{-4}	[43]
	CuCl	MClAc	3.3×10^{-6}	[142]
DMCBCy	CuCl	MClAc	9.9×10^{-5}	[142]



Kinetics of ATRP



$$P_n\text{-}X + Mt^n/L \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^* + X\text{-}Mt^{n+1}/L$$

$K = k_a/k_d$; K ~ equilibrium constant; less tha

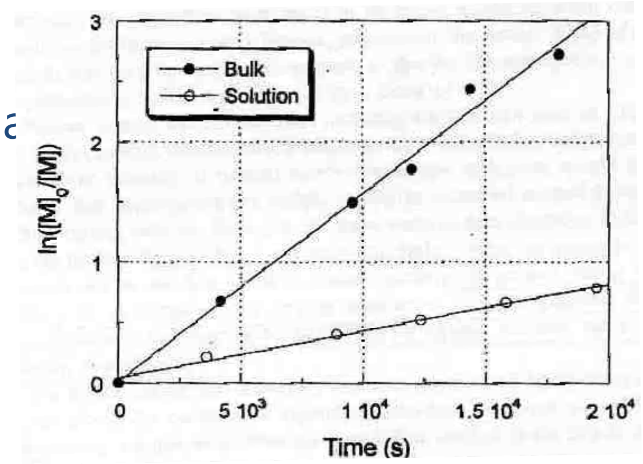
$$k_a[PX][Cu^+]=k_d[R\cdot][Cu^{2+}]$$

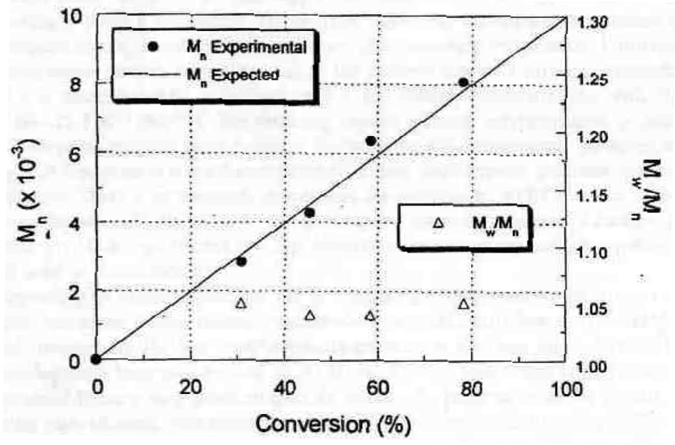
$$[R\cdot]=\frac{K[PX][Cu^+]}{[Cu^{2+}]} \fallingdotseq \frac{K[I][Cu^+]}{[Cu^{2+}]}$$

$$R_p = k_p[M][R\cdot] \fallingdotseq \frac{k_pK[M][I][Cu^+]}{[Cu^{2+}]}$$

$$\ln\frac{[M]_0}{[M]} = \frac{k_pK[I][Cu^+]}{[Cu^{2+}]}t$$

$$Mn = \frac{p[M]_0}{[I]_0}$$





Effect of components

- Initiator
  - Organic halides are used as initiator
  - Reactivity of halogen I≫Br＞Cl ≫F
  - Usually, organic halides having similar structure with monomer are used as initiator
- Metal catalyst and Ligands
  - The equilibrium constant of ATRP is mainly determined by metal catalysts.
  - Proper functioning of a metal catalyst requires appropriate ligands.
- Temperature
  - k_p and K increases with increasing temperature

    -> increasing Rp and bimolecular termination

  There is an optimum temperature for any specific ATRP reaction system.

Summary

- ATRP involves an organic halide undergoing a Reversible redox process catalyzed by a transition metal compound.

- Rapid reversible deactivation of propagating radicals is needed.

- Metal catalyst is the key to ATRP.

- Various monomers can be polymerization by ATRP, but low reactive monomers, such as ethylene, vinyl chloride, vinyl acetate, and acidic monomers such as acrylic acid have not been polymerized.

The direction of research of ATRP

- Metal residue should be removed.

The direction of research of ATRP

ICAR-ATRP

Summary

- Radical generation in atom-transfer radical polymerization involves an organic halide undergoing a reversible redox process catalyzed by a transition metal compound.
- Rapid reversible deactivation of propagating radicals is needed to maintain low radical concentrations and minimize normal termination of living polymers.
- Metal catalyst is the key to ATRP since it determines the position of equilibrium(K) and rate of exchange between dormant and propagating species.
- Various monomers can be polymerization by ATRP, but low reactive monomers, such as ethylene, vinyl chloride, vinyl acetate, and acidic monomers such as acrylic acid have not been polymerized.
- Metal residue should be removed.

Block copolymer

- Methods to synthesize block copolymers

$$A \xrightarrow[\text{Cux}]{\text{RX}} RA_nX \xrightarrow{\text{B}} RA_n\text{-}B_mX$$

- One-pot sequential method.
  - Adding second monomer when most of first monomer has reacted.
  - Simpler method than isolated macroinitiator method but second block can be a random polymer.
- Isolated macroinitiator metholds
  - halogen-terminated polymer of first monomer is isolated and then used as an initiator.
- Conditions
  - Usually, 90% conversion of first monomer is the maximum conversion.
  - If the two monomers are in the same family, either addition sequence works. However, if the two monomers are in the different families, specific sequence is allowed because of the reactivities of monomers

MMA-styrene, MMA-MA (O)

Styrene-MMA, MA-MMA (X)

Block copolymer

- Syntheses of tri- or more block copolymers.
- Continuation of the sequential method.

  one-pot sequential method and isolated-macroinitiator method

$$A \xrightarrow[Cux]{RX} RA_nX \xrightarrow{B} RA_n\text{-}B_mX \xrightarrow{C} RA_n\text{-}B_m\text{-}C_lX$$

- Using difunctional initiator.

$$A \xrightarrow[Cux]{XRX} XA_nRA_nX \xrightarrow{B} XB_m\text{-}A_nRA_n\text{-}B_mX$$

- Well defined star, graft, comb, hyperbranched polymer can be synthesized

SFRP

- Stable Free Radical Polymerization(SFRP)

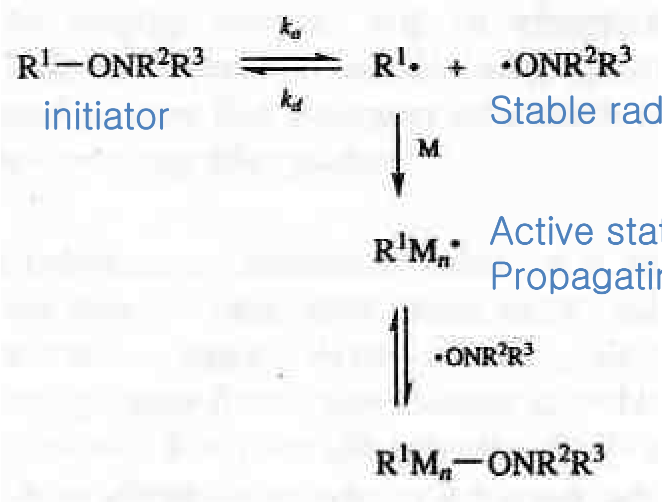
- Prevention bimolecular termination by reversible termination with stable radical.

- Initiator(reactive radical + stable radical), monomer, (solvent)

- Dormant state (deactivated propagating chain) is dominant.
  - low equilibrium constant $K \sim 10^{-11}$

Mechanism of SFRP

Mechanism of SFRP

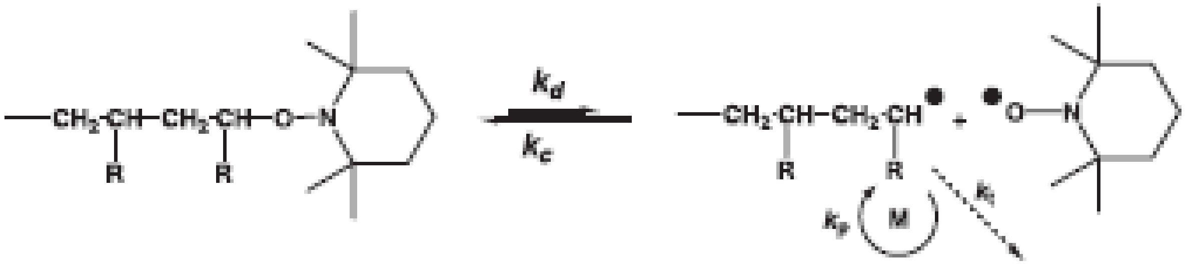


initiator

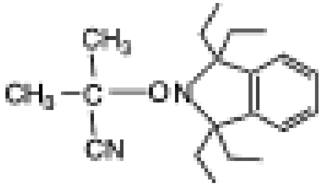
Stable radical

Active state
Propagating radical

Dormant state



Initiators of SFRP



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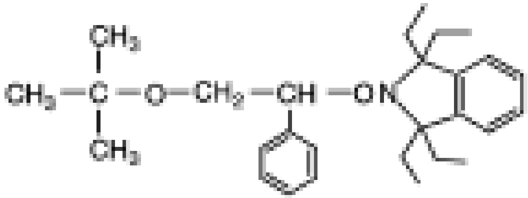

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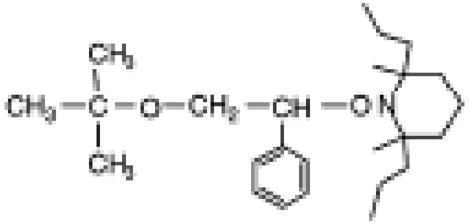

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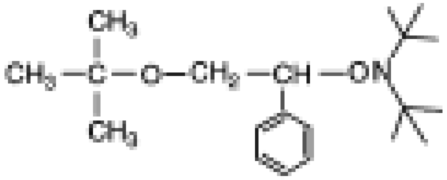

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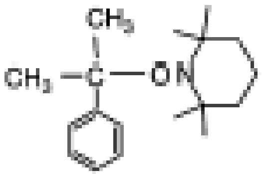

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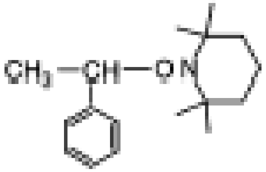
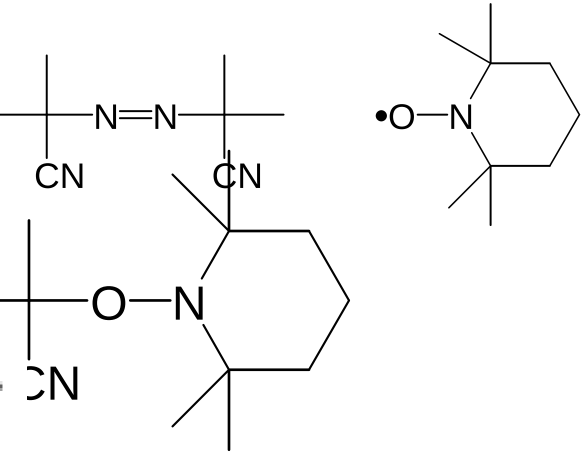


6: S-TEMPO

7

AIBN−TEMPO



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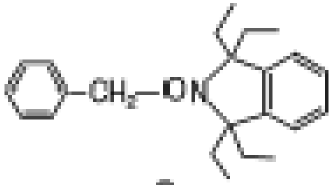


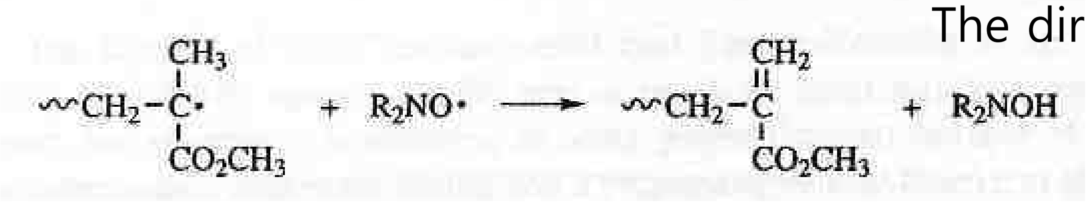
9

2,2,6,6,−tetramethy−1−piperidinoxyl(**TEMPO**)

Summary

- Nitroxide, triazolinyl, (arylazo)oxy, and dithiocarbamate, etc.
- Nitroxide Mediated Polymerization (NMP) – esp. TEMPO
- Synthesized initiators
- Very low equilibrium constant. Higher temperatures (125-145℃) and longer reaction time.
- Limited monomers.
- (styrenes, acrylates, acrylamides, 1,-dienes, and acrylonitriles are OK)
- (Well defined PMMA is difficult to be synthesized by SFRP)

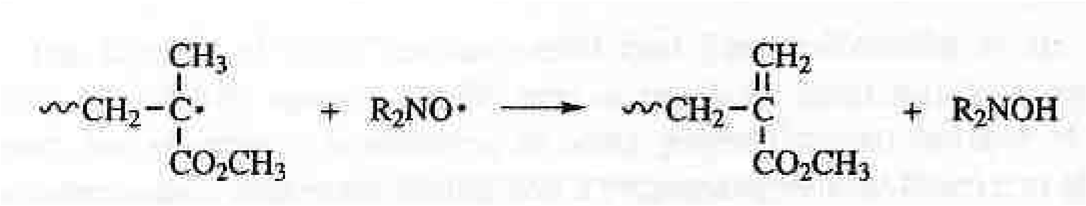
The direction of research of SFRP



β−hydrogen abstraction

Summary

- Various stable radicals such as nitroxide, triazolinyl, trityl, and dithiocarbamate have been used as the mediating or persistent radical for SFRP.
- Nitroxide Mediated Polymerization (NMP) – esp. TEMPO
- Synthesized initiators(active radical and stable radical), (conventional initiators such as AIBN), monomers, solvent are components in SFRP
- Very low equilibrium constant. It requires higher temperatures (125-145℃) and longer reaction time compared to ATRP.
- Limited monomers can be polymerized by SFRP
- (styrenes, acrylates, acrylamides, 1,-dienes, and acrylonitriles are OK)
- (Well defined PMMA is difficult to be synthesized by SFRP)



$$\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CO_2CH_3}{C\cdot}} + R_2NO\cdot \longrightarrow \sim CH_2-\overset{\displaystyle CH_2}{\underset{\displaystyle CO_2CH_3}{C}} + R_2NOH$$

β−hydrogen abstraction

Block copolymer

- Methods to synthesize block copolymers

$$\text{R1-ONR2R3} \xrightarrow{\text{A}} \text{R1-AnONR2R3} \xrightarrow{\text{B}} \text{R1-AnBmONR2R3}$$

- Both One-pot sequential and isolated macromonomer methods are available.

- The order of addition of monomer is often important.

  Styrene-isoprene, MA-styrene, acrylate-isoprene

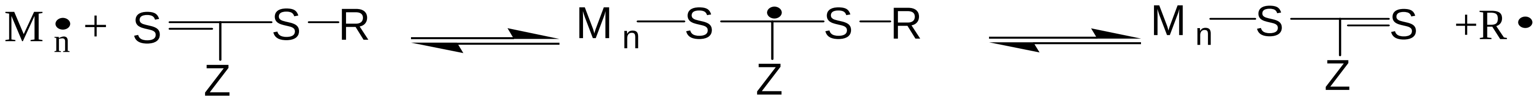
- Well defined star, graft, comb, hyperbranched polymer can be synthesized

RAFT

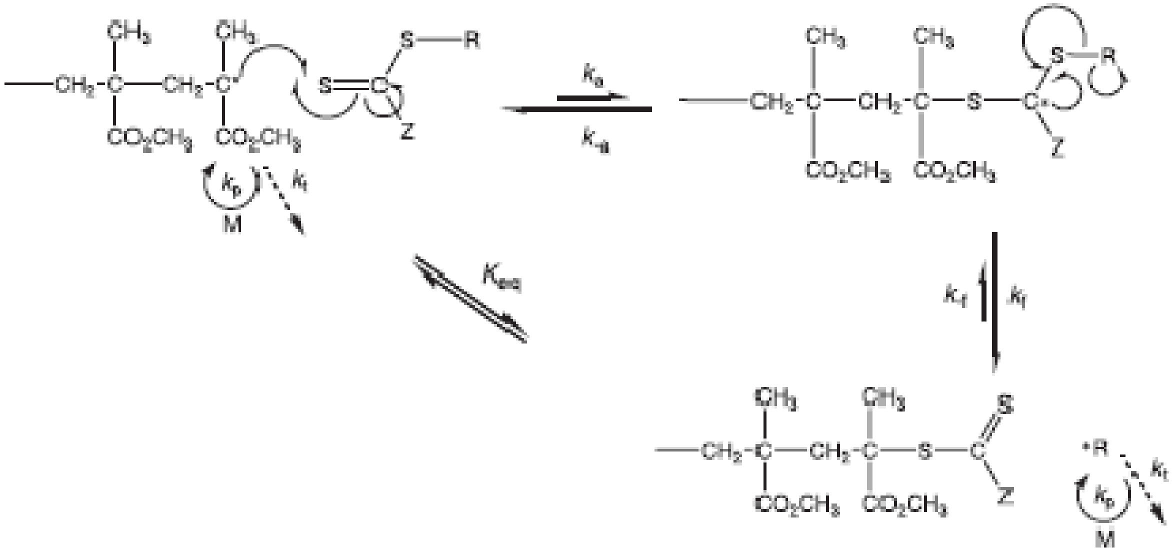
- Reversible Addition Fragmentation Transfer (RAFT)
  - Prevention bimolecular termination by reversible transfer with thiocarbonylthio group as chain transfer agent.
  - Initiator, chain transfer agent, and monomer, (solvent)
  - High equilibrium constant; $K \sim 1$

Mechanism of RAFT

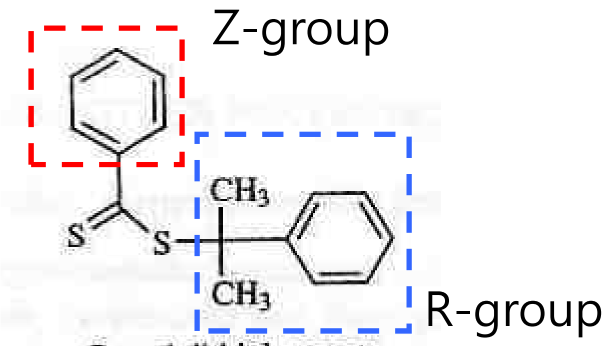
Mechanism of RAFT



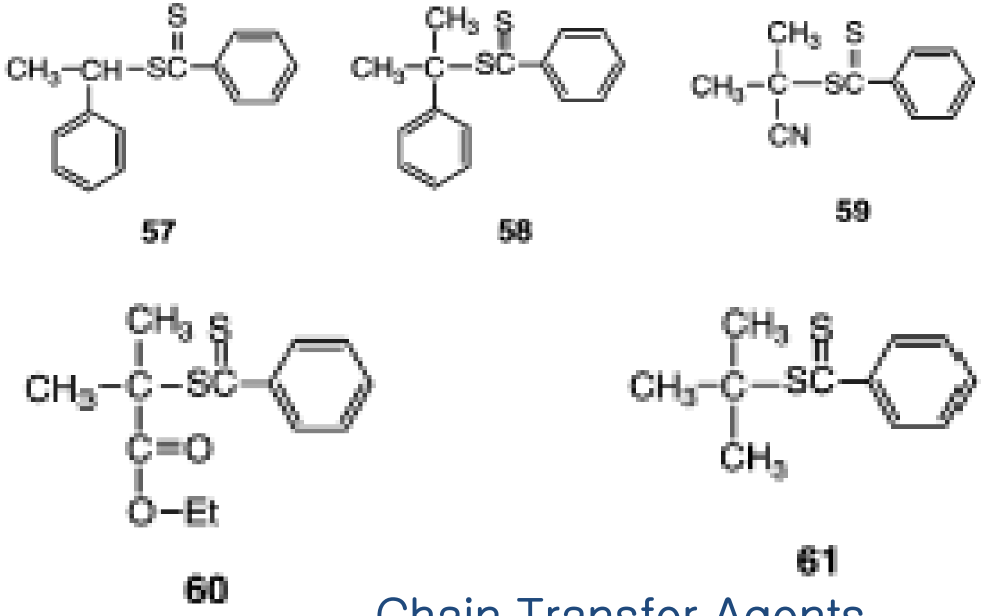
$M_n^{\bullet} + S{=}\underset{Z}{|}{-}S{-}R \rightleftharpoons M_n{-}S{-}\underset{Z}{\overset{\bullet}{|}}{-}S{-}R \rightleftharpoons M_n{-}S{-}\underset{Z}{|}{=}S + R^{\bullet}$



Chain Transfer Agents of RAFT



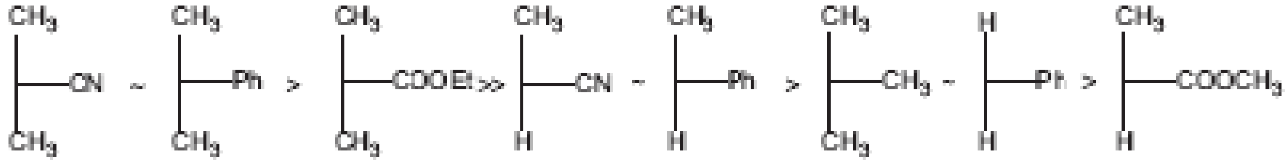
Cumyl dithiobenzoate



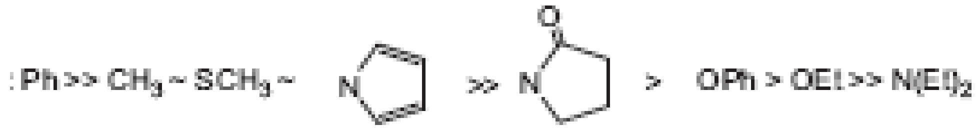
57 58 59 60 61

Chain Transfer Agents

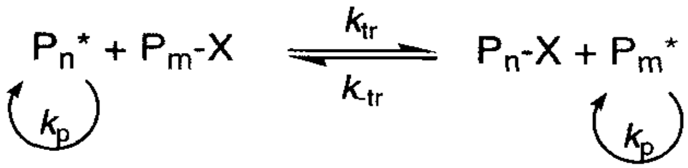
Reactivity of R–group



Reactivity of Z–group



Kinetics of RAFT



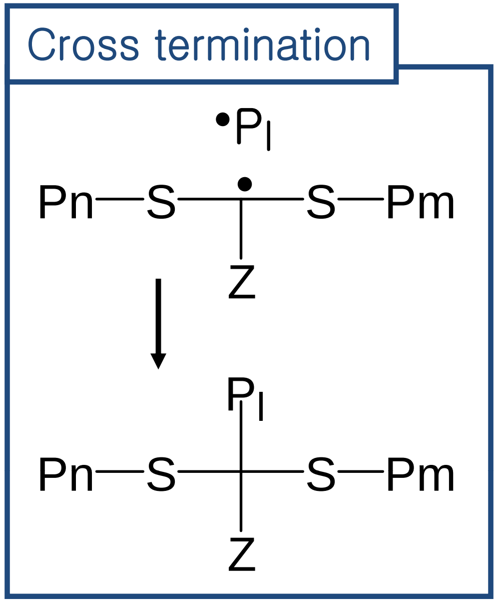
$$R_p = R_{p,0}\left(\frac{1}{1+2K_{RAFT}(k`_t/k_t)[P\text{-}X]_0}\right)^{1/2}$$

-A. Goto, T. Fukuda -

$R_{p,0}$ = polymerization rate without CTA
$[P\text{-}X]_0$=concentration of CTA
k_t = termination rate constant
$k`_t$ = cross-termination rate constant
$K = k_{ad}/k_{fr}$

Explanation of retardation

Slow fragmentation – Davis et al.
Cross termination - Monteiro et al.



Mn of polymer synthesized by RAFT

$$Mn = \frac{[M]}{[CTA]} \times M.W._{monomer} \times p$$

p : conversion

Effect of components

- Initiator

  - Higher concentration, higher Rp

- Chain Transfer agents

  - CTA controls Rp
  - Higher concentration, lower Rp

- Temperature

  - Higher temp., higher Rp, higher PDI

Summary

- RAFT transfer agent.
- Synthesized CTA
- # of chains = (# of CTA + # of decomposed initiator)
- Various monomers
- Modification of CTA

The direction of research of RAFT

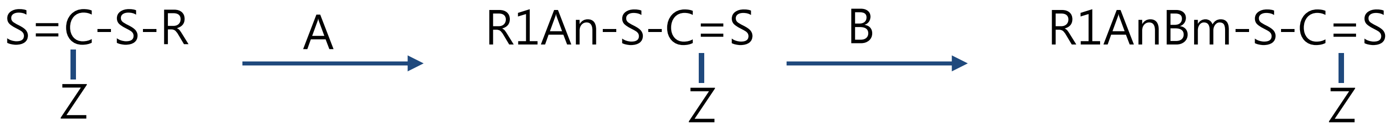
- Removal of thiocarbonylthio end group.

Summary

- RAFT living polymerizations control chain growth through reversible chain transfer.
- Equilibrium constant is about 1.
- The key that makes RAFT a living polymerization is the choice of the RAFT transfer agent.
- Usually commercial CTAs are not available, so they need to be synthesized.
- The number of chains is determined by the amount of RAFT agent consumed and the amount of conventional initiator decomposes.
- Various monomers can be polymerized by RAFT polymerization.
- Z and R groups in CTA can be functionalized by modification.
- Polymers synthesized via RAFT polymerization have color because of CTA, so thiocarbonylthio end group should be removed.

Block copolymer

- Methods to synthesize block copolymers



$$\mathrm{S{=}\underset{\displaystyle Z}{\underset{|}{C}}{-}S{-}R} \xrightarrow{\mathrm{A}} \mathrm{R1An{-}S{-}\underset{\displaystyle Z}{\underset{|}{C}}{=}S} \xrightarrow{\mathrm{B}} \mathrm{R1AnBm{-}S{-}\underset{\displaystyle Z}{\underset{|}{C}}{=}S}$$

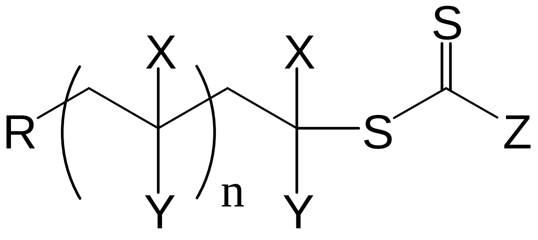
- Both One-pot sequential and isolated macromonomer methods are available.

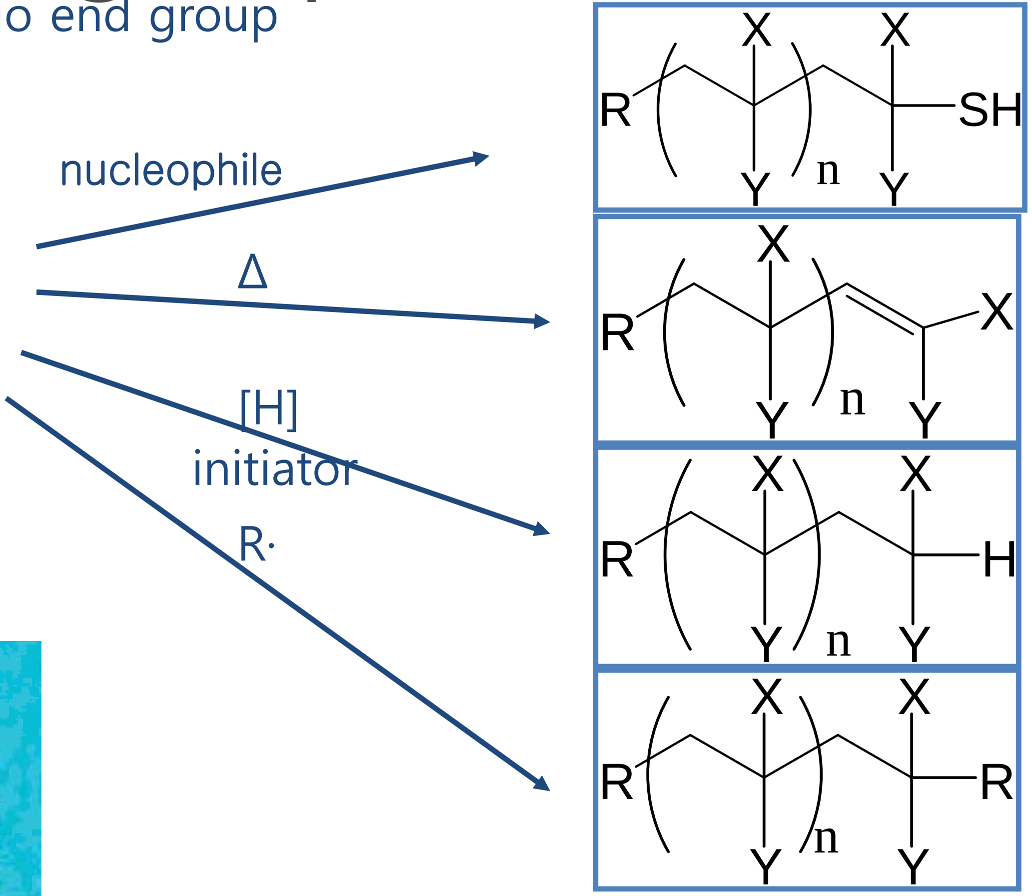
- The order of addition of monomer is often important.
  MMA-styrene, MMA-MA

- Well defined star, graft, comb, hyperbranched polymer can be synthesized

Removing thiocarbonylthio end group

- Removing thiocarbonylthio end group



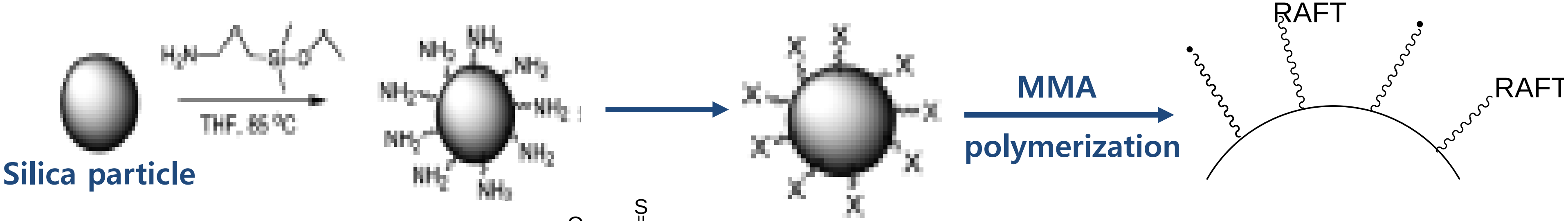


PMMA-CDB

20eq. AIBN, 120℃

Macromolecules 2005, 38, 2033

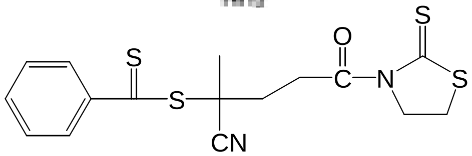
CTA modification



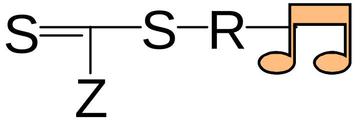
Silica particle

MMA

polymerization

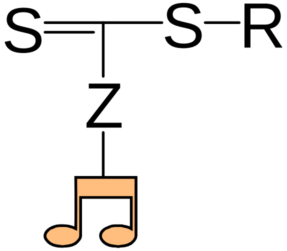


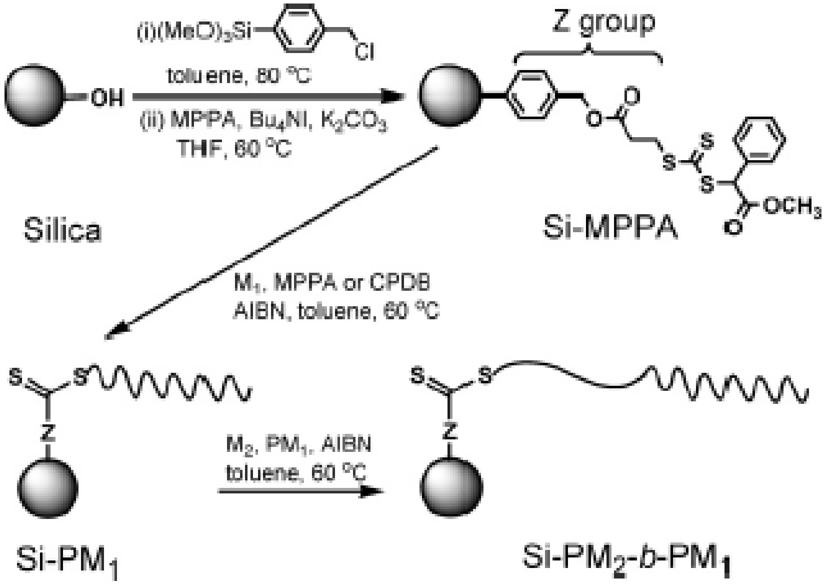
RAFT chain transfer agent



R group modification

Z group modification





ATRP vs. SFRP vs. RAFT

	ATRP	**SFRP**	**RAFT**
Living method	Reversible termination	Reversible termination	Reversible chain transfer
Advantages	▪ Commercial initiator, catalyst, and ligand. ▪ Various monomers	▪ No metal residue	▪Various monomers ▪No metal residue
Disdavantages	▪Metal containing polymer ▪Color of metal oxide	▪Limited monomers ▪Synthesis of initiator	▪Synthesis of CTA ▪Odor of CTAs and color of polymers

Ch4. Emulsion Polymerization

4-1. Description of Process

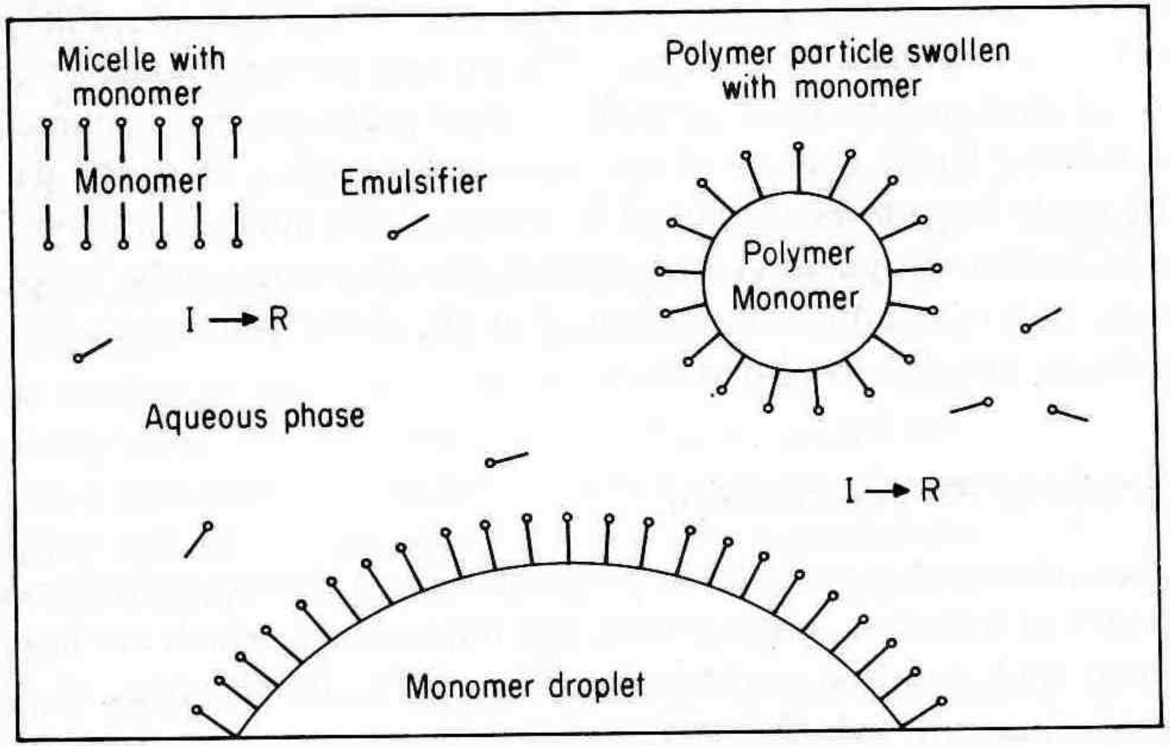


Fig. 4-1 Simplified representation of an emulsion polymerization system.

Ch4. Emulsion Polymerization

4-1. Description of Process

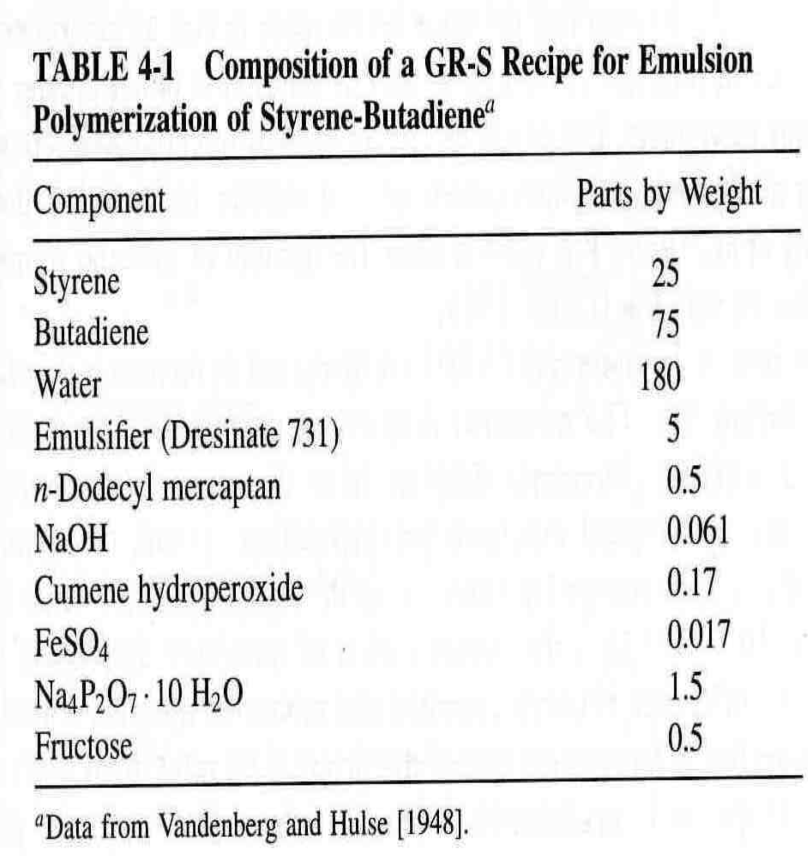
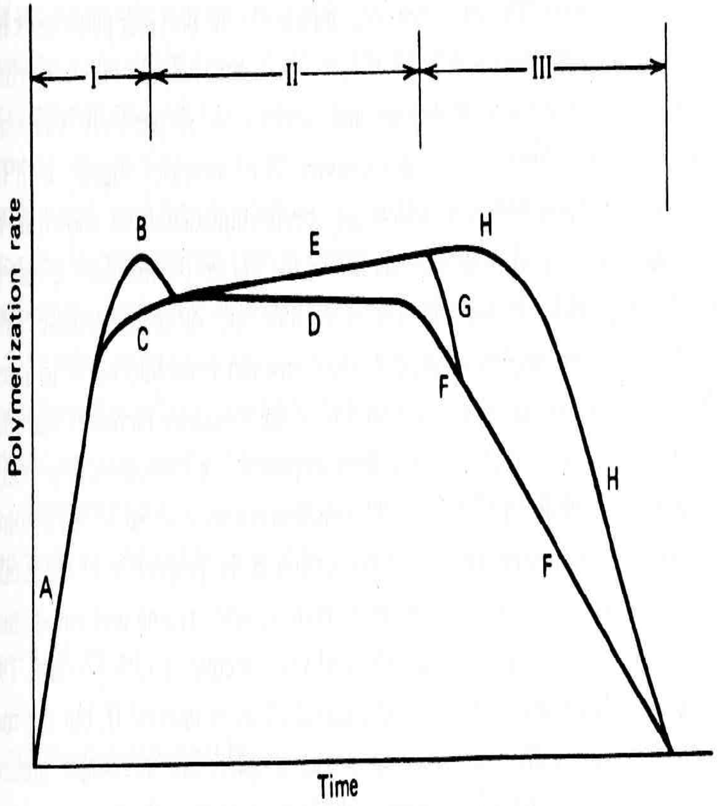


TABLE 4-1 Composition of a GR-S Recipe for Emulsion Polymerization of Styrene-Butadiene[a]

Component	Parts by Weight
Styrene	25
Butadiene	75
Water	180
Emulsifier (Dresinate 731)	5
n-Dodecyl mercaptan	0.5
NaOH	0.061
Cumene hydroperoxide	0.17
$FeSO_4$	0.017
$Na_4P_2O_7 \cdot 10\ H_2O$	1.5
Fructose	0.5

[a] Data from Vandenberg and Hulse [1948].



Ch4. Emulsion Polymerization

4-2. Quantitative Aspects

a. Rate of Polymerization

$$r_p = k_p[\mathbf{M}] \qquad R_p = k_p[\mathrm{M}][\mathrm{P}\cdot]$$

$$[\mathbf{P}\cdot] = \frac{N'\bar{n}}{N_A}$$

$$R_p = \frac{N'\bar{n}k_p[\mathrm{M}]}{N_A} \qquad R_p = \frac{N\bar{n}k_p[\mathrm{M}]}{N_A}$$

Ch4. Emulsion Polymerization

4-2. Quantitative Aspects

b. Degree of Polymerization

$$r_i = \frac{R_i}{N}$$

$$\overline{X}_n = \frac{r_p}{r_i} = \frac{Nk_p[\mathrm{M}]}{R_i} \qquad \overline{X}_n = \frac{r_p}{r_i + \sum r_{tr}}$$

$$r_{tr} = k_{tr}[\mathrm{XA}]$$

Ch4. Emulsion Polymerization

4-2. Quantitative Aspects

c. Number of Polymer Particles

$$N \propto R_i^{2/5} S^{0.4-1.2}$$

$$N = k\left(\frac{R_i}{\mu}\right)^{2/5} (a_s S)^{3/5}$$