Chapter 1

Introduction

- Polymers: Macromolecules build up by the linking together of large numbers of much smaller molecules.

- Monomers: The small molecules that combine with each other to form polymers.

- Polymerization: The reactions of small molecules to form polymers

1,1 Types of polymers and polymerization

- **Classification of polymers**
  - **Based on polymer structure**
    condensation and addition polymers
  - **Based on polymer mechanism**
    step and chain polymerization

- Most condensation polymers are produced by step polymerization
- Most addition polymers are produced by chain polymerization

* Although this is not always the case

1-1a Polymers Composition and structure

Classification by Carothers: **condensation** and **addition** polymers
→ based on the composition differences between the polymers and monomers

- Condensation polymers

→ formed from polyfunctional monomers by the condensation reactions of organic chemistry with the elimination of small molecules such as H_2O, HCl, CH_3OH…

- Cellulose, starch, wool, and silk are condensation polymers

-Protein (polyamide)
-DNA, RNA (polyphosphate)
→ condensation polymers

- Addition polymers

→ formed from monomers without the elimination of small molecules

- then the repeating unit of an addition polymer has the same composition as monomer

- Polyurethane ?

no by product,

then Addition polymer?

Condensation Polymers: repeating units are joined together by functional units such as ester, amide, sulfide, urethane, sulfide , ether,….

Addition polymers: No such functional groups

Phenol-formaldehyde polymer and poly(*p*-xylene) ?

No functional groups but small molecules are eliminated,

Condensation Polymers

1. Elimination of small molecules

2. Contains functional groups as part of the polymer chain

3. Repeating unit lacks certain atoms in the monomer

Addition polymers: not fulfill any of these requirements

1-1b Polymerization Mechanism (by Flory) step and chain polymerization

- Step polymerization

→ proceed by the stepwise reaction **between the functional groups of the reactants ,** then the size of the polymer molecules increases slowly.

→ The reaction occurs between any of the different-sized species as a step-wise manner.

- Chain polymerization

→ polymer growth proceeds only bwteen monomers and reactive sites

***reactive sites: radical, cation, or anion**

- For most step polymerizations there is less than 1% of the original monomer remaining when the polymer chain contains about 10 monomer units

- Ring opening polymerization vs. Chain polymerization

1-2 Nomenclature of Polymers

1-2a Nomenclature based on Sources

→ applicable for polymers synthesized from a single monomer (addition and ring opening polymerization)

ethylene → polyethylene

acetaldehyde → polyacetaldehyde

3-methyl-1-pentene → poly(3-methyl-1-pentene)

vinyl chloride → poly(vinyl chloride)

Ethylene oxide→ poly(ethylene oxide)

propylene oxide → poly(propylene oxide)

Polyethylene oxide (II) vs poly(ethylene oxide) (III)

- Name from hypothetical monomer (poly(vinyl alcohol)
- (6-aminocaproic acid) and poly(ε-caprolactam) are the same polymer

1-2b Nomenclature based on Structure (Non-IUPAC)

→ applicable for polymers synthesized from two different monomers (condensation polymers)

A suggestion was made to name condensation polymers synthesized from two different monomers by following the prefix poly(the two reactants separated by the term –co-).
Thus, the polymer in Eq. 1-7 would be named poly(phenol-*co*-formaldehyde).
This suggestion did not gain acceptance.

1-2c IUPAC Structure-Based Nomenclature System

→ Poly(CRU), CRU: constitutional repeating unit

CRU is also the structural repeating unit

CRU is synonymous with repeating unit except a few cases

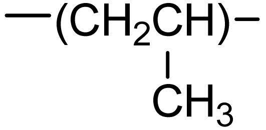
EX)

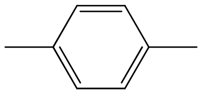
Polyethylene and polytetrafluoroethylene

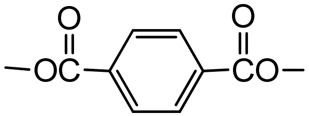
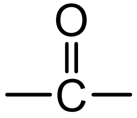
CRU: CH_2 and CF_2

Repeating unit : CH_2CH_2 and CF_2CF_2

Nomenclature of subunits (same as used in Organic Chemistry)

-CH_2- : methylene, -CH_2CH_2- : ethylene, 
$$—(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}H})–$$
: propylene


: 1,4-phenylene , -S- : thio , -NH- : imino


: terephthaloyl , -O- : oxy 
$$—\overset{\displaystyle O}{\overset{\|}{C}}—$$
: oxo

Alkane : - α,ω-diyl except methylene and ethylene

-Steps to be followed to name the polymers

1. Identify the CRU
2. Orient the CRU according to the priority (seniority) rule
3. Name the Polymer

CRU is the smallest possible repeating unit of the polymer composed of several units, poly(x, y, z), How to orient the x, y, z
→ follow the priority (seniority) rule

Priority (seniority) rules

1. heterocyclic rings > chains with heteroatoms > carbocyclic ring > carbon chains

2. Heterocyclic ring seniority

ring with nitrogen (N) > ring with other than N (heteroatom seniority **rule ,3**)

> ring with greatest number of heteroatom > ring with the largest individual ring

> Ring with greatest variety of heteroatoms

3. heteroatom seniority rule

O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, Hg

4. For carbocyclic rings

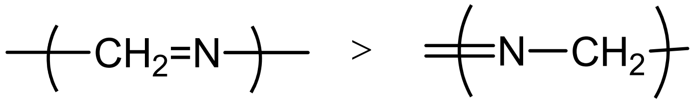
greatest number of rings > largest individual ring > greatest number of atoms

5. For carbocyclic and heterocyclic ring differing only in unsaturation,

seniority **increase with degree of unsaturation**.

For the same ring, higher seniority for the subunits having **the lowest location number** (locant)

6. Minimizing the number of free valence supersedes any of the seniority rule



※ Nomenclature of the copolymers

- poly(A-*co*-B) unspecified copolymer
- poly(A-*ran*-B) random copolymer
- poly(A-*alt*-B) alternating copolymer
- Poly(A)-*block*-poly(B) diblock copolymer
- Poly(A)-*block*-poly(B)-*block*-poly(C) triblock copolymer
- Poly[poly(A)-block-poly(B)] multiblock copolymer

- Other commonly used commercial polymers with common names

SBR : poly(styrene-*co*-butadiene) not specified copolymer
Kraton® : polystyrene-*block*-polybutadiene-*block*-polystyrene
HIPS (High impact polystyrene): polybutadiene-graft-polystyrene
ABS : polybutadiene-graft-poly(styrene-co-acrylonitrirle)

※ Nomenclature of Nylon

- Nylon is the trade name of polyamide invented by Carothers at DuPont
- It was announced on 22 September in 1938 by the New York Times

- Why Nylon?
- Firstly suggested names are novasilk, synthesilk among 400 suggested names because it could replace the silk (mostly from Japan and East Asia at that time)
- To put something new (applications in stocking were in mind, so *stockings of new fiber would run !*), 'Nuron"
- American "noo"(=new) as in "noon", British "new" would bee seemed like neuron. Then r was replaced by l, so nulon.
- Nulon → Nilon → Nylon
- Or Now You Lousy Old Japan ! (Nylon)

※ Nomenclature of Nylon

$$-\left[NH(CH_2)_6NHCO(CH_2)_4CO \right]_n$$

poly(iminohexane-1,6-diylimino-1,6-dioxohexane-1,6-diyl))
Poly(hexamethylene adipamide)
Nylon 6,6

$$-\left[NHCO(CH_2)_5 \right]_n$$

Poly[imino(1-oxohexane-1,6-diyl)]
Poly(ε-caprolactam) or poly(ε -aminocaproic acid)
Nylon 6

$$-\left[NH(CH_2)_{10}NHCO(CH)_4CO \right]_n-$$

Nylon 10,6

1-3 Linear, Branched, And Crosslinked Polymers

Branched (A): long branched
Branched (B): short branched
Branched (C): branched branched

Typical features of the branches in the polymer
Crystallinity ↓
solubility (processability) ↑
thermal transition (Tm, Tg)↓
mechanical property ↓

Branched polymer does not refer to linear polymers containing side groups that are part of the monomer structure.

Light crosslinking is used to impart good recovery (elastic properties (to be used as rubbers)

High degrees of crosslinking are used to impart high rigidity and dimensional stability.

Preparations of the crosslinking

- step polymerizations: monomers with three or more functional groups are used.

- chain polymerization: monomers with two or more vinyl groups are used.

1-4 Molecular Weight

Molecular weights could be determined based on colligative property, light scattering, viscosity, and so on.

Different values could be obtained from different methods

-some are biased toward the large-sized polymers and others are biased toward smaller sized polymers.

- **colligative properties:** vapor pressure lowering, freezing point depression, boiling point elevation and osmotic pressure (삼투압 membrane osmometry).

Example for MW

Molecular Weight (g)	1	2	3	4	5
Number (N)	1	1	1	1	1
NM	1	2	3	4	5
NM^2	1	4	9	16	25
X_i: number fraction	1/5	1/5	1/5	1/5	1/5
W_i : weight fraction	1/15	2/15	3/15	4/15	5/15

$$\mathbf{M_n = 15/5 = 3}$$

$$\mathbf{M_w = 55 / 15 = 3.6666}$$

Extreme case for MW

M_i (g/mol)	N_i (mol)	w_i (g)	N_iM_i (g)	$N_iM_i^2$ (g^2mol)	X_i: number (mol) fraction	W_i : weight fraction
1.0×10^3	1.0	1,000	1,000	1.0×10^6	1/1.001	1/2
1.0×10^6	0.001	1,000	1,000	1.0×10^9	0.001/1.001	1/2
Total (Σ)	1.001		2,000	1.001×10^9		

$$\overline{M}_n = \sum_i X_iM_i = \frac{\sum_i N_iM_i}{\sum_i N_i}$$

$$\overline{M}_w = \sum_i W_iM_i = \frac{\sum_i w_iM_i}{\sum_i w_i} = \frac{\sum_i N_iM_i^2}{\sum_i N_iM_i}$$

Mn ~ 2000 g/mol
Mw ~ 500,000 g/mol

1-5 Physical State

1-5a Crystalline and Amorphous Behavior

⇒ Solid polymers generally contains amorphous and crystalline phases

⇒ X-ray and electron diffraction: the crystalline phases have sharp peaks, while the amorphous phases have broad and diffuse peaks (crystallinity could be estimated by comparing the area)

The nature of polymer crystallinity

1. Fringed-micelle model

   Crystallites are imbedded in the amorphous matrix

2. Fringed-micelle theory

Polymer single crystals are in the form of thin platelets termed “lamella”

a. Adjacent reentry model

b. Switchboard model

Spherulites are easily observed from the polymers and they are formed from the micelles

1-5b Determinant of Polymer Crystallinity

⇒ what kinds of chemical structures can give the crystal packing structure easily

1. Simple, compact, and regular structure
2. Some degree of flexibility to give the changes of the conformation

PE: highly crystalline

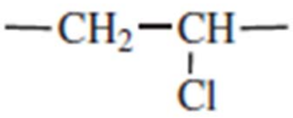
PDMS: too flexible to maintain the chain conformation and Si-O is bulky

3. Secondary attractive forces between the polymer chains

Polyamide: $-\!\left[\mathrm{NHCO(CH_2)_5}\right]\!-$

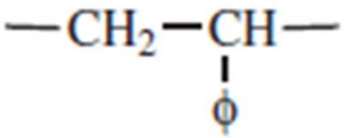
- highly crystalline polymers.
- The amide group is a polar one and leads to much larger secondary attractive forces in polyamides (due to hydrogen bonding) compared to polyethylene; this is most favorable for crystallization.
- However, the polyamide chains are not as simple as those of polyethylene and packing requires that chain segments be brought together so that the amide groups are aligned.

PVC



$$-\mathrm{CH_2}-\underset{\mathrm{Cl}}{\underset{|}{\mathrm{CH}}}-$$

PS



$$-\mathrm{CH_2}-\underset{\phi}{\underset{|}{\mathrm{CH}}}-$$

Crysallinity is possible only for the stereoregular polymers
Ex) syn-PS or iso-PS: crystalline, atactic-PS; amorphous

Their crystallinity is lower than PE because, 1) less flexible, 2)less compact,
Although there is more interactive forces

Aromatic Polymers; Backbones are more rigid, then not easily crystallized
although their interactions could help the crystallization
→ liquid crystalline phases could be observed

1-5c Thermal Transitions

Amorphous polymer: only glass transitions (T_g)

Semicrystalline polymer: glass transitions and melting temperature (T_m)

Fig 1-9

Empherical relationship (unit in kelvin)

Symmetric polymer: $T_g/T_m \cong 1/2$
Unsymmetricpolymer : $T_g/T_m \cong 3/4$

⇒ what kinds of chemical structures can give the crystal packing strucrue eaily

1. **Simple, compact, and regular structure**
2. **Some degree of flexibility to give the changes of the conformation**

1-6 Applications of Polyemrs

1-6a Mechanical Properties: The mechanical behavior ; stress–strain properties

1. Modulus. The resistance to deformation as measured by the initial stress divided by = ΔL/L.
2. Ultimate Strength or Tensile Strength. The stress required to rupture the sample.
3. Ultimate Elongation. The extent of elongation at the point where the sample ruptures.
4. Elastic Elongation. The elasticity as measured by the extent of reversible elongation.

General Rule

1. High extensibility and low strength; low mechanical properties

→ Low Tg and low crystallinity, low degree of cross-linking

2. Low extensibility and high crystallinity; high mechanical properties

→ Hgh Tg and high crystallinity, high degree of cross-linking

1-6b Elastomers, Fibers, and Plastics

1. Elastomer

- very large, reversible elongations (≤ 500– 1000%) at relatively low stresses
- almost completely amorphous with a low glass transition temperature
- low secondary forces (high chain mobility)

Ex) Polyisoprene (natural rubber); amorphous (low crystallinity), easily crosslinked, low Tg (- 73 °C), and low Tm (28 °C).

When slightly crosslinked, initial modulus less than 70 Ncm^{-2};

at 400% elongation 1500 $N\ cm^{-2}$, at 500% 2000 Ncm^{-2}.

2. Fiber; high resistance to deformation

- low elongations (<10–50%), very high moduli (>35,000 N Ncm^{-2}) and tensile strengths (>35,000 Ncm^{-2})
- highly crystalline containing polar groups with secondary forces
- ex) Poly(hexamethylene adipamide) (Nylon 6,6)

- high tensile strength (70,000 Ncm^{-2}), very high modulus (500,000 Ncm^{-2}), low elongation (<20%). Tm and Tg values of of 265 and 50 °C, respectively.

3. Plastics: a large group of polymers that have a wide range of mechanical behaviors in between those of the elastomers and fibers

a) Flexible plastic

moderate to high degrees of crystallinity and a wide range of Tm and Tg values.

moderate to high moduli (15,000– 350,000 Ncm^{-2}), tensile strengths (1500–7000 Ncm^{-2}), and ultimate elongations (20–800%)

. Ex) Polyrethylene; a tensile strength of 2500 Ncm^{-2}, a modulus of 20,000 Ncm^{-2}, ultimate elongation of 500%.

b) Rigid plastic:

high rigidity and high resistance to deformation

high moduli (70,000–350,000 Ncm^{-2}) and moderate to high tensile strengths (3000–8500 Ncm^{-2}), very small ultimate elongation (<0.5–3%)

- The high chain rigidity (by extensive crosslinking)

Ex), phenol–formaldehyde, urea–formaldehyde, and melamine–formaldehyde polymers.

- The high rigidity from bulky side groups (high Tg values)

Ex) polystyrene (T_g = 100 ^oC) and poly(methyl methacrylate)(T_g = 105 ^oC).

Chapter 2
Step Polymerization

- Two Groups

1. Two different bifunctional and/or polyfunctional monomers in which each monomer possesses only one type of functional group

2. A single monomer containing both types of functional groups.

Both types have the same characteristics in kinetics and polymerization mechanisms

Very different from the synthesis of low molecular weight organic compounds

Ex) 90% conversion of the functional groups is disaster in polymerization

2-1 Reactivity of Functional Groups

2-1a Basis of Analysis of Polymerization Kinetics

-Step polymerization proceeds by a relatively slow increase in molecular weight of the polymers

ex) the synthesis of a polyester from a diol and a diacid

- The rate of a step polymerization is, therefore, the sum of the rates of reaction between molecules of various sizes, that is, the sum of the rates for reactions such as

innumerable separate reactions would normally be difficult to analyze

→ too many variables to derive the kinetic equation

→ equal reactivity of functional groups

2-1b Experimental Evidence

2-1c Theoretical Consideration

$$A + B \underset{\text{diffusion}}{\rightleftharpoons} \overset{\text{Collided state}}{(A + B)} \xrightarrow[\text{combination}]{} A{-}B$$

- Molecular size ↑ , diffusion rate ↓

- Once the molecules are close enough, the combination rate is identical

i) diffusion rate > combination rate, then combination step is RDS
→ the total rxn rate is independent of the size
ii) diffusion rate < combination rate
→ the total rxn rate is dependent of the size

Normally 10^{13} collision per one combination ⇒ diffusion >> combination

Therefore reaction rate is independent of the size

Exceptions: when the reactivities of the groups are very high and/or the molecular weights of the polymer are very high. Then the polymerization becomes **diffusion-controlled** in these cases because mobility is too low to allow maintenance of the equilibrium concentration of reactive pairs and of their collision frequencies.

2-1d Equivalence of Groups in Bifunctional Reactants

Reactivity might be affected when x is smaller than 4 or 5, while not much affected when x is 6 or larger.

2-2 Kinetics of Step Polymerization

The rate of polymerization *R* = the rate for the formation of –COO–
→ more difficult to measure (NMR ?)
= the rate for the disappearance of COOH
→ easier to estimate (Titration)

2-2a Self-Catalyzed Polymerization

2-2a-2 Reasons for Nonlinearity in Third-Order Plot

2-2a-2-a Low-Conversion Region

i) The reaction system is very polar
The association of OH and COOH groups by the H-bonding can lower the reactivity

ii) $2\frac{1}{2}$ reaction order at low conversion?
Why? The proton concentration ($[H^+]$) is relatively high and $[H^+]$ is a more effective catalyst than the unionized carboxylic acid in the polar and low conversion region.
Then
where K_{HA} is the ionization constant for the for –COOH (at low conversion HA).

$K_{HA} = [H^+][A^-]/[HA]$ where $[H^+] = [A^-]$

iii) Equations were made by the assumption that concentration $\propto$ reactivity
It is true for diluted system.
At high concentration of reactants (at low conversion), it is not true.

possible other explanations in page 49.

2-2a-2-b high-Conversion Region

i) Partial vacuum (and/or purging nitrogen gas) is used to drive the system toward high molecular weight.
Then, small amounts of any monomers may be lost (degradation or volatilization).

Ex) dehydration of diols $HOCH_2CH_2OH \rightarrow CH_3COH + H_2O$
decarboxylation of diacid

At high conversion, such small changes of the stoichiometric affect the reaction rate very much

ii) The system becomes very viscous, then 100 % removal of water is very difficult, (2-19) was made by this assumption.

Possibly diffusion-controlled reaction might occurs

2-2a-3 Molecular Weight of Polymer

$\overline{X_n}$: number-average degree of polymerization
N : total number of molecules at t (= the number of unreacted COOH groups when stoichiometric diols and diacids are used in the polymerization)
N_0 : total number of molecules at t = 0

$\bar{M}_n$: number-average molecular weight

M_{eg} : the molecular weight of the end groups.

2-2b External Catalysis of Polymerization

By using small amounts of strong acids, [HA], (such as sulfuric acid or p–toluene sulfonic acid) catalysts, then [HA]= constant

2-2c Step Polymerizations Other than Polyesterification: Catalyzed vs. Uncatalyzed

1. Polyamidation ； reasonable rates as uncatalyzed reactions.

2. urea, melamine, or phenol with formaldehyde ： externally added acid or base catalyst

3. Polyurethane formation:
base-catalyzed system ； very high rate of polymerization with some side reacti
uncatalyzed system ； slower but side reactions could be avoided

2-2d Nonequivalence of Functional Groups in Polyfunctional Reagents

2-2d-1 Examples of Nonequivalence

If n ≥ 6, neighboring groups do not affect the reactivity of OH groups

neighboring groups can affect the reactivity of OH groups

neighboring groups (Electron density) can affect the reactivity of OH groups

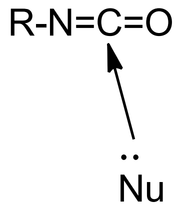
$O^{-} > CO_2^{-} > CR_3 > D > H > CH{=}CH_2 > OH > SH > R > COOR > CN > SO_2R > NH_3^{+} > SR_2^{+} > NR_3^{+}$

$\longleftarrow$

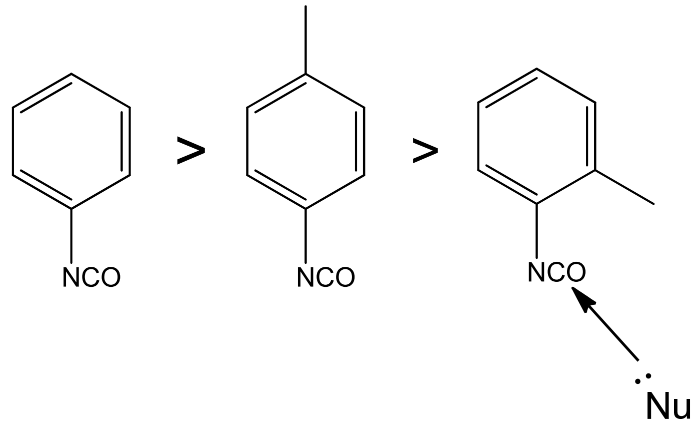
e^{-} density

The increase of the e^{-} density can increase the nucleophilicity, while decrease the electrophilicity

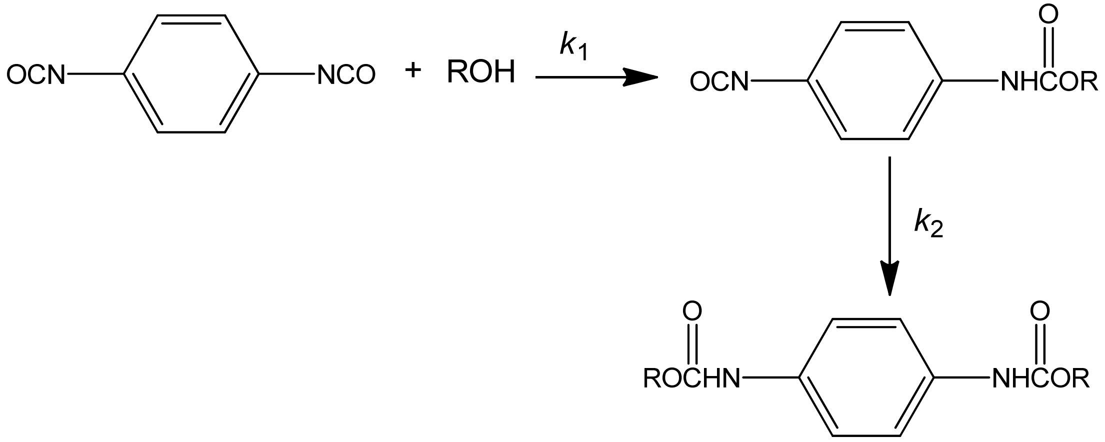
The reactivity of the isocyanate groups



Isocyanate : electrophile



CH_3 is the e⁻ donating groups, and it can decrease the electrophilicity



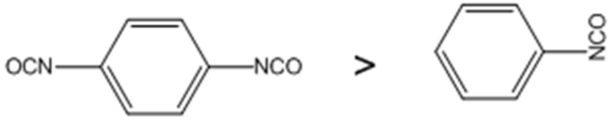
$k_1 > k_2$

Why?

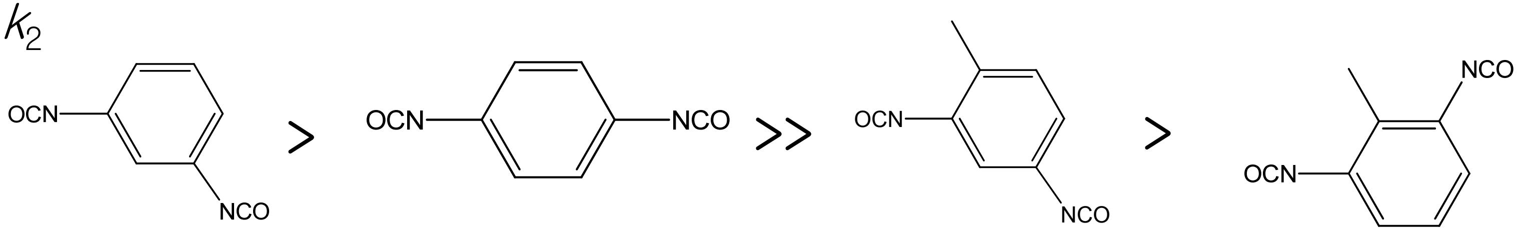
e⁻ withdrawing strength

$-NCO > -NHCO_2R$

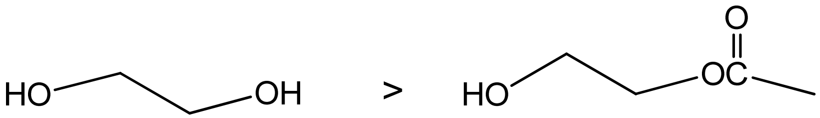
therefore



k_1 and k_2

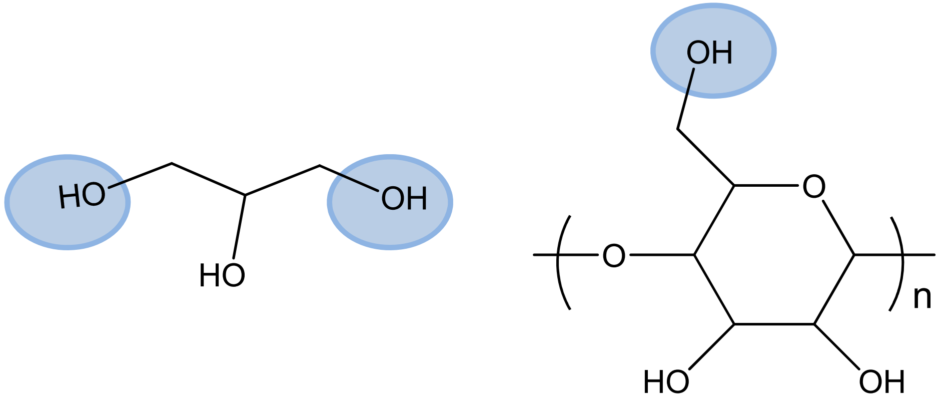


Reactivity of short hydroxy groups



OH ; nucleophile

Why?
e^- donating strength
OH > $-$OCOR



1° OH > 2° OH > 3° OH

Thus polar solvents enhance the rate of a polymerization with a transition state more polar than the reactants. Polar solvents are not desirable for reactions involving transition states that are less polar than the reactants.

2-4 Equilibrium Consideration

2-4a Closed System

Many, if not most, step polymerizations involve equilibrium reactions, and it becomes important to analyze how the equilibrium affects the extent of conversion and, more importantly, the polymer molecular weight.

2-4b Open, Driven System

Therefore step polymerizations must be carried out as an open, driven system. To remove the byproduct to drive the equilibrium toward polymers.

A concentration of 5 M is fairly typical of a step polymerization that is often carried out with only the reactant(s) present (without solvent). The lowering of [H_2O] to achieve a particular X_n is less the more favorable the equilibrium (that is, the larger the K value). Thus the synthesis of polyamides (with typical K values > 10^2) is clearly easier from the equilibrium viewpoint than polyester synthesis ($K \sim 0.1–1$).

2-4c Kinetics of Reversible Polymerization

p_e is experimentally determined, or calculated from Eq. 2–61 if K is known. From experimental values of p as a function of time, Eq. 2–68 yields a straight line when the left side of the equation is plotted against time. The slope of the line then allows one to calculate k_1.

2-5 cyclization vs. Linear Polymerization

2-5a Possible Cyclization reactions

Ring formation is possible in the polymerizations of both the A–B and A–A plus B–B types

1. A–B type: through the intramolecular cyclization of the monomers and others

2.. A–A plus B–B types: intramolecular cyclization after the formation of dimer or larger oligomers

The extent to which cyclization occurs during polymerization depends on whether the polymerization proceeds under equilibrium control or kinetic control, the ring sizes of the possible cyclic products, and the specific reaction conditions.

2-5b Cyclization Tendency vs. Ring Size

Thermodynamic stability

The strain in ring structures:

1. angle strain
2. conformational strain (torsional strain and transannular strain)

3, 4– : angle strain

5– and 7–; somewhat strained because of the torsional strain arising from eclipsed conformations on adjacent atoms of the ring.

8 or larger; transannular strain from repulsive intxns between H's or other groups forced to crowed positions in the interior of the ring structure.

The general order of thermodynamic stability of different–sized rings is given by 3, 4 << 5, 7–13 < 6, 14 and larger.

Kinetic feasibility

→ the probability of having the functional end groups of the reactant molecules approach each other.

As the ring size increases, the probability of ring formation decreases as the probability of the two functional groups encountering each other decreases.

Considering both the Thermodynamic stability and Kinetic feasibility
5-, 6-, 7- membered rings can be formed easily!

2-5c Reaction Conditions

High concentrations of monomers favor linear polymerization since cyclization is a unimolecular (intramolecular) reaction, while linear polymerization is a bimolecular (intermolecular) reaction.

k_p does not change as linear polymerization proceeds (the equal reactivity of functional groups assumption), but k_c decreases as the linear polymer increases in molecular weight (kinetic feasibility decreases with increasing ring size).

The effect of the monomer structure

1. phthalic acid (ortho isomer) is more prone to cyclization than terephthalic acid (para isomer)

2. Aromatic monomers are much less prone to cyclization than the flexible chains

2-5d Thermodynamic versus Kinetic Control

1. Thermodynamic control: Polymerizations proceed with an equilibrium between cyclic and linear products.
   ex) polyesterification between diacids and diols

   - most industrial step polymerizations proceed under thermodynamic control.
   - most frequently the equilibrium favors linear polymerization over cyclization
   - the total cyclic content in polyesterification and polyamidation has been found to be as high as 1–3%
   - The cyclic oligomers are formed mostly by backbiting, which involves an intramolecular (interchange) nucleophilic substitution reaction,

2. Kinetic control: Polymerizations without an equilibrium between cyclic and linear products.

ex) polyesterication between diacyl chlorides and diols (no reversal because the by-product HCl is not reactive with ester linkages) , low temperature reaction

- a continuous increase in cyclic products with increasing conversion even though the rate of cyclization decreases which the increases with conversion because the cyclic products formed by reaction between end groups of linear chains are inert under the polymerization conditions.

Cyclization decrease the molecular weight of the polymer

Without any cyclization

If there is any cyclizaton
where X is a constant greater than 1 and dependent on the reactant concentration. a is the ratio of the rate of linear polymerization to the rate of cyclization.

2-5e Other Considerations

The optimum ring size is the 8- membered ring because of the large size of the Si atom, the longer length of the Si-O bond, and the larger SiOSi bond angle.
Still the formations of 8- membered during the polymerization of the monomer (6-membered ring)is not overwhelming because of the kinetic factor (larger-sized rings are not as favored).

2-6 Molecular Weight Control in Linear Polymerization

2-6a Need for Stoichiometric Control

- Desired molecular weight can be obtained by quenching the reaction!

→ However, the polymer obtained in this manner is unstable in that subsequent heating leads to changes in molecular weight because the ends of the polymer molecules contain functional groups (referred to as end groups) that can react further with each other.
So the "Stoichiometric Control"

“Stoichiometric Control”

1. One of the reactants is present in slight excess.

The polymerization then proceeds to a point at which one reactant is completely used up and further polymerization is not possible !

2. Addition of a small amount of a monofunctional monomer (chain stopper)

2-6b Quantitative Aspects

Type 1: For the polymerization of the bifunctional monomers A–A and B–B (e.g., diol and diacid or diamine and diacid) where B–B is present in excess

$$\underset{\text{A}}{\text{HO–R–OH}} + \underset{\text{B excess}}{\text{HOOC–R'–COOH}} \longrightarrow \text{HOOC–R'---------------R'–COOH}$$

N_A and N_B : numbers of OH and COOH functional groups (twice the number of ecah monomer)

$r = (N_A/N_B)$: stoichiometric ratio ≤ 1 because B is excess

$(N_A+N_B)/2$ or $N_A(1+1/r)/2$: total number of monomer molecules

p : extent of reaction of A , then $1-p$: faction of unreacted A

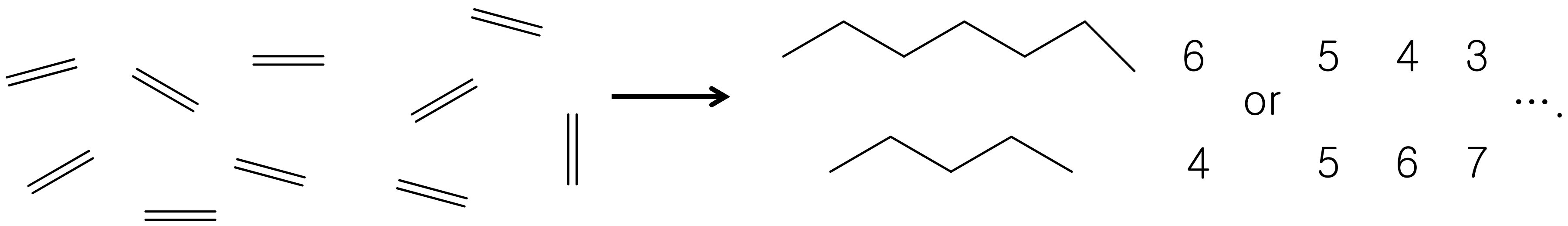
rp : fraction of reacted B, then $(1-rp)$: faction of unreacted B

$N_A(1-p)$: total numbers of unreacted A, $N_B(1-rp)$: total numbers of unreacted B

$[N_A(1-p) + N_B(1-rp)]/2$: total number of polymer molecules then

$$\overline{X}_n = \frac{\text{total number of monomer molecules}}{\text{total number of polymer molecules}}$$

Ex) 10 monomers 2 polymers



Expected $\overline{X_n}$ = 10/2 = 5

$$\overline{X}_n = \frac{N_A(1 + 1/r)/2}{[N_A(1 - p) + N_B(1 - rp)]/2} = \frac{1 + r}{1 + r - 2rp}$$

Type 2: For the polymerization of equimolar mixture A–A and B–B by the addition of small amounts of a monofunctional B reactant

Type 3: For the polymerization of A–B type monomers by addition of small amounts of a monofunctional B reactant

2-7 Molecular Weight Distribution in Linear Polymerization

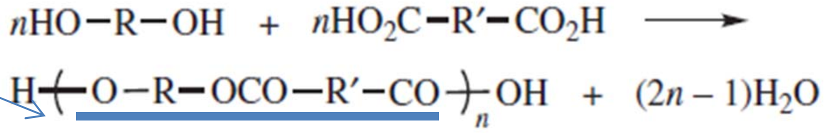
The product of a polymerization is a mixture of polymer molecules of different molecular weights.

The molecular weight distribution (MWD) has been derived by Flory by a statistical approach based on the concept of equal reactivity of functional groups.

The derivation that follows is essentially that of Flory and applies equally to A–B and stoichiometric A–A plus B– B types of step polymerizations.

2-7a Derivation of Size Distribution

the mole or number fraction of molecules in the polymer mixture that are x-mers (i.e., that contain x structural units)



$$n\mathrm{HO{-}R{-}OH} + n\mathrm{HO_2C{-}R'{-}CO_2H} \longrightarrow \mathrm{H}\!\left(\underline{\mathrm{O{-}R{-}OCO{-}R'{-}CO}}\right)_{\!n}\mathrm{OH} + (2n-1)\mathrm{H_2O}$$

$$\underline{N}_x = p^{x-1}(1-p)$$

Ex) B-BA-AB-BA-AB-BA-AB-BA-A; 4 structural units, 3 times reacted, 1 time unreactd

$$N_x = Np^{x-1}(1-p)$$

where N is the total number of polymer molecules at t and N_x is the number of x-mers.

$$N_x = N_0(1-p)^2 p^{x-1}$$

Where N_0 is the total number of structural units at t = 0, then N = N_0 (1-p)

$$w_x = x(1-p)^2 p^{x-1}$$

w_x : the weight fraction of x-mers (i.e., the weight fraction of the molecules that contains x structural units) is given by $w_x = xN_x/N_0$

2-7b Breadth of Molecular Weight Distribution

The number average molecular weights have been defined by

Dividing the number−average molecular weights by the weight M_o of a structural unit yields the number−average degree of polymerization

The breadth of the molecular weight distribution is then given by polydispersity index (PDI)

For many different step polymerizations, this ratio has been found to be close to 2 because p ≅ 1, r ≅ 1.

2-7c Interchange Reactions

Polyesters, polyamides, polysulfides, and others can undergo interchange reactions between the terminal functional group of one polymer molecule with the interunit repeating linkage of another polymer molecule.

Free interchange corresponds to all interunit linkages in all polymer molecules having equal probabilities of interchange.

This is analogous to the concept of functional group reactivity independent of molecular size as applied to the interchange reaction.

It is apparent that the presence of interchange during a polymerization will not affect the size distribution from that expected for the random polymerization.

2-8 Process Conditions

2-8a Physical Nature of Polymerization Systems

To achieve high molecular weights in step polymerizations

-Polymerization with an absence or at least a minimum of side reactions

-Polymerizations are carried out at high concentrations to minimize cyclization and maximize the reaction rate

- High purity reactants in stoichiometric or near-stoichiometric amounts

- The equilibrium in the direction of the polymer product (removal of the by product by vacuum or heating)

Bulk polymerization is widely used for step polymerizations.

Advantages of the bulk polymerization

- Minimum of potentialities for contamination
- Simple product separation
- Viscosity is relatively low throughout most of the course of the polymerization
- Thermal control is also relatively easy, since the typicaly reaction has both a modest activation energy and enthalpy of polymerization.

When highly exothermic with high activation energies and where the viscosity becomes very large,
Solution polymerization can be used. (ex, Chain polymerization)

2-8c Interfacial Polymerization

Many of the polymers that are produced by the usual high–temperature reactions could be produced at lower temperatures by using the faster Schotten–Baumann reactions of acid chlorides.

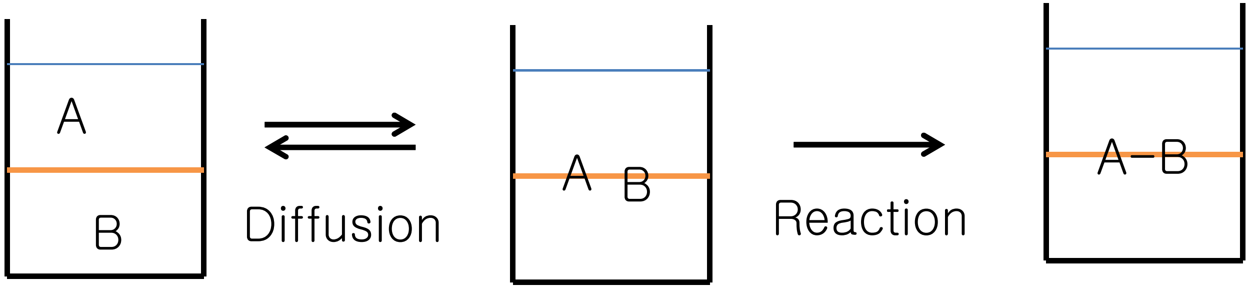
–Polymerization temperatures in the range 0 – 50 °C.

–Polymerization of two reactants is carried out at the interface between two liquid phases, each containing one of the reactants.

–The rate constants for these reactions are orders of magnitude greater than those for the corresponding reactions of the diacid or diester reactants

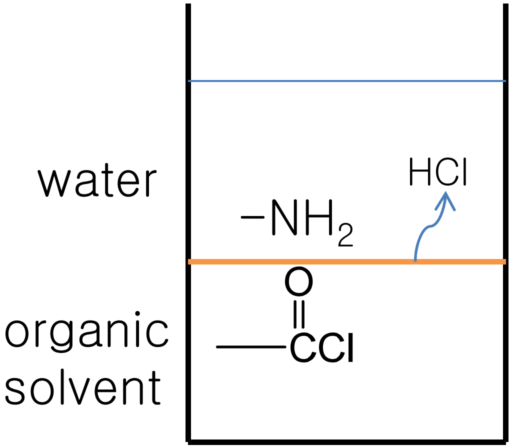
2-8c-1 Description of Process

- Diffusion controlled reaction
  → reaction rate > diffusion rate



- Stoichiometry automatically exist
  → high molecular weight can be obtained regardless of the amount of diacylchloride and diamine (when one of the compounds are consumed, then reaction is over)

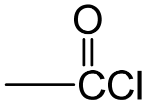
- Inorganic base in aqueous phase
  → HCl is the by product



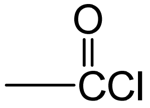
$-NH_2 + HCl \rightarrow -NH3^{+}Cl^{-}$

Not reactive any more

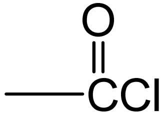
- Then reaction between acylchloride groups with water ?



$—\overset{\overset{O}{\|}}{C}Cl + -NH_2 \rightarrow k \cong 10^{4} - 10^{5}\ L\ mol^{-1}\ s^{-1}$



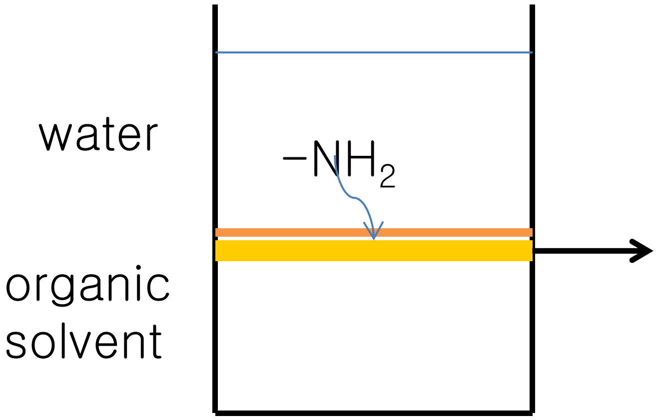
$—\overset{\overset{O}{\|}}{C}Cl + H_2O \rightarrow k \cong 10^{-3}\ L\ mol^{-1}\ s^{-1}$

→ Therefore interfacial polymerization $-OH$ with  $—\overset{\overset{O}{\|}}{C}Cl$ is not possible
While $-ONa$ with acylchloride is possible

- The Choice of the organic solvent

→ should be phase separated with water

The polymerization site is the organic phase
→ diamine is soluble in water and in organic solvent, while diacylchloride is only soluble in the organic solvent,
Then diamine can diffuse into the organic phase



polymers in organic phase
Polymerization proceeds until the polymer precipitates

→ High molecular weight polymers can be precipated in the the organic solvent,
While small molecular weight polymers should be dissolved in the organic phase.

Xylene, CCl4 cannot be used although they are not miscible with water.
$CHCl_3$ is a good choice

- Advantages of the interfacial polymerization
  i) low temperature polymerization
  ii) no tedious stoichiometric control
  iii) high-molecular weight polymers can be easily obtained

- Disadvantages
  i) Cost (acylchlorides are expensive)
  ii) limited monomers available

Therefore Commercial utilization has been limited to some polycarbonates, aliphatic polysulfides, and aromatic polyamides, the more expensive polymers.

2-8d Polyester

Possible synthetic pathways

Water must be continuously removed to achieve high conversions and high molecular weights → High temperature reaction

Possible side reactions at high temperatures

i) dehydration

→ Changes of the stoichiometry: Molecular weight is decreased

→ Diethylene glycol units in the polymer structure: T_m is decreased

ii) β scission of the polyester

Acetaldehyde as an impurity causes problems for food and beverage containers. Acetaldehyde also results in discoloration in the final polymer product, due to the formation of aldol-type by-products.

The carboxyl functional groups for synthesizing polyesters can be supplied by using diacids, acid anhydrides, diacid chlorides, or dimethyl esters.

Direct reactions of diacids or anhydrides with diols are often avoided because of the high temperatures required to completely eliminate water.

Diacid chlorides have been used with dihydric phenols to produce polycarbonates

Ester interchange of dimethyl ester (or diacid) is used because the reaction is fast and the dimethyl ester is often more easily purified and has better solubility characteristics. Various weak bases such as the oxides and acetates of manganese, antimony, and zinc are used.

Commercialized Polymerization Process

i) Ester interchange:heated at temperatures increasing from 150 to 210 ^{o}C

ii) Polymerization : heated at temperatures to 270 – 280 ^{o}C with a partial vacuum of 0.5–1 torr (66–133 Pa).

Stoichiometric balance is inherently achieved at the end of the second stage of the process (an excess of ethylene glycol is initially used to increase the rate of formation of bis(2-hydroxyethyl)terephthalate)

A dual catalyst system is used in PET synthesis. The first-stage catalyst is an acetate of manganese, zinc, calcium, cobalt, or magnesium. Antimony(III) oxide is usually added as the second-stage catalyst; it is ineffective alone for the first-stage reaction. The first stage catalyst is often inactivated by the addition of an alkyl or aryl phosphite or phosphate.

Poly(ethylene terephthalate), known by the trade names Mylar, Dacron, and Terylene.

- highly crystalline melting temperature (270C) and stiff polymer chains
- good mechanical strength, toughness, and fatigue resistance up to 150-175C as well as good chemical, hydrolytic, and solvent resistance

i) Fibers
  - 45% of the total PET production
  - crease and abrasion resistance

ii) Plastics
  - blow-molded bottles for soft drinks, beers, spirits, and other food products (outstanding barrier properties)

iii) Films
- photographic, magnetic, and X-ray films or tapes, metallized films, and electrical insulation

iv) engineering plastic
  - reinforced with glass fiber or compounded with silicones, graphite, or Teflon to improve strength and rigidity
- replacing steel and other metals in electrical devices, and automobile parts

Poly(butylene terephthalate) [IUPAC: poly(oxybutane-1,4-diyloxyterephthaloyl)] (PBT),

- 1,4-butanediol for ethylene glycol.
- crystallizes much faster than PET, and competes with PET in engineering plastics applications.
- Its maximum use temperature is 120-140C, slightly lower than that of PET.

Poly(ethylene 2,6-naphthalate) [IUPAC: poly(oxyethyleneoxycarbonylnaphthalene-2,6- diylcarbonyl)] (PEN)

- produced from ethylene glycol and 2,6-naphthalenedicarboxylic acid (2,6-naphthalic acid).

- increased strength, heat stability, and barrier properties compared to PET.
- -specialty photographic and electronic films, and food and beverage bottles that require filling at higher temperatures.

2-8e Polycarbonates

interfacial polymerization in the most industrial processes

- The bisphenol A is usually dissolved in aqueous alkali to form the phenolate salt and then the organic solvent (chlorobenzene, 1,2-dichloroethane, THF, anisole, and dioxane) added followed by phosgene.
- The organic solvent prevents the loss of phosgene by hydrolysis and precipitation of the polymer before it has reached the desired molecular weight.
- Reaction temperatures : 0 – 50 °C
- Phase-transfer catalysts (quaternary ammonium and sulfonium salts and crown ethers) may be added to enhance the transfer of the phenolate salt across the interfacial boundary into the organic phase.

The IUPAC name of the polycarbonate based on bisphenol A is poly(oxycarbonyloxy-1,4-phenylenedimethylmethylene-1,4-phenylene) (trade names: Lexan , Merlon, Calibre)

- mostly amorphous; Tg = 150 °C
- high T_g with Stiff polymer chain : benzene rings and bulky tetrasubstituted carbons
- good combination of mechanical properties in the range of 15 – 130 °C
- excellent resistance to acids and oxidants, better than PET, but is somewhat less resistant to bases compared to PET
- resistance to organic solvents at RT; comparable to PET
- more resistant to aliphatic and aromatic solvents but less resistant to polar organic solvents compared to PET

Applications

compact disks, glazing (windows, doors, face shields, sunglasses, aircraft interiors), automotive (instrument panels and components, exterior panels, wheel covers), medical (components for dialysis, blood collection, and surgical devices), and other uses (power tool and appliance housings, refrigerator interiors, safety helmets, electrical connectors).

2-8f Polyamides

Preparation

i) direct amidation of a diacid with a diamine

ii) self–amidation of an amino acid. (not useful because of a greater tendency toward cyclization)

iii) Ring–opening polymerization of lactams

Poly(hexamethylene adipamde) [IUPAC: poly(iminohexanedioyliminohexane-1,6-diyl) or poly(iminoadipoyliminohexane-1,6-diyl)], nylon 6/6,

-A stoichiometric balance of amine and carboxyl groups is obtained by the formation of a 1 : 1 ammonium salt (XIII) (called as nylon salt) in aqueous solution at a concentration of 50%.

-Polymerization is carried out by raising the temperature under a steam pressure of 250 psi (1.7 MPa). The pressure also prevents salt precipitation and subsequent polymerization on heat-transfer surfaces.

Poly(hexamethylene adipamide): (nylon 6/6)

- excellent fiber and engineering plastic with a high-crystalline melting temperature (265 °C).
- high strength, flexibility, toughness, abrasion resistance, dyeability, low coefficient of friction (self-lubricating), low creep, and resistanceto solvents, oils, bases, fungi, and body fluids.
- The main limitation is its moisture pickup with resulting changes in dimensional and mechanical properties
- Applications include transportation (auto fender extensions, engine fans,,), electrical/electronics (toggle switches, plugs, sockets,,,), films (meat and cheese packaging, cook-in-pouches, multilayer nylon-polyolefin protective barrier materials for oil and moisture resistance), and so on.

Nylon 6 has a lower Tm (223 °C)

Those with more methylene groups (nylons 6/9, 6/10, 6/12, 11, 12, 12/12) than nylons 6/6 and 6 have better moisture resistance, dimensional stability, and electrical properties, but the degree of crystallinity, Tm, and mechanical properties are lower.

The United States production of polyamides was more than 4 billion pounds in 2001.About two-thirds of that is nylon 6/6; the second most important polyamide is nylon 6.

The United States production of PET fiber and plastic was over 9.5 billion pounds in 2001. The global production is about 6 times that of the United States.

The United States production of polycarbonates was
more than 800 million pounds in 2001; the global production was about 3 billion pounds.

Aromatic polyamides (referred to as aramid polymers)

- lower reactivity of aromatic amines compared to aliphatic (The aromatic ring decreases the electron density of nitrogen through resonance interaction.
- The elevated temperatures required to achieve polymerization (extensive side reactions that limit polymer molecular weight).

Therefore Aromatic polyamides are produced by using the faster reaction of a diamine with a diacid chloride in solution.
Ex) poly(*m*-phenylene isophthalamide) or poly(imino-1,3 phenyleneiminoisophthaloyl) (trade name: Nomex)

Aromatic Polyamide : The present U.S. market is about 20 million pounds per year.

Applications;

- very high flame resistance (clothing for firefighters and welders, welder's protective shield, upholstery and drapes),
- heat resistance (ironing board covers, insulation film for electrical motors and transformers, aerospace and military),
- dimensional stability (fire hose, V- and conveyor belts)
- strength and modulus (circuit boards, bulletproof vests, fiber optic and power lines, ship mooring ropes, automobile tire cord, puncture-resistant bicycle tires).

2-9 Multichain Polymerization

2-9a Branching

Polymerization of an A–B reactant in the presence of a small amount of a monomer A_f containing f functional groups per molecule. The value of f is the functionality of the monomer. If f = 3,

- Cross–linked species will not be formed.

- Branch chains from one molecule cannot react with those from another.

2-9b Molecular Weight Distribution

The distribution functions for this polymerization have been derived statistically by Peebles (1971) and Flory (1948), and the results are,

$\bar{X}_w/\bar{X}_n$ decreases
from 2 for f = 1 to 1.25 for f = 4 (at p = 1)

2-10 Crosslinking

The branch joining the two chains is referred to as a crosslink.

when $f > 2$ in the following reactions

In order to control the crosslinking reaction so that it can be used properly, it is important to understand the relationship between gelation and the extent of reaction.

Two general approaches have been used to relate the extent of reaction at the gel point to the composition of the polymerization system—based on calculating when $\bar{X}_w$ and $\bar{X}_n$, respectively, reach the limit of infinite size.

2-10a Carothers Equation: $\bar{X}_n \to \infty$

2-10a-1 Stoichiometric Amounts of Reactants

Carothers derived a relationship between **the extent of reaction at the gel point** and **the average functionality (f_{avg}) of the polymerization system** of the two functional groups (A and B) with the equivalent amounts.

Ex) 2 mol of glycerol (a triol) and 3 mol of phthalic acid (a diacid), then there is a total of 12 functional groups per five monomer molecules, and $f_{avg} = 12/5 = 2.4$.

2-10a-2 Extension to Nonstoichiometric of Reactant Mixtures

cannot be applied to the reaction mixtures with nonequivalent numbers of the functional groups.

Ex) a mixture of 1 mol of glycerol and 5 mol of phthalic acid.
f_{avg} = 13/6 = 2.14, P_c = 0:922.
Since r = 0.3 (the gross stoichiometric imbalance), the polymerization will stop with the large portion of the acid functional groups being unreacted.

Therefore the average functionality of nonstoichiometric mixtures has been deduced as being equal to twice the **total number of functional groups that are not in excess** divided by the total number of all molecules present.

Because the extent of polymerization (and crosslinking, if it can occur) depends **on the deficient reactant.**

The average functionality of nonstoichiometric mixtures containing more than two monomers.

Monomers with A functional groups; N_A moles of A_{fA} and N_C moles of A_{fC}
Monomer with B functional group: N_B moles of B_{fB}
f_A, f_C : functionality of monomers with A functional groups
f_B : functionality of monomers with A functional groups
B groups are in excess.

2-10b Statistical Approach to Gelation; $\bar{X}_w \rightarrow \infty$

The branching coefficient α; defined as the probability that a given functional group of a branch unit at the end of a polymer chain segment leads to another branch unit.

The multifunctional monomer A_f ; branch unit
The segments between branch units ; chain segments.
If f =3 f = 4

The criterion for gelation in a system containing a reactant of functionality f is that at least one of the (f−1) chain segments radiating from a branch unit will in turn be connected to another branch unit.

The probability for this occurring is simply 1/(f−1) and the critical branching coefficient α_c for gel formation is

When $\alpha(f-1) = 1$, a chain segment will, on the average, be succeeded by $\alpha(f-1)$ chains. Of these $\alpha(f-1)$ chains a portion a will each end in a branch point so that $\alpha^2(f-1)^2$ more chains are created.

The branching process continues with the number of succeeding chains becoming progressively greater through each succeeding branching reaction. The growth of the polymer is limited only by the boundaries of the reaction vessel.

If, on the other hand, $\alpha(f-1)$ is less than 1, chain segments will not be likely to end in branch units.

For a trifunctional reactant ($f=3$) the critical value (α_c) of a is simply 1/2.

2-10c Experimental Gel Points

Carothers Equation; $\bar{X}_n \rightarrow \infty$

Statistical Approach to Gelation; $\bar{X}_w \rightarrow \infty$

diethylene glycol ($f = 2$), 1,2,3-propanetricarboxylic acid ($f = 3$)

either succinic or adipic acid ($f = 2$)

Carothers > Observed > Statistical

2-11 Crosslinking Technology

Preparations of thermosetting polymers (crosslinked polymers)

1. Fabrication of prepolymer (incompletely polymerized polymer)
   - molecular weight range 500–5000 either liquid or solid state

2. Prepolymers are poured into an appropriate mold to form the desired finished object.

Or three stages
The A-stage: soluble and fusible $p < p_c$
The B-stage: fusible but is barely soluble. $p \cong p_c$
The C-stage : infusible and insoluble (highly crosslinked, $p >> p_c$)

2-12a Polyesters, Unsaturated Polyesters, and Alkyds

Crosslinked polyesters : direct esterification of acid or acid anhydride with alcohol.

Unsaturated polyester: Typically maleic anhydride with ethylene glycol

Crosslinking by radical copolymerization with alkene monomers (styrene, vinyl toluene, methyl methacrylate, triallyl cyanurate, and diallyl phthalate)

Alkyds : unsaturated polyesters in which the unsaturation at chain ends

Various unsaturated fatty acids containing i) a single double bonds (oleic, ricinoleic) ii) two or more double bonds, either isolated (linoleic, linolenic) or conjugated (eleostearic).

Alkyd prepolymers are crosslinked via oxidation with atmospheric oxygen. So The crosslinking process is referred to as drying.

Application: architectural enamels, exterior paints, top-side marine paints, and various metal primers and paints

Alkyds with carboxyl end groups reacted with hydroxy groups of nitrocellulose : lacquers

2-12b Phenolic Polymers

Product from phenol (f = 3) with formaldehyde (f =2)
The polymerization rate is pH-dependent, with the highest rates occurring at high and low pH.

2-12b-1 Resole Phenolics

-The strong base-catalyzed polymerization yields resole prepolymers (resole phenolics),

- The polymerization is carried out using a molar ratio of formaldehyde to phenol of 1.2–3.0 : 1 (1.2 : 1 ratio is the typical formulation) → formaldehyde excess

- Heating at 80 – 95 °C for 1–3 h to produce the prepolymers (Vacuum dehydration is carried out quickly to prevent overreaction and gelation.)

- Crosslinking (curing) is carried out by heating at temperatures up to 180 °C.

2-12b-1 Novolac Phenolics

Resole: 1.2–3.0 : 1 using base catalyst

Prepared by formaldehyde to phenol in the ratio of 0.75–0.85 : 1
→ phenol excess
– heatied for 2–4 h at or near reflux temperature in the presence of an acid catalyst.

The polymerization involves electrophilic aromatic substitution, first by hydroxymethyl carbocation and subsequently by benzyl carbocation–each formed by protonation of OH followed by loss of water.
There is much less benzyl ether bridging between benzene rings compared to the resole prepolymers.

2-12b-3 Applications

Phenolic polymers, the first commercial synthetic plastics, were introduced by Leo Baekeland in 1909 through his Bakelite Company.

- The largest-volume application of phenolic polymers is the adhesive bonding material for the manufacture of plywood, particle board, wafer board, and fiberboard.

- adhesive applications in the furniture, automotive, construction, and footwear industries.

- Coatings on cans, drums, metal pipe, electrical insulation, varnishes, and metal primers.

The melamine (f=6, aromatic structure) resins are better than the ureas (f=4) in hardness and resistance to heat and moisture.

The melamine resins produced with adequate molding and laminating techniques; colored dinnerware and dinnerware with decorative patterns.

A combination of phenolic and melamine plastics: decorative laminated plastic sheets for tabletop and counters (a phenolic backing imparts superior mechanical properties while a top melamine layer imparts outstanding clarity and hardness).

Amino resins ; crease resistance and wash-and-wear properties to cellulosic fabrics. Ex) a garment with its appropriate creases and containing the low-molecular-weight amino resin isheated to achieve curing. Curing involves reaction of the amino resin with hydroxyl groups of the cellulosic fabric, and this ‘‘sets’’ the garment into its shape.

Automotive paints; the cheaper ureas are used as primers while the melamines are used as topcoats.

2-12d Epoxy Resins

- Prepared by the reaction of epichlorohydrin and bisphenol A

Prepolymer having two epoxy groups

diepoxy : f = 2
Diamine : f = 4 Then crosslinking is possible
Possible amines : diethylene triamine (f=5), triethylene tetramine (f =4), 4,4'-diaminodiphenylmethane (f=4), and polyaminoamides (e.g., the diamide formed from diethylene triamine and a dimerized or trimerized fatty acid).

- Further crosslinking with anhydride compounds (tetrahydrophthalic, nadic methyl, and chloroendic anhydrides

Epoxy resins possess high chemical and corrosion resistance, toughness and flexibility, good mechanical and electrical behavior, and outstanding adhesion to many different substrates.

Coatings applications : marine, maintenance, drum, automotive, can coatings.

Structural composites; military (missile casings, tanks), aircraft (rudders, wing skins, flaps), automobiles (leaf springs, drive shafts), and pipe in the oil, gas, chemical, and mining industries.

2-12e Polyurethanes

Many polyurethanes are synthesized using mixtures of diols and diamines.

Polymerization temperatures are moderate, often near ambient and usually no higher than 100-120C. At higher temperatures o several different types of degradation reactions occur

Further crosslinking of the polymers possible by the reactions of -NH- with -NCO

The production of flexible polyurethane foams.

Trimerization of isocyanate groups to form isocyanurates also occurs and serves as an additional source of branching and crosslinking

The wide variations possible in synthesis give rise to a wide range of polyurethane products including flexible and rigid foams and solid elastomers, extrusions, coatings, and adhesives.

2-12f Polysiloxanes

Applications wide temperature range (−100 to 250 °C).
- Very low Tg value (−127C) ; good low-temperature flexibility
- Si- O bond is stronger than the CC bond (450 vs. 350 kJ/mol); stable to high temperature, oxidation, and chemical and biological environments.

Preparation

crosslinking of the polysiloxane

2-12g Polysulfides

Curing to a solid elastomer is accomplished
by oxidation of thiol to disulfide links by oxidants such as lead dioxide and p-quinone dioxime.

2-13 STEP COPOLYMERIZATION

2-13a Types of Copolymers

Naming copolymers

The specific type of copolymer is noted by insertng -*alt*-, -*stat*-, or -*ran*- in between the names of the two repeating units; -*co*- is used when the type of copolymeris not specified:
poly(A-*co*-B), poly(A-*alt*-B), poly(A-*stat*-B), poly(A-*ran*-B).

The di-, tri-, tetra-, and multiblock copolymers are named as polyA-*block*-polyB, PolyA-*block*-polyB-*block*-polyA, polyA-*block*-polyB-*block*-polyA-*block*-polyB, and poly(polyA-*block*-polyB),

* copolymer involves different functional groups in the two repeat units are also possible
for example, an amide-ester copolymer such as

2-13b Methods of Synthesizing Copolymers

2-13b-1 Statistical Copolymers

2-13b-2 Alternating Copolymers

two-stage process

i) a diamine is reacted with an excess of diacid to form a trimer

ii) The trimer is then reacted with an equimolar amount of a second diamine

Alternating Copolymers

The silyl ether derivative of the alcohol is used since the corresponding alcohol cannot be isolated because of the high degree of reactivity of isocyanate and alcohol groups toward each other.

2-13b-3 Block Copolymers

The two methods

i)two-prepolymer methods

the separate synthesis of two different prepolymers, each containing appropriate end groups, followed by polymerization of the two prepolymers

Block Copolymers

ii) one-prepolymer method

Polymerization of prepolymers with two ‘‘small’’ reactants.

Telechelic polymer : containing one or more functional end groups that have the capacity for selective reaction to form bonds with another molecule.

2-14 HIGH-PERFORMANCE POLYMERS

2-14a Requirements for High-Temperature Polymers

synonyms of high-performance polymer; heat-resistant polymer, thermally stable polymer, high-temperature polymer,

1. The strengths of the primary bonds
   - → Aromatic ring systems (carbocyclic and heterocyclic) possess the highest bond strengths due to resonance stabilization
   - → Certain functional groups (ether, sulfone, imide, amide, CF_2) are much more heat-resistant than others (alkylene, alicyclic, unsaturated, NH, OH)
2. Ladder or semiladder polymer structures
3. High molecular weight and crosslinking
4. Strong secondary attractive forces (including dipole-dipole and hydrogen bond interactions) improve heat resistance.
5. Crystallinity increases heat resistance by serving as physical crosslinks

2-14b Aromatic Polyethers by Oxidative Coupling

The oxidative coupling polymerization of 2,6-disubstituted phenols with bubbling oxygen in an organic solvent (toluene) containing a catalytic complex of a cuprous salt and amine

Phenols with one or more bulky *o*-substituents (isopropyl or *t*-butyl) and with two *o*-methoxy substituents undergo dimerization (carbon-carbon) coupling instead of polymerization (carbon-oxygen coupling).

The amine/cuprous ion ratio and the reaction temperature determine the extent of polymerization relative to dimerization, probably by affecting the nature of the complex formed among cuprous ion, amine, and reaction intermediate.

The polymer from 2,6-dimethylphenol is the commercial product referred to as poly(pphenylene oxide) or PPO. The IUPAC name is poly(oxy-2,6-dimethyl-1,4-phenylene). (T_m = 262-267 ^oC, T_g = 205-210 ^oC).

Neat PPO cannot be used commercially because its high melt viscosity makes processing too difficult.

The commercially available products are blends of PPO with high-impact polystyrene (HIPS) (polybutadiene-graft-polystyrene).

Blending overcomes the processing problem by lowering the melt viscosity and also increases the impact strength.

2-14c Aromatic Polyethers by Nucleophilic Substitution

Preparation of polyetherketones (polyketones) and polyethersulfones (polysulfones)

Polyetheretherketone (PEEK)

polyetherketone (PEK)

bisphenol A polysulfone

polyethersulfone

2-14d Aromatic Polysulfides

Poly(*p*-phenylene sulfide) [IUPAC: poly(sulfanediyl-1,4-phenylene) (trade name: Ryton) (PPS) is synthesized by the reaction of sodium sulfide with *p*-dichlorobenzene in a polar solvent such as 1-methyl-2-pyrrolidinone (NMP) at about 250 °C and 1.1 MPa (160 psi).

Uncrosslinked PPS is a highly (60%) crystalline polymer with T_m = 285 °C and T_g = 85 °C. It is rated for continuous service at 200–240 °C, placing PPS between the polysulfones and the polyketones.

PPS undergoes a slow curing process when heated above the melting point in air. Curing involves chain extension, oxidation, and crosslinking, but is poorly understood. There is spectroscopic evidence for crosslinking via sulfur, oxygen, and aromatic bridges between polymer chains

2-14e Aromatic Polyimides

The direct production of high-molecular-weight aromatic polyimides in a one-stage polymerization cannot be accomplished because the polyimides are insoluble and infusible.

Two step reactions

1. Amidation reaction in a polar aprotic solvent (NMP, DMAC) to produce a high-molecular-weight poly(amic acid)
2. The poly(amic acid) is cyclodehydrated to the polyimide by heating at temperatures above 150C.

Polyetherimides (PEI) (trade name: Ultem)

→ polyimides containing sufficient ether as well as other flexibilizing structural units to impart melt processability by conventional techniques, such as injection molding and extrusion.

Polyamideimides (PAIs) (trade name: Torlon)

2-14g Liquid Crystal Polymers

They exhibit liquid crystal characteristics either in solution (lyotropic liquid crystal) or in the melt (thermotropic liquid crystal).

They show the flow behavior of isotropic liquids but appear to possess some kind of long-range molecular order greater than the isotropic liquid state but less than the true crystal state.

2-14h 5-Membered Ring Heterocyclic Polymers

polybenzimidazoles (PBI)

Polymerization of 3,3’-diaminobenzidine and diphenyl isophthalate yields poly[(5,5’-bi-1*H*-benzimidazole]- 2,20-diyl)-1,3-phenylene]

The formation of PBI : a sequence of two nucleophilic reactions:

i) a nucleophilic substitution to form an amine-amide
ii) cyclization via nucleophilic addition

Polybenzoxazoles (PBO) and polybenzthiazoles (PBT)

Synthesis of PBO (LIV) and PBT (LV) is accomplished by the reactions of a dicarboxyl reactant with a bis-*o*-aminophenol (X = O) and bis-o-aminothiophenol (X = S), respectively.

2-14j Conjugated Polymers

- conjugated π-electron systems possibly used as semiconducting, conducting, and light-emitting (optoelectronic) materials.

- high electron affinities and low ionization potentials, so easily oxidized or reduced

- charge-transfer agents (dopants) (electron acceptors or electron donors) can oxidize or reduce the polymers

- electron acceptors can produce poly(radical-cation))-doped conducting materials (p-type)

- electron donors can produce poly poly(radical-anion)-doped conducting materials (n-type)

- These doped polymers can have near-metallic conductivity in some cases.

Oxidative dopants: AsF_5, I2, $AlCl_3$, and $MoCl_5$
Reductive dopants: Sodium, potassium, and lithium naphthalides

2-14j-1 Oxidative Polymerization of Aniline

Polyaniline [IUPAC: poly(imino-1,4-phenylene)] is obtained by the oxidative polymerization of aniline in aqueous HCl solution, either by electrochemical polymerization or by using a chemical oxidant such as ammonium persulfate, $(NH_4)_2S_2O_8$.

2-14j-2 Poly(p-phenylene)

oxidative polymerization of benzene to poly(p-phenylene) [IUPAC: poly(1,4-phenylene)]

Unfortunately, the oxidative route yields an insoluble and intractable product of low molecular weight and irregular structure (a mixture of *o* and *p* substitution).

Alternate approaches to the poly(*p*-phenylene) :
→ Suzuki coupling between arylboronic acids (or their esters) and aryl bromides

2-14j-3 Poly(p-phenylene Vinylene)

Poly(p-phenylene vinylene) [IUPAC: poly(1,4-phenyleneethene-1,2-diyl)] (PPV) is obtained by the sequence involving successive base- and heat-induced eliminations of dialkyl sulfide and hydrogen halide

2-16 DENDRITIC (HIGHLY BRANCHED) POLYMERS

Dedritic Polymers	Linear polymers
globular shape: dimensions of the polymer molecule are about the same in all directions So, lower hydrodynamic volume and lower viscosity	elongated shapes : the dimensions are much greater in one direction than the other directions
low secondary forces: higher solubility and miscibility with other materials	greater attractive secondary forces: molecules pack together and attract each other over a larger surface area
chain entanglements are not easy; rarely have sufficient strength to be useful as fibers, rubbers, and plastics.	chain entanglements can increase the strength of the polymers
much larger number of chain ends	Only two chain ends
Ex) Globular proteins : catalytic, transport, regulatory, hormonal, and other functions that require solubility in blood and the other aqueous media of cells and tissures.	Ex) The fibrous proteins : strong secondary attractive forces used to construct bone, skin, and nails.

CHAPTER 3

RADICAL CHAIN POLYMERIZATION

Initiation : chain Polymerization is initiated by a <u>reactive species R*</u> produced from some compound I termed an initiator:

Propagation: The reactive species (free radical, cation, or anion) adds to a monomer molecule by opening the p-bond to form a new active. The process is repeated as many more monomer molecules are successively added to continuously propagate the reactive center

Termination : Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the particular reaction conditions.

3-1 NATURE OF RADICAL CHAIN POLYMERIZATION

3-1a Comparison of Chain and Step Polymerizations

Chain Polymerizations	Step Polymerizations
only monomer and the propagating species can react with each other	two molecular species present can react each other
The monomer concentration decreases throughout the course of the reaction	Monomer disappears much faster
The MW of the polymer is relatively unchanged during the polymerization (Radical)	The MW increases throughout the course of the reaction

3-1b Radical versus Ionic Chain Polymerizations

3-1b-1 General Considerations of Polymerizability

- C=C (Vinyl monomers) and C=O (aldehydes and ketones) bonds are the two main types of linkages that undergo chain polymerization.

- Aldehydes and ketones are polymerized by both anionic and cationic initiators

- Vinyl monomers can undergoes polymerization by both radical and ionic initiators.

3-1b-2 Effects of Substituents

Electrondonating substituents (alkoxy, alkyl, alkenyl, and phenyl)
→ cationic polymerization

isobutylene, styrene, methyl vinyl ether, and isoprene :
- cationic polymerization by cationic initiators.

Electron-withdrawing substituents (such as cyano, aldehyde, ketone, acid, or ester) → anionic polymerization

Alkenyl and phenyl substituents can resonance stabilize the anionic propagating
Species → anionic polymerization

Halogens : withdraw electrons inductively and push electrons by resonance, but both effects are relatively weak: neither anionic nor cationic polymerization vinyl chloride → radical polymerization

Radical species : neutral and no stringent requirements for the stabilization of the propagating radical species.

Almost all substituents can stabilize the propagating radicals,

3-2 STRUCTURAL ARRANGEMENT OF MONOMER UNITS

3-2a Possible Modes of Propagation

two possible points of attachment on monosubstituted (X=H) or 1,1-disubstituted monomers for a propagating radical

Possible polymer structure

head-to-tail (H-T)

head-to-head (H-H)

Regioselective process : H-T is favored over H-H

Why? resonance effects + steric hinderence

Isoregic : exclusive H-T
Syndioregic : alternating arrangements of H-T and H-H
Aregic: random arrangements of H-T and H-H

3-2b Experimental Evidence

Less than 1-2% H-to-H placement in poly(vinyl acetate)
-hydrolysis to poly (vinyl alcohol) and periodate oxidation

H-T propagation is the predominant (>98-99%) in chain polymers

Exceptions: H-H placements of
poly(vinyl fluoride) : 10 %
poly(vinylidene fluoride): 5%
poly(trifluoroethylene) : 12%
poly(chlorotrifluoroethylene) : 2%

- substituents are small (not much steric hindrance) and not much resonance stabilizing → F (fluorine)

The effect of polymerization temperature

H-H in

poly(vinyl acetate) : 40 ^{o}C → 1 % ,100 ^{o}C → 2 %

poly(trifluoroethylene) : −80 ^{o}C → 10 % ,80 ^{o}C → 14 %

The effect of increasing the polymerization temperature is an increase in the extent of H-H placement, but the effect is small.

3-2c Synthesis of Head-to-Head Polymers

H-H poly(vinyl chloride) is obtained by chlorination of 1,4-poly-1,3-butadiene

H-H polystyrene by hydrogenation of 1,4-poly-2,3-diphenylbutadiene

3-3 RATE OF RADICAL CHAIN POLYMERIZATION

3-3a Sequence of Events

Radical chain polymerization is a chain reaction consisting of a sequence of three steps — initiation, propagation, and termination.

1. Initiation

2. Propation

3. Termination

combination (coupling) disproportionation

k_t : rate constant for termination 10^6–10^8 L mol^{-1} s^{-1},
much larger than for propagation (10^2–10^4 L mol^{-1} s^{-1})

Still the propagation is the main event in the polymerization due to the effect of the concentration!

3-3b Rate Expression

Assumption: k_p and k_t are independent of the size of the radical.

Although Very small radicals are more reactive than propagating radicals, but this effect is not important because the effect of size vanishes at the dimer or trimer size.

The rate of monomer disappearance = the rate of polymerization

the number of monomer molecules reacting in the initiation step is very very small

Then the polymerization rate is given simply by the rate of propagation

[M] : monomer concentration

$[M\cdot]$: total concentration of all chain radicals

$[M\cdot] = [M_1\cdot] + [M_2\cdot] + [M_3\cdot] + \cdots\cdots\cdots.. + [M_n\cdot] + \cdots\cdots$

The radical concentration ($[M\cdot]$) is very difficult to measure quantitatively, since they are very low (10^{-8} M) and is very reactive.

Therefore it is desirable to eliminate $[M\cdot]$
How?
"steady-state assumption" : The rate of change of the concentration of radicals quickly becomes and remains zero during the course of the polymerization.

The use of the factor of 2 (conventional number) in the termination rate equation follows the generally accepted convention for reactions destroying radicals in pairs.

$R_p \propto k_p$, [M], $(R_i)^{1/2}$, $(k_t)^{-1/2}$

3-3c Experimental Determination of R_p

3-3c-1 Physical Separation and Isolation of Reaction Product

Isolating (followed by drying and weighing) the polymer from aliquots of the polymerization system as a function of reaction time.

i) Precipitation using non-solvent (while solvent for monomer) for polymers
ii) Distillation of monomers

3-3c-2 Chemical and Spectroscopic Analysis

i) titration of the unreacted double bonds with bromine for vinyl monomers
ii) Infrared (IR), ultraviolet (UV), and nuclear magnetic resonance (NMR) and other spectroscopies.

3-3c-3 Other Techniques

Dilatometry, the heat of polymerization (using DSC)

3-4 INITIATION

-The term catalyst is often used synonymously with initiator, but it is incorrect in the classical sense, since the initiator is consumed.
-Radicals can be produced by a variety of thermal, photochemical, and redox methods.

3-4a Thermal Decomposition of Initiators

3-4a-1 Types of Initiators

- compounds with bond dissociation energies in the range 100-170 kJ mol^{-1} (ex, O-O, S-S, N-O), C-C : ~300 kJ mol^{-1}, C-H : ~340 kJ mol^{-1}

peroxides (O-O) are mostly used

acyl peroxides : acetyl and benzoyl peroxides alkyl peroxides : cumyl and *t*–butyl peroxides

hydroperoxides : *t*–butyl and cumyl hydroperoxides

peresters : *t*–butyl perbenzoate

acyl alkylsulfonyl peroxides, dialkyl peroxydicarbonates,
diperoxyketals, and ketone peroxides

azo compounds: 2,2’-Azobisisobutyronitrile (AIBN)

The C– N bond dissociation energy is high (290 kJ mol^{-1}), but the driving force for homolysis is the formation of the highly stable nitrogen molecule.

other initiators

disulfides

tetrazenes

different initiation temperatures for different structures depending on rates of decomposition (proper k_d values: $10^{-4} - 10^{-6}$ s^{-1})

2,2'−Azobisisobutyronitrile (AIBN) : 50 − 70 ^{o}C

acetyl peroxide : 70 − 90 ^{o}C

benzoyl peroxide: 80 − 95 ^{o}C

t−butyl and cumyl hydroperoxides : 120 − 140 ^{o}C

k_d is larger for acyl peroxides than for alkyl peroxides since the RCOO· radical is more stable than the RO· radical

for R−N=N−R,
k_d increases in the order R = allyl, benzyl > tertiary > secondary > primary

initiator half-life $t_{1/2}$

The rate of initiator disappearance $$t_{1/2} = \frac{0.693}{k_d}$$

3-4a-2 Kinetics of Initiation and Polymerization

initiation

The rate of producing primary radicals by the thermal homolysis

where [I] is the concentration of the initiatorand f is the initiator efficiency.

The use of the factor of 2 (conventional number) because two radicals are generated

In most polymerizations, the second step (the addition of the primary radical to monomer) is much faster than the first step.

Then, the rate of initiation is

$$R_p \propto k_p,\ [M],\ (k_d)^{1/2},\ [I]^{1/2},\ (kt)^{-1/2}$$

3-4a-3 Dependence of Polymerization Rate on Initiator

$R_p \propto [\mathrm{I}]^{1/2}$

i) at very high initiation concentration and $k_d > k_i$

→ RDS step then $R_\mathrm{i} = k_\mathrm{i}[\mathrm{R\cdot}][\mathrm{M}]$

Then the possible termination is

Because [I] is very large

This could occurs when concentration of R· is very large and/or when [M] is very small

Then the steady state for [M·] is

$R_\mathrm{i} = k_\mathrm{i}[\mathrm{R\cdot}][\mathrm{M}] = R_\mathrm{t} = k_{tp}[\mathrm{M\cdot}][\mathrm{R\cdot}]$ then $[\mathrm{M\cdot}] = [\mathrm{M}]k_\mathrm{i}/k_{tp}$

$R_p \propto [\mathrm{M}]^2$

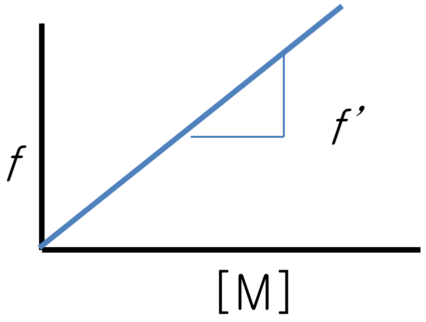
$R_p \propto [\mathrm{I}]$

3-4a-4 Dependence of Polymerization Rate on Monomer

Monomer : methyl methacrylate (MMA)
initiator : t-butyl perbenzoate-diphenylthiourea redox system

$$R_p \propto [M]$$

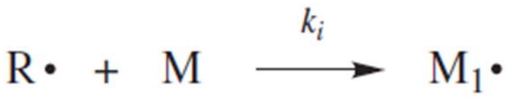
When the initiator efficiency f may vary directly with the monomer concentration



then, becomes $R_i = 2f'[M]k_d[I]$

$R_p \propto [M]^{3/2}$

Why?



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

$$R\cdot + R\cdot \longrightarrow R{-}R$$

If [I] is very large (or [M] is very small), R·+R· reaction occurs more than R· + M reaction

If the second step of the initiation reaction is RDS

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

$R\bullet + M \xrightarrow{k_i} M_1\bullet$ → RDS, then $k_i < k_d$

$R_i = k_i[R\cdot][M] = k_t 2[M\cdot]^2 = R_t$, steady state assumption

therefore $R_p \propto [M]^{3/2}$

This happens

1) Photochemcial Initiation
2) Initiation by ionizing radiation
3) Redox initiation

Molecule-induced homolysis

Some initiators need very high initiation temperature,
then at nominal polymerization temperature, radicals are generated by the reaction of the initiator and monomer

Then, initiation step is $\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{R}\cdot + \mathrm{M}_1\cdot$

$R_\mathrm{i} = k_i [\mathrm{I}][\mathrm{M}]$ $R_i = R_t = 2k_t [\mathrm{M}\cdot]^2$, steady state assumption

therefore $R_p \propto [\mathrm{M}]^{3/2}$

3-4b Redox Initiation

Oxidation-reduction reactions produce radicals that can be used to initiate polymerization.

radicals can be produced at reasonable rates over a very wide range of temperatures even at moderate temperatures of 0-50°C and even lower.

A wide range of redox initiation systems are possible

1) initiated photolytically as well as thermally

2) both inorganic and organic components either wholly or in part

3) direct electron transfer between reductant and oxidant, or the intermediate formation of reductant-oxidant complexes

3-4b-1 Types of Redox Initiators

1. Peroxides in combination with a reducing agent

the combination of benzoyl peroxide and an N,N-dialkylaniline

k_d for benzoyl peroxide in styrene by heating (thermal initiation)

$1.33 \times 10^{-4}\ \mathrm{s}^{-1}$ at 90°C

k_d for the benzoyl peroxide-N, N-diethylaniline redox system

$1.25 \times 10^{-2}\ \mathrm{L\ mol^{-1}\ s^{-1}}$ at 60°C and $2.29 \times 10^{-3}\ \mathrm{L\ mol^{-1}\ s^{-1}}$ at 30°C.

2. The combination of inorganic reductants and inorganic oxidants

Other possible oxidants and reductants

This system is generally possible for aqueous solution.

3. Organic–inorganic redox pairs initiate polymerization

4. monomer itself acts as one component of the redox pair.

thiosulfate ($S_2O_3^{2-}$, reductant) + acrylamide or methacrylic acid

N,*N*–dimethylaniline (oxidant)+ methyl methacrylate

3-4b-2 Rate of Redox Polymerization

1) Termination is by bimolecular reaction of propagating radicals

$$Ri = R_t = 2k_t[M\cdot]^2$$, steady state assumption

2) Termination is by monomolecular reaction

The propagating radical loses a hydrogen to form a dead polymer with a C=C end group.

3-4c Photochemical Initiation

Photochemical or photoinitiated polymerizations occur when radicals are produced by ultraviolet and visible light irradiation of a reaction system.

How radicals are generated?

1. Some compound in the system undergoes excitation by energy absorption and subsequent decomposition into radicals.
2. Some compound (photosensitizer) undergoes excitation and the excited species interacts with a secondcompound (by either energy transfer or redox reaction) to form radicals derived from the latter and/or former compound(s).

Advantages of photoinitiation

1. Polymerization can be spatially directed (i.e.,confined to specific regions) by turning the light off and on.
2. The initiation rates can be very fast and are controlled by a combination of the source of radicals, light intensity, and temperature.

→ thin coating of bulk monomers in industrial applicatios

Disadvantege

penetration of light energy through a thickness of material is low. (not possible for the preparation of thick sample)

3-4c-2 Irradiation of Thermal and Redox Initiators

Aromatic ketones are useful photoinitiator, since their absorptions occur at longer wavelength (lower energy) and their quantum yields are higher.

1) **α-Scission** : bond scission between the carbonyl carbon and the α-carbon

2) electron transfer : electron transfer followed by proton transfer from the amine (alcohols, amides, amino acids, and ethers) to the ketone

Other commercial photoinitiators (usually used together with an amine)

benzoin (VIII), benzyl ketals (IX), aroylphosphine oxides (X), and α -aminoalkylphenones (XI).

The relative amounts of α -scission and electron transfer vary with the initiator (which determines the relative stabilities of the radicals formed from the two processes) and also the electron donor used.

3-4c-3 Rate of Photopolymerization

The rate of photochemical initiation

$$R_i = 2\phi I_a$$

I_a : intensity of absorbed light (the volumetric light intensity with units of $\text{mol cm}^{-3}\ \text{s}^{-1}$ or $\text{mol L}^{-1}\ \text{s}^{-1}$

ϕ : quantum yield for initiation

2 : two radicals are produced per molecule.

ϕ is synonymous with f in $R_i = 2fk_d[\text{I}]$

3-4c-3-a Measurement of Absorbed Light.

Chemical, thermal, and electrical ***actinometers*** are used

3-4c-3-b General Observations

If the term $\alpha[\text{A}]D$ is sufficiently small

and there is negligible attenuation of light intensity in traversing the reaction system

3-4d Initiation by Ionizing Radiation

- Initiation by radioactive sources and particle accelerators

radioactive sources : gamma and X rays

particle accelerators : electrons, neutrons, and α-particles (He^{2+})

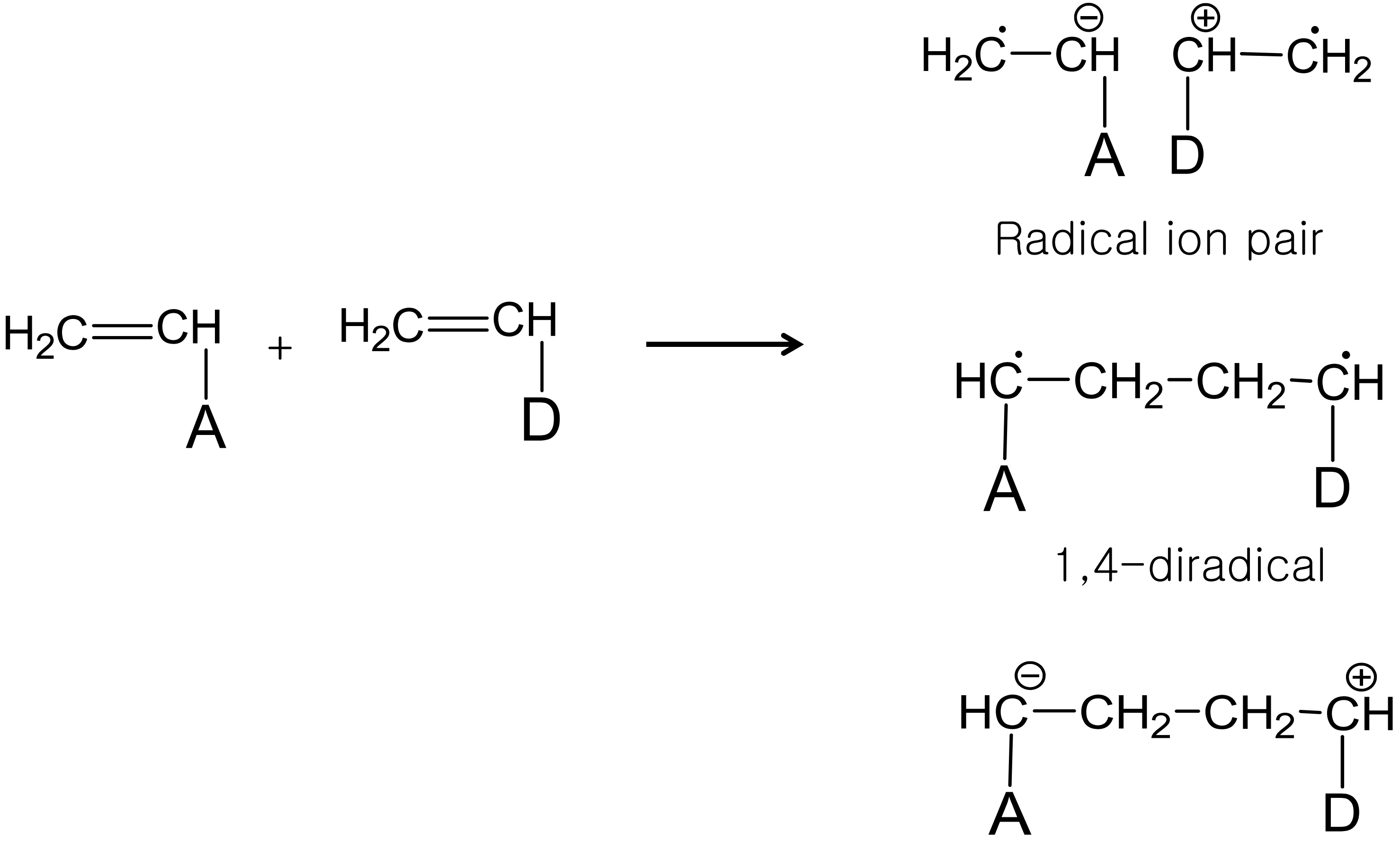
Then radical, anion, and or cation can be generated.
Polymerization type can be decided by the types of the monomers

3-4e Pure Thermal Initiation

Most monomers, when exhaustively purified (and in exhaustively purified reaction vessels), do not undergo a purely thermal, self-initiated polymerization in the dark.

self-initiated polymerization are substituted styrenes, acenaphthylene, 2-vinylthiophene, 2-vinylfuran, and methyl methacrylate.

Spontaneous polymerization is also observed in certain pairs of monomers such as styrene–acrylonitrile and maleimide–vinyl ether



Radical ion pair

1,4–diradical

1,4–zwitterion

A; electron accepting (withdrawing) group
D; electron donating group

3-4g Initiator Efficiency, *f*

3-4g-1 Definition of *f*

There is wastage of initiator due to two reactions.

1) Chain Transfer

→ chain transfer to initiator
→ does not change the radical concentration during the polymerization,

2) the side reaction(s) of the radicals formed in the primary step of initiator decomposition.

Definition of *f* : the fraction of radicals formed in the primary step of initiator decomposition, which are successful in initiating polymerization

3-4g-2 Mechanism of $f < 1$: Cage Effect

The values of f : 0.3–0.8. Why?

the primary step of initiator decomposition
into two radicals, within the solvent cage.

brackets : solvent cage (traps the radicals for some short period
before they defuse out.

The average life of neighboring radicals in the cage : $10^{-10} - 10^{-9}$ s

The rate constants for radical–radical reactions : 10^{7} L mol^{-1} s^{-1}

The rate constants for radical–monomer reactions : $10–10^{5}$ L mol^{-1} s^{-1}

The concentration of radicals in the solvent cage : 10 M

The concentration of radicals outside of the solvent cage : 10^{-8} M

The concentration of monomers : 10^{-1} – 10 M

In the solvent cage: radical–radical reactions >> radical–monomer reaction

But the life time is very short

Outside of the solvent cage: radical–radical reactions << radical–monomer reaction

So the prime reason for $f < 1$ is the reactions occurring within the solvent cage.

The cage effect is much less in the redox initiation

→ No radical pairs
still the reaction between radical and other species in the cages are possible

acetyl peroxide

The initiator efficiency and quantum yield (for photo initiation) for initiation are generally independent of monomer concentration. However, one can observe a variation of *f* with the monomer concentration at low monomer concentrations.

Effect of styrene concentration on the initiator efficiency of azobisisobutyronitrile (AIBN)

Other factors affecting the initiator efficiency

viscosity ↑ : f ↓

With increasing viscosity, the lifetimes of radicals in the solvent cage are increased, leading to greater extents of radical–radical reactions within the solvent cage.

f = 0.22 in benzene , f = 0.086 in diethyl phthalate
for bis-azo-1,1'-cyclohexane nitrile at 0 ^{o}C

f = 0.75 at conversions up to 30%, f = 0.20 at 90–95% conversion
for AIBN in the polymerization of styrene

solvent reacting with radicals : f ↓

f in carbon tetrachloride or 1-chlorooctane < f in aromatic solvents

f for AIBN :
methyl methacrylate, vinyl acetate, styrene, vinyl chloride, and acrylonitrile

$$0.6 \xrightarrow{\hspace{10cm}} 1.0$$

the relative rates with which radicals add to the different monomers

3-4g-3 Experimental Determination of f

1) Direct Measurements of the initiator decomposition and the polymers.

- Measurement of the initiator decomposition
  ex) NMR, IR spectroscopy
  the evolution of nitrogen of AIBN decomposition

- Measurement of the polymer number-average molecular weight +
  knowledge of termination mechanism (coupling or disproportionation)

- Polymer end groups analysis by NMR, IR spectroscopy

  → 50,000-molecular-weight polymer, the end groups constitute only 0.1% of the total weight of the sample.

  The sensitivity could be increased by using isotopically labeled initiators such as ^{14}C-labeled AIBN and benzoyl peroxide and ^{35}S-labeled potassium persulfate

2) The use of radical scavengers

(the number of radicals can be counted by rapidly stopping their growth)

i) Stable radicals

ex) 2,2-diphenylpicrylhydrazyl (DPPH) obtained by oxidation of diphenylpicrylhydrazine

DPPH

Other stable radicals : TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), 1,3,5-triphenylverdazyl, and galvinoxyl

ii) Fast hydrogen or halogen transfer

Using thiols, iodine, bromine, and dihydroanthracene.

iii) spin traps

→ reaction with radicals to form stable radicals.

Ex) 2-Methyl-2-nitrosopropane (XIII) and phenyl-*N*-t-butylnitrone (XIV)

Electron spin resonance (ESR) spectroscopy can be used to measure the
radical concentrations of the nitroxide radicals (XVand XVI).

3) dead-end polymerization technique

The determination of k_d is possible!

Polymerization with a limited concentration of initiator, then polymerization stops short of completion.

In general $t \rightarrow \infty$, $p \rightarrow 1$
If [I] is small $t \rightarrow \infty$, $p < 1$

3-5 MOLECULAR WEIGHT

3-5a Kinetic Chain Length (ν)

Definition in radical chain polymerization
→ the average number of monomer molecules consumed (polymerized) per each radical

at steady state

Kinetic Chain Length (ν) $\propto$ $[I]^{1/2}$

3-5b Mode of Termination

termination by coupling

termination by disproportionation

a : the fractions of propagating chains terminated by coupling
(1−*a*) : the fractions of propagating chains terminated by disproportionation
b : the average number of initiator fragments per polymer molecule.

n : number of propagating chains

coupling

disproportionation

Coupling is the major termination mode !

styrene, methyl acrylate, and acrylonitrile : almost by coupling
methyl methacrylate : by a combination of coupling and disproportionation

Disproportionation : - sterically hindered propagating radical
- many β-hydrogens available for transfer
- higher temperature
- highly reactive radicals (vinyl acetate and ethylene)

Ex) The extent of disproportionation in methyl methacrylate increases from 67% at 25 ^oC to 80% at 80 ^oC.

3-6 CHAIN TRANSFER

3-6a Effect of Chain Transfer

The degree of polymerization with chain tranfer

the rate of a chain-transfer reaction

The degree of polymerization without chain transfer

XA : monomer, initiator, solvent, or other substance

chain-transfer constants

Mayo equation

3–6b Transfer to Monomer and Initiator

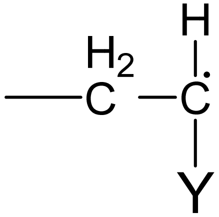
3–6b–2 Monomer Transfer Constants

C_M is generally very small (10^{-5} to 10^{-4}) because the reaction involves breaking the strong vinyl CH bond.

C_M values for ethylene, vinyl acetate and vinyl chloride are relatively large

Ethylene, vinyl acetate and vinyl chloride has very high propagating radical reactivity, while low monomer reactivity !

radical reactivity vs monomer reactivity



$$-\overset{H_2}{C}-\overset{\overset{H}{|}}{\underset{\underset{Y}{|}}{\dot{C}}}$$

Stability of the radical by Y increases from the following order

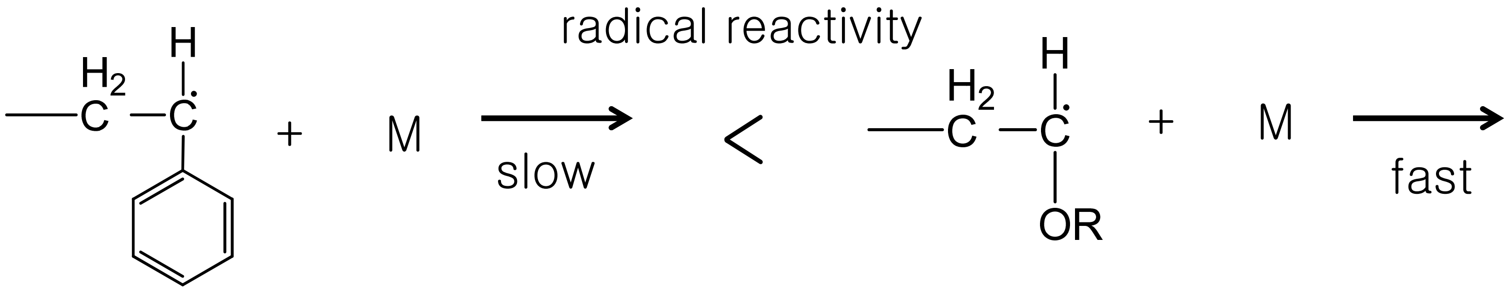
stable ←

$-\phi$, $-CH{=}CH_2$ > $-CN$, $-COR$ > $-COOH$, $-COOR$ >

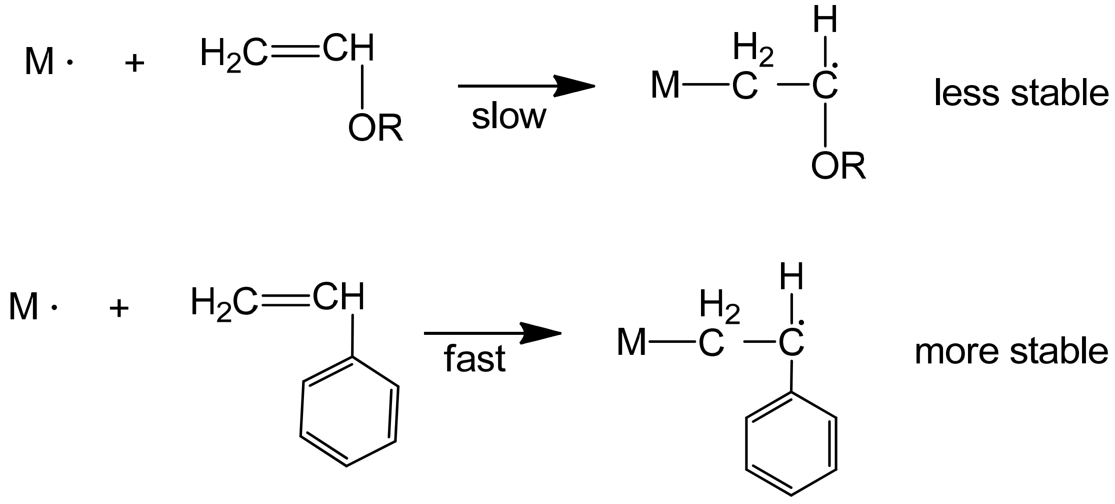
$-Cl$ > $-OCOR$, $-R$ > $-OR$, $-H$

→ more reactive

ex)



monomer reactivity



Styrene is more reactive monomer

The most reactive pair is vinyl acetate radical and styrene monomer
Details in chapter 6 “copolymerization”

Highly reactive radicals generated from ethylene, vinyl acetate and vinyl chloride can have more chain transfer reactions.

Still vinyl acetate and vinyl chloride have larger C_M values than ethylene although their radical reactivity is close or even lower!

vinyl acetate has the acetoxy methyl group for the chain transfer

vinyl chloride is attributed to a reaction sequence involving the propagating center formed by head-to-head addition (Intramolecular migration of Cl·)

The maximum number-average molecular weight of PVC is 50,000–100,000.

C_M for PVC is about 0.001

In PVS, the amounts of allyl chloride and 1,2-dichloroalkane end groups are approximately equal (0.7–0.8 per polymer molecule).

3-6b-3 Initiator Transfer Constants

C_I varies with the reactivity of the propagating radical
ex) C_I *for* cumyl hydroperoxide

3–6c Transfer to Chain–Transfer Agent

3–6c–1 Determination of CS

In Mayo equation

By using low concentrations of initiators or initiators with negligible C_I values (e.g., AIBN) and keeping $R_p/[\mathrm{M}]^2$ constant by appropriately adjusting the initiator concentration

Mayo equation

Then, C_S can be determined by the slope of $(1/\overline{X}_n)$ versus [S]/[M]

C_S values for sulfur compounds are very large

i) Weak C–S or S–H bonds, ii) S· radicals are stable

i) the weak carbon–halogen bonds.
ii) excellent stabilization of the trihalocarbon radicals formed by resonance involving the halogen free pairs of electrons

$CCl_4 < CBr_4$ C– Cl : ~ 85 Kcal/mol CBr_4 : ~ 70 Kcal/mol

C_S values for vinyl acetate are larger than those of styrene
→ more reactive vinyl acetate radical

The order of radical reactivity is vinyl chloride > vinyl acetate > acrylonitrile > methyl acrylate > methyl methacrylate > styrene > 1,3–butadiene.

$(CH_3CH_2)_3$–N (Triethylamine, TEA) : electron donating and electron rich compound

⇒ highly reactive with electron poor monomers such as acrylonitrile, MMA

CCl_4 : electron poor compound

⇒ highly reactive with electron rich monomers such as vinyl axetate, styrene

3-6d Chain Transfer to Polymer

Since C_I, C_M , and C_S values are obtained in the steady state when the polymer concentration is not high, chain transfer to polymer could be ignored!

However, transfer to polymer cannot be neglected for the practical situation where polymerization is carried to complete or high conversion.

The extent of branching is greater in polymers, such as poly(vinyl acetate), poly(vinyl chloride), and polyethylene (having very reactive propagating radicals) due to the chain transfer to polymer.

ex) The extent of branching but may reach as high as 15-30 branches per 500 monomer units for polyethylene.

How ?

3-6e Catalytic Chain Transfer (CCT)

two advantages over conventional transfer agents

(1) low-molecular weight polymers can be produced without having to use large amounts of conventional chain-transfer agents or high initiator : monomer ratios or high temperatures

(2) polymers with unsaturated end groups (macronomers) are produced. Very good for coating applications

3-7 INHIBITION AND RETARDATION

Inhibitors:
stop every radical, and polymerization is completely halted until they are consumed.

$k_p << k_{tr}$ $k_p >>> k_a$ $k_a \cong 0$

Retarders:
stop only a portion of the radicals and they polymerize at a slow rate

$k_p << k_{tr}$ $k_p \geq k_a$ $k_a \neq 0$

self-initiated polymerization of styrene at 100 °C

Plot 1: no inhibitor

plot 2: 0.1% benzoquinone
Inhibitor

plot 3: 0.5% nitrobenzene
Retarder

plot 4, 0.2% nitrosobenzene
Inhibitor + Retarder + α

3-7b Types of Inhibitors and Retarders

p-Benzoquinone and chloranil (which are electron-poor) act as inhibitors toward electron rich propagating radicals (vinyl acetate and styrene) but only as retarders toward the electron-poor acrylonitrile and methyl methacrylate propagating radicals.
chloranil (2,3,5,6-tetrachlorobenzoquinone) is electron poorer !
See neutral oxygen!

Aromatic nitro compounds (electron poor):

- effective retarder(inhibiter) for electron-rich monomers.
- Inhibition of vinyl acetate, retardation of styrene
- Not effective for methyl acrylate and methyl methacrylate

3–9 ENERGETIC CHARACTERISTICS

3–9a Activation Energy and Frequency Factor

Arrhenius-type relationship

where A is the collision frequency factor, E the Arrhenius activation energy, and T the Kelvin temperature.

A plot of ln k versus $1/T$ allows the determination of both E and A from the slope and intercept, respectively.

The variations of A_p (the frequency factor) are much greater than those in E_p, → steric effects are more important factor in determining the k_p.

Thus the more hindered monomers (methyl methacrylate and dimethyl itaconate (dimethyl 2-methylenebutanedioic acid)), have lower k_p and A_p values than the less hindered monomers (methyl acrylate and vinyl acetate).

3–9a–1 Rate of Polymerization

The composite or overall activation energy for the rate of polymerization

For thermal decomposition initiation

E_d : 120 – 150 kJ mol^{-1} E_p : 20 – 40 kJ mol^{-1} E_t : 8 – 20 kJ mol^{-1}

Then, $E_R = 80 - 90$ kJ mol^{-1} 10 °C ↑, two– or threefold rate ↑

For redox initiation, E_d : 40 – 60 kJ mol^{-1} , then, $E_R = \sim 40$ kJ mol^{-1}

For photoinitiation, E_d : ~0 kJ mol^{-1} , then, $E_R = \sim 20$ kJ mol^{-1}

Much less sensitive to the temperature

3–9b Thermodynamics of Polymerization

3–9b–1 Significance of ΔG, ΔH, and ΔS

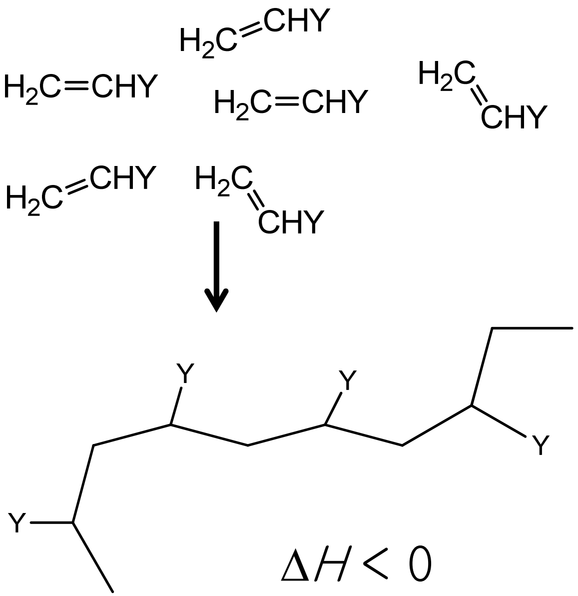
$\Delta G = \Delta H - T\Delta S$

For polymerization

$\Delta G < 0$

$|\Delta H| > |T\Delta S|$

In polymerization



$\Delta H < 0$

$\Delta S < 0$

favorable from the ΔH

unfavorable from the ΔS

wide range of ΔH values   a narrower range of ΔS values

3-9b-2 Effect of Monomer Structure

1. resonance stabilization

Styrene	73
Acrylonitrile	76.5
1,3-Butadiene	73

conjugated structure

vs

Ethylene[c]	93
Vinyl acetate	88

non-conjugated structure

→ the conjugated structure is lost after the polymerization

The decrease the exothermicity of the polymerization

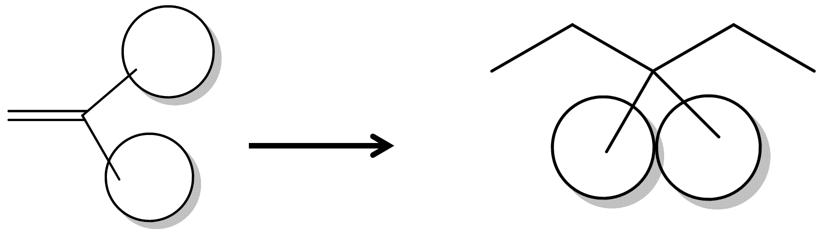
2. Steric strain differences

α-Methylstyrene	35
Maleic anhydride	59
Methyl methacrylate	56

vs

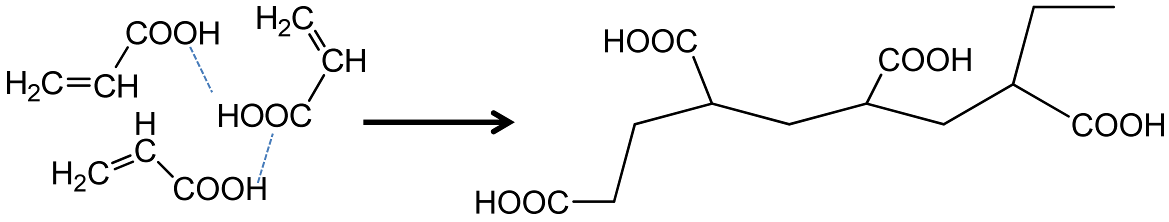
Ethylene[c]	93
Tetrafluoroethylene	163

sterically hindered monomers



3. Differences in hydrogen bonding or dipole interactions in the monomer and polymer.

Acrylic acid 67 vs Methyl acrylate 78



3-9b-3 Polymerization of 1,2-Disubstituted Ethylenes

1,2-disubstituted ethylenes exhibit little or no tendency to undergo polymerization. the ΔH value for maleic anhydride is $-59\ \mathrm{kJ\ mol^{-1}}$
Not due to the steric effect (, favorable for the polymerization)

Less 1,3-interactions

But by the kinetic reason : The propagation step is extremely slow because of steric interactions between the β-substituent of the propagating species and the two substituents of the incoming monomer.

- Only low-molecular-weight polymers are produced from maleic anhydride even when high initiator concentrations are used

- *N*-substituted maleimides,dialkyl fumarates (and fumaramides), and vinylene carbonate have been polymerized to higher molecular weights, many in the 10^3–10^4 range.

Fumarate esters with trans form polymerize because there is less steric hindrance.

Both k_p and k_t are lowered in fumarate esters compared to MMA or MA, but the decrease in k_t is much greater than the decrease in k_p, and polymerization is facilitated.

3-9c Polymerization–Depolymerization Equilibria

ceiling temperature T_c	the propagation and depropagation rates are equal

3-9c-2 Floor Temperature

$$\Delta G = \Delta H - T\,\Delta S$$

ΔS is endoentropic ($\Delta S = +$) and ΔH is very small (either $+$ or $-$) or zero.

floor temperature (T_f) : below which polymerization is not possible.

	ΔH kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
ex) cyclic sulfur	9.5	27
selenium octamers	13.5	31
octamethylcyclotetrasiloxane	6.4	190

3-10 AUTOACCELERATION

3-10a Course of Polymerization

benzoyl peroxide-initiated polymerization of methyl methacrylate in benzene at 50 °C.

Normal polymerization: time ↑, polymerization rate ↓ ∵ [M] ↓, < 40%

60 % < autoacceleration (gel effect) time ↑, polymerization rate ↑

Plotting $R_p/[\mathrm{M}][\mathrm{I}]^{1/2}$ instead of conversion to take into account the changes of [M] and [I] with time.

Stage I : constant rate (IA) or declining rate (IB) with time.

Stage II : autoaccelerative gel effect region

Stage III : constant (IIIA) or declining (IIIB) rate.

3-10b Diffusion-Controlled Termination

three-step process of termination

1. Translational diffusion (affected by macroviscosity)

2. Segmental diffusion : rearrangement of the two chains so that the two radical ends are sufficiently close for chemical reaction (affected by microviscosity)

   The movement of (end) segments of a polymer chain relative to other segments

3. Chemical reaction of two radical ends

Theoretical considerations indicate that k_c (about 8x10^9 L mol^{-1} s^{-1}) is much larger than k_t (10^6 – 10^8)
Once $M_n\cdot$/ $M_m\cdot$ is formed, dead polymer is formed immediately

Thus diffusion is the rate–determining process for termination,
$k_c >> k_4$

then $[M_n\cdot{-}{-}{-}{-}\, M_m\cdot] = \dfrac{k_1[M\cdot]2}{k_2+k_3}$

R_t : the rate for the formation of the polymer
or the rate for the disappearance of propagating radical

$$R_t = \frac{d[\text{polymer}]}{dt} = k_3\,[M_n\cdot{-}{-}{-}{-}\, M_m\cdot]$$

$$R_t \propto \frac{k_1 k_3}{k_2+k_3}$$

1. slow translational diffusion, $k_3 >> k_2$

2. slow segmental diffusion, $k_3 << k_2$

Conversion ↑, polymer concentration ↑, viscousity ↑
translational diffusion ↓
Segmental diffusion ↑

As conversion increases, polymerization medium becomes a poorer solvent, then the size of the randomly coiled up propagating radical in solution (referred to as coil) becomes smaller and there is an effective higher concentration gradient across the coil. Then the chance of the radical end to meet another radical increases (Segmental diffusion ↑) .

Stage IA：the increase in segmental
diffusion (k_3) is exactly counterbalanced by the decrease in translational diffusio
(k_1 and k_2)
(k_1 and k_2 ↓ k_3 ↑ i.e., k_t remains constant).

Stage IB：the increase in segmental diffusion is greater than the decrease in translational diffusion, k_t increases and the polymerization rate decreases.
(k_1 and k_2 ↓ k_3 ⇑)

Stage II：translational diffusion decreases faster than the increase in segmental diffusion(k_1 and k_2 ⇓ k_3 ↑)
→ autoacceleration (gel effect)
gel effect is caused by a decrease in k_t relative to k_p

Stage IIIA：k_p and k_t becomes very small

Stage IIIB： glass or vitrification effect when glass transition temperature exceeds the reaction temperature
or f becomes very small ! [Russel et al., 1988; Sack et al., 1988]

k_p and k_t were carried out assuming
constant f independent of conversion

τ: lifetime of a growing radical

k_p is not much changed until 50% conversion, while k_t has decreased by almost 2 orders of magnitude.
The $k_p/k_t^{1/2}$ and the polymerization rate increase rapidly at first.
At higher conversion (60% <) and then taper off as k_p is also decrease much.

3-10c Effect of Reaction Conditions

Thus segmental diffusion **increases** by any factor that decreases the coil size of the propagating radical, therefore
segmental diffusion ↑
Polymer molecular weight ↑, conversion ↑, solubility ↓

Stage I
At very low conversion,
k_t is larger in a poor solvent than k_t in a good solvent.

At higher conversion
k_t is larger in the good solvent than k_t in the poor solvent.

Because coil size decreases with increasing polymer concentration, but the decrease is steeper in better solvents

Stage II : Diffusion controlled reaction due to the very large decrease of translational diffusion

Vinyl acetate (lower-molecular-weight polymers due to CT to monomer) does not show as dramatic a gel effect as styrene or methyl methacrylate.

Higher temperatures (decreasing the viscosity) delays the gel effect.

3-10d Related Phenomena

3-10d-1 Occlusion (Heterogeneous) Polymerization

1. Bulk polymerization of monomers whose polymers are insoluble or weakly soluble in their own monomers.
ex) acrylonitrile, vinyl chloride, trifluorochloroethylene, and vinylidenechloride

2. Solution polymerizations using solvents that are nonsolvents for the polymer ex) methanol for polystyrene, hexane for poly(methyl methacrylate)]

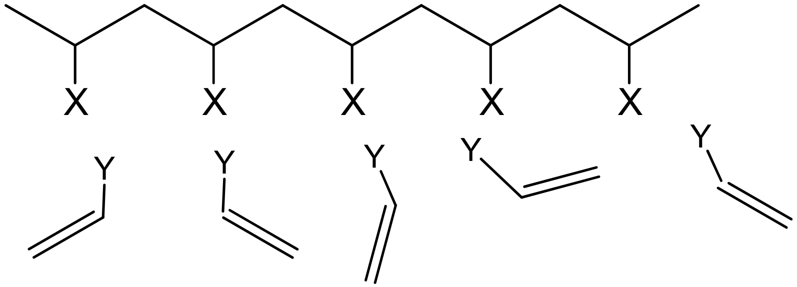
→ accelerative effects (gel effect) observed.

Termination between radicals again becomes progressively more difficult, while propagation may still proceed reasonably well.
Because monomers are soluble, while polymers are coiled up.

The decrease of the segmental diffusion is much more than the decrease of the translational diffusion.

3–10d–2 Template (matrix) Polymerization

ex) acrylic acid with polyethyleneimine and poly(N–vinylpyrrolidinone),
N–vinylimidazole with poly(methacrylic acid)
acrylonitrile with poly(vinyl acetate)
methyl methacrylate with poly(methyl methacrylate).



X and Y has specific interactions

The rate enhancements are typically by 2–5 times from the zip mechanism.

the increase in k_p

1. The alignment of monomer molecules on the parent polymer
2. The decrease in k_t due to slower translational and segmental diffusion of propagating radicals.

3-10f Other Accelerative Phenomena

The polymerizations of acrylonitrile, N-vinylpyrrolidinone, and acrylic acid are faster in the presence of water or hydrogen-bonding solvents.

ex) k_p for acrylonitrile at 25 °C
2.8×10^4 $\mathrm{Lmol^{-1}s^{-1}}$ in water, 400 $\mathrm{Lmol^{-1}s^{-1}}$ in DMF.

→ hydrogen-bonds of water between monomers and propagating radicals (through the CN group)
i) increasing the effective local monomer concentration at the radical site
ii) increasing the reactivity of the monomer and/or radical by a polar effect.

→ *water template effect*

Carboxylic acid monomers (acrylic and methacrylic acids and trans butadiene-1- carboxylic acid) have lower polymerization rates in good solvents and/or at higher pH where monomer exists in ionized form due to the repulsions between the carboxylate anion groups.

The addition of Lewis acids ($ZnCl_2$ and $AlCl_3$) can increases the polymerization
rate of monomers with electron-withdrawing substituents (acrylamide, methyl methacrylate, and acrylonitrile) by complexation of the propagating

3-11 MOLECULAR WEIGHT DISTRIBUTION

3-11a Low-Conversion Polymerization

one polymer is produced from each kinetic chain
(disproportionation or chain transfer or a combination of the two, but without combination

Exactly same as the step polymerization exempt p

$N_x = Np^{x-1}(1-p)$ the number that are x-mers (N: total number of polymers)

If the total number of structural units is N_0, then $N = N_0(1-p)$

the weight fraction w_x of x-mers : $w_x = xN_x/N_0$

polydispersity index (PDI)

100 % coupling ($R_{tr} = 0$): one polymer is produced from two kinetic chain

If x-sized polymer by the coupling of y-sized and z-sized propagating radicals
$(x = y + z)$

The probability $\underline{N}_{y+z}$ is the product of the probabilities, $\underline{N}_y$ and $\underline{N}_z$, of forming the y- and z-sized propagating radicals.

There (x-1) possible pathways of producing an x-sized polymer molecule when x is an even number.
y+z, z+y, (y-1)+(z+1), (z-1)+(y+1), (y-2)+(z+2), (z-2)+(y+2),,,,,, total x-1 times

Altough when x is an odd number, there are x pathways, he differences are unimportant for systems that yield high polymer

3-11b High-Conversion Polymerization

In practical radical chain polymerizations, conversion is about 100 %, then size distributions become much broader than 1+P or (2+P)/2.

Conversion ↑, [I] and [M} ↓ then molecular weight ↓ ∵

MW $\propto$ $[M]/[I]^{1/2}$

At high conversion $\overline{X}_w/\overline{X}_n$ ratio = ~ 2 – 5

In commercial polymerization processes, initiator and/or monomer are added several times during the polymerization.

When autoacceleration occurs, $k_p/k_t^{1/2}$ ↑, MW ↑ $\overline{X}_w/\overline{X}_n$ ratio = 5 – 10

When chain transfer occurs $\overline{X}_w/\overline{X}_n$ ratio becomes up to 50

get effect and chain transfer are the major reasons for the broadening, not easy to control.
ex) low temperature polymerization can minimize chain transfer to polymer but maximize the gel effect

3-12 EFFECT OF PRESSURE

The commercial polymerizations of most gaseous monomers are done under pressure.

ex) vinyl chloride, vinylidene chloride, tetrafluoroethylene, vinyl fluoride at about 5 – 10 MPa (49.3 – 98.7atm)

Ethylene to low-density polyethylene 100 – 300-MPa

(1 MPa = 145 psi = 9.87 atm)

3-12a Effect on Rate Constants

3-12a-1 Volume of Activation

The quantitative effect of *P* (at constant temperature) on a rate constant is given by

When > 0, the pressure ↑, *k* $\Delta V^{\ddagger}$

When < 0, the pressure ↑, *k* $\Delta V^{\ddagger}$

the change in volume ($cm^3 mol^{-1}$) in going from the reactant(s) to the transition state

Initiation

pressure ↑, k_d ↓: decomposition involving a volume expansion

Propagation

pressure ↑, k_p ↑ : in propagation two species coming together (volume decrease)

Termination (diffusion controlled, pressure ↑, viscosity ↑, termination ↓)

pressure ↑, k_t ↓: diffusion controlled

Although volume decreases (two radicals come together), since the termination step is diffusion controlled, increased pressure decreases k_t by increasing the viscosity of the reaction medium

3-13 PROCESS CONDITIONS

3-13a Bulk (Mass) Polymerization

Advantage: simplest process with a minimum of contamination of the product.

Disdvantages: difficulties in temperature control
the need for strong and elaborate stirring equipment
(Their highly exothermic nature and the tendency toward the gel effect in the radical polymerization combine to make heat dissipation difficult)

ethylene, styrene, and methyl methacrylate are polymerized in bulk system in industry

3-13b Solution Polymerization

Advantage: easy heat transfer with normal stirring conditions

Disdvantages: chain transfer to solvent, the removal of the solvent.

Vinyl acetate, acrylonitrile, and esters of acrylic acid are polymerized in solution system in industry

3-13c Heterogeneous Polymerization

Precipitation (powder or granular) **polymerizations** begin as homogeneous polymerizations but are quickly converted to heterogeneous polymerizations.

ex) Bulk polymerization of vinyl chloride and solution polymerization of acrylonitrile in water

Suspension (bead or pearl) **polymerization** :
suspending the monomer (discontinuous phase) as droplets (50–500 mm in diameter) in water (continuous phase) with monomer soluble initiator and less than 0.1 weight percent of suspension stabilizers (much lower than the surfactant concentration in emulsion polymerizations (typically as high as 1–5%)

Two types of stabilizers

i) water-soluble polymers: poly (vinyl alcohol), hydroxypropyl cellulose, sodium poly(styrene sulfonate), and sodium salt of acrylic acid-acrylate ester copolymer

ii) water-insoluble inorganic compounds: talc, hydroxyapatite, barium sulfate, kaolin, magnesium carbonate and hydroxide, calcium phosphate, and aluminum hydroxide

ex) Styrene, acrylic and methacrylic esters, vinyl chloride, vinyl acetate, and tetrafluoroethylene are polymerized in industry

Inverse suspension polymerization

an organic solvent as the continuous phase with droplets of a water-soluble monomer (e.g., acrylamide), either neat or dissolved in water.

Microsuspension polymerization

suspension polymerizations in which the size of monomer droplets is about 1 μm

Dispersion polymerization

initially homogeneous system of monomer, organic solvent, initiator, and particle stabilizer (usually uncharged polymers such as poly(N-vinylpyrrolidinone)
and hydroxypropyl cellulose).
The system becomes heterogeneous on polymerization because the polymer is insoluble in the solvent.
polymer particles with sizes in between those obtained by emulsion and suspension polymerizations—about 1–10 μm in diameter.

type	Particle radius	Droplet size	initiator	Continuos phase	Discrete phase (particle)
emulsion	50-300 nm	~ 1 – 10 μm	Water-soluble	water	Initially absent, monomer-swollen polymer ptcles form
precipitation	50-300 nm	N/A	Soluble in monomer	Monomer or water	As in ordinary emulsion polymerization, but mono-mer doesnot swell polymer
suspension	≥ 1 μm	~ 1 – 10 μm	Soluble in monomer	water	Monomer + formed polymer in preexisting droplet
disersion	≥ 1 μm	N/A	Soluble in solvent	solvenr	Initially absent, monomer-swollen polymer particles form
microemulsion	10-30 nm	10-100 nm	Water-soluble	water	Monomer, co-surfactant + formed polymer
inveremulsion	100-1000 nm	~ 1 – 10 μm	Water- or monomer - soluble	monomer	Monomer, water + formed polymer
miniemulsion	30-100 nm	~ 50 – 1000 nm	Water-soluble	water	Monomer, co-surfactant + formed polymer

3-15 LIVING RADICAL POLYMERIZATION

3-15a General Considerations

- 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. –

Using the living polymerizations, block copolymers could be prepared by the sequential addition of different monomers

In conventional (nonliving) radical polymerization, the lifetime of propagating radicals is very short (typically less than a second or, at most, a few seconds) due to the termination (coupling and/or disproportionation) of the two propagating chains. Then block copolymers cannot be prepared.

Living radical polymerizations have been achieved by minimizing normal bimolecular termination and prolonging the lifetime of living polymers (hours or longer) through the introduction of dormant states.

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, hyperbranched polymers can be prepared

Most well known living radical polymerization

1. atom-transfer radical polymerization (ATRP)
2. stable free-radical polymerization (SFRP): reversible termination
3. reversible addition–fragmentation transfer (RAFT) : reversible chain transfer

3-15b Atom Transfer Radical Polymerization (ATRP)

3-15b-1 Polymerization Mechanism

- Prevention of 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 $K = k_a/k_d. \sim 10^{-7}$

- the dormant species concentration exceeds the propagating radical concentration by a factor of 10^6

ATRP polymerizations of styrene at 110 °C with CuBr, 1-phenylethyl bromide (I), and 4,4-di-5-nonyl-2,2'-bipyridine(L)

Bulk polymerization (o): [M]= 8.7 M, $[CuBr]_0$ =$[L]_0$/2 = [I] = 0.087 M
Solution polymerization in diphenyl ether (•): [M]= 4.7 M, $[CuBr]_0$ =$[L]_0$/2 = [I] = 0.045 M

From this equation a polymer of number average degree of polymerization of 50 having a Poisson distribution, the PDI would be 1.02.

In reality, many ATRP polymerizations have somewhat broader distributions (PDI $\leq$ 1.2–1.3) for two reasons.

1. There is a initial period (as much as 5% conversion) before the persistent radical (deactivator) concentration has grown sufficiently large to suppress normal termination. (by initially adding $CuBr_2$ ~10 mol% of CuBr, it could be supressed).

2. At very high conversion (90%), the polymerization rate decreases significantly such that normal termination is not sufficiently suppressed.

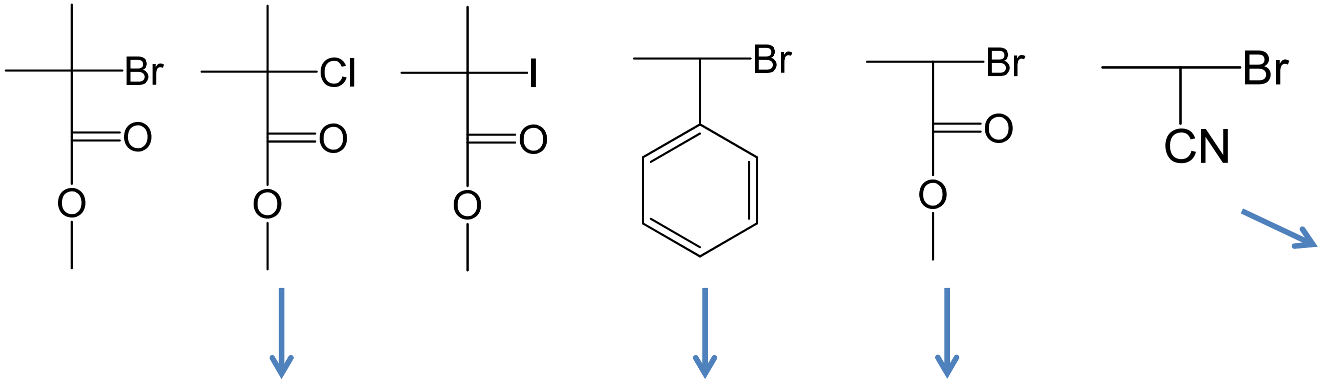
3-15b-2 Effects of Components of Reaction System

Monomers for ATRP

styrene, acrylonitrile, (meth) acrylates, (meth) acrylamides, 1,3-dienes, and 4-vinylpyridine

Initiators for ATRP

Organic halides such as $CHCl_3$ and CCl_4, allyl and benzyl halides, α-haloesters, α -haloketones, α -halonitriles, and sulfonyl halides



acrylonitrile

methyl methacrylates

styrene

methyl acrylates

Bromides are more reactive than chlorides, iodides are highly reactive but undergo light-induced side reactions, and fluorides are unreactive.

metal catalyst

must have two oxidation states
Cu, Fe, Ru ets. ; Various middle and late transition metals (group 6–11)

Cu has been found to be most useful irrespective of the monomers.

Ligands

solubilize the transition metal salt in organic media and adjust the redox potential of the metal center for appropriate activity

For copper: bidentate and multidentate, but not monodentate, nitrogen ligands

3-15b-4 Block Copolymers

1. One-pot sequential method

- Polymerizing monomer A and Monomer B is then added when most of A has reacted (less than 90 % conversion)

Advantage: simple

Disadvantage : ‘‘contamination’’ of the second block

2. Isolated macroinitiator methods

- halogen-terminated polyA (RA_nX) is isolated (less than 90 % conversion) and then used as an initiator (the macroinitiator) together with CuX to polymerize monomer B.

- halogen-terminated macroinitiator is stable and can be stored for long periods

Advantage: pure second block

Disadvantage : additional step for the separation process of the macroinitiator

The exact sequence of monomer addition

Possible sequence

1. Similar reactivity of A and B blocks
methyl acrylate–butyl acrylate
methyl methacrylate–butyl methacrylate
styrene–acetoxy styrene)

2. Equilibrium constant K (A > B) (A monomer has larger reactivity)
methacrylate–acrylate
methacrylate–styrene blocks

Impossible sequence

Equilibrium constant K (A < B) (B monomer has larger reactivity)
Acrylate–methacrylate
styrene–methacrylate

Why? How to make such sequence?
See textbook!

Tri- and higher block copolymers

Star polymers

Graft copolymers

Hyperbranched polymers from copolymerization of vinyl and divinyl monomers
Where smaller amount of divinyl mpomers are used
(not easily from normal radical chain polymerization)

Summary of ATRP

- ATRP involves an organic halide undergoing a reversible redox process catalyzed by a transition metal/ligand complex.

- Rapid reversible deactivation of propagating radicals is needed.

- Metal/ligand 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.

- Metal residue should be removed.

3-15c Stable Free-Radical Polymerization (SFRP)

Prevention of bimolecular termination by reversible termination with stable radical.

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

Dormant state (deactivated propagating chain) is dominant.

- very low equilibrium constant $K \sim 10^{-11}$

→nitroxide, triazolinyl, trityl, and dithiocarbamate are used as the mediating or persistent radical (deactivator)

ex) Cyclic nitroxide radical: 2,2,6,6-tetramethyl-1-piperidinoxyl (TEMPO)

2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine

SFRP with nitroxides is called nitroxide mediated polymerization (NMP)

- NMP with TEMPO generally requires higher temperatures (125–145 °C) and longer reaction times (1–3 days) compared to ATRP
- only styrene and 4-vinylpyridine polymerizations proceed with good control of molecular weight and polydispersity.

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 are needed.
- Limited monomers.
- (styrenes, acrylates, acrylamides, 1-dienes, and acrylonitriles are OK)
- (Well defined PMMA is difficult to be synthesized by SFRP)

β−hydrogen abstraction

3-15d Radical Addition-Fragmentation Transfer (RAFT)

The control of chain growth

- reversible termination in ATRP and NMP
- reversible chain transfer in RAFT

Typical chain-transfer agent in RAFT ex)

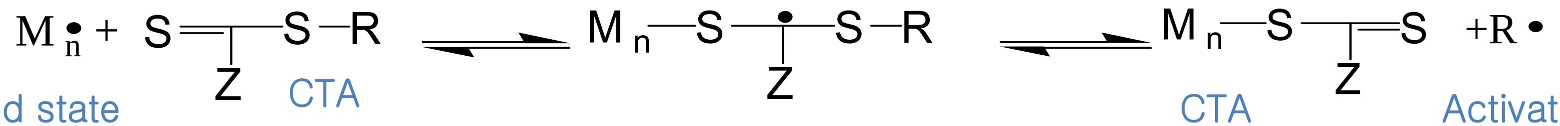
-Prevention of bimolecular termination by reversible transfer with dithioester group as chain transfer agent.

-Initiator, chain transfer agent, and monomer, (solvent)

-High equilibrium constant; $K = \sim 1$

- High concentrations of RAFT agents relative to initiator and RAFT agents with large chain-transfer constants

Mechanism of RAFT



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

Dormant state

Activated state
Propagating radical

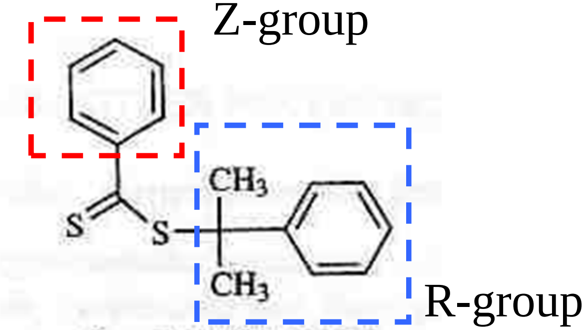
CTA

Dormant state

CTA
end group

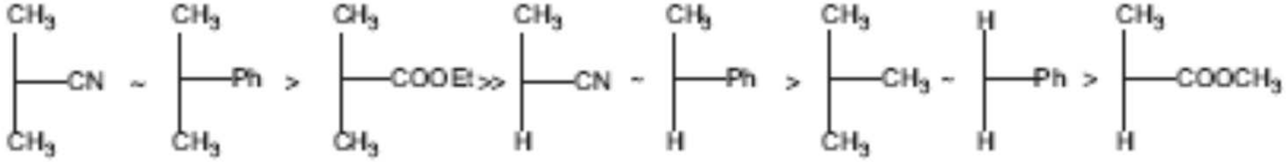
Activated state

Chain Transfer Agents of RAFT

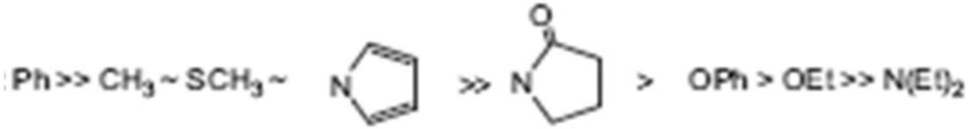


Cumyl dithiobenzoate

Reactivity of R-group



Reactivity of Z-group



The degree of polymerization

$[M]_0$: the initial concentrations of monomer
$[RAFT]_0$: the initial concentrations of RAFT transfer agent
$[I]_0$: the initial concentrations of
p : fractional conversions of monomer
p' : fractional conversions of RAFT agent
p'' : fractional conversions of initiator

-The chain transfer constant of dithioesters : > 1000
-RAFT agent is consumed ($p' = 1$) within the first few percent of monomer conversion $(p'[\mathrm{RAFT}]_0 \gg 2fp''[\mathrm{I}]_0)$.

Kinetics of RAFT

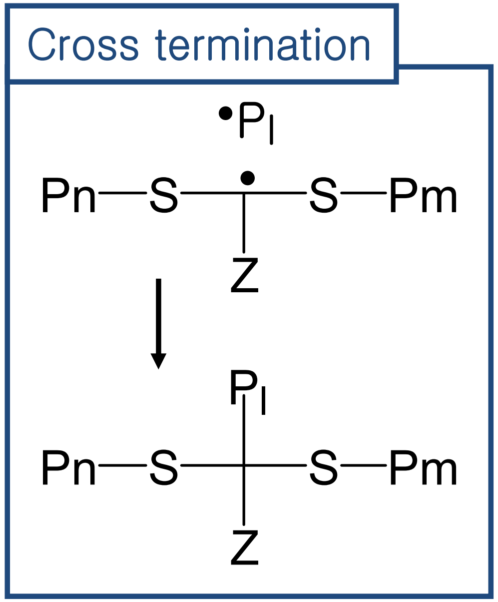
$$R_p = R_{p,0}\left(\frac{1}{1+2K_{RAFT}(k`_t/k_t)[P\text{-}X]_0}\right)^{1/2}$$

-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.


Cross termination

Effect of components

Initiator
-Higher concentration, higher R_p

Chain Transfer agents :
-CTA controls R_p
-Higher concentration, lower R_p

Temperature
-Higher temp., higher R_p, higher PDI

Summary

- RAFT ~ chain transfer agent.
- Synthesized CTA
- # of chains = (# of CTA)
- Wider range of monomers than NMP and ATRP
- Modification of CTA
- Removal of dithioester end group.

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 catalyst	▪Limited monomers ▪Synthesis of initiator	▪Synthesis of CTA ▪Odor of CTAs and color of polymers

CHAPTER 4

EMULSION POLYMERIZATION

4-1b Qualitative Picture

4-1b-1 Components and Their Locations

mercaptan :chain-transfer
agent to control the polymer molecular weight.

hydroperoxide-ferrous ion
redox initiation system

sodium pyrophosphate :
to solubilize the iron salts

fructose : to regenerate
ferrous ion by reducing the
ferric ion

The main components: monomer(s), dispersing medium (water), emulsifier,
and water-soluble initiator.

Polymer particels
; 50–300 nm

initiator in the water phase
(oil–insoluble initiators)

surfactant concentrations: 0.1–3 wt% (larger than critical micelle concentration (CMC)

Typical micelles dimensions : 2–10 nm (spherical and rodlike, 50–150 surfactants)

monomer droplets (>95% of monomer) : diameters of 1–100 μm

Therefore concentration of micelles is 10^{19}–10^{21} L^{-1},
concentration of monomer droplets : 10^{12}–10^{24} L^{-1}

4-1b-2 Site of Polymerization

Initiator in the water phase (oil-insoluble initiators)

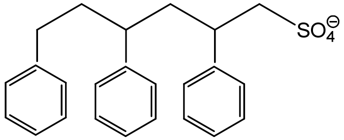
$$^{-}O_3S-O-O-SO_3^{-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\bullet$$

$$SO_4^{-}\bullet + M \rightarrow \cdot MSO_4^{-}$$

Polymerization in the micelles not in the monomer droplets
- The micelles is the meeting place for the organic (oil-soluble) monomer and the water-soluble initiator.

$$\cdot MSO_4^{-} \;\begin{array}{c} M \\ \rightarrow \\ \longrightarrow \\ \longrightarrow \end{array}\; \cdot M_3SO_4^{-}$$

If deg. of polym. is >3, then it works as a surfactant



Polymerization of the monomer in solution can occur but not much, since the monomer concentration is low.

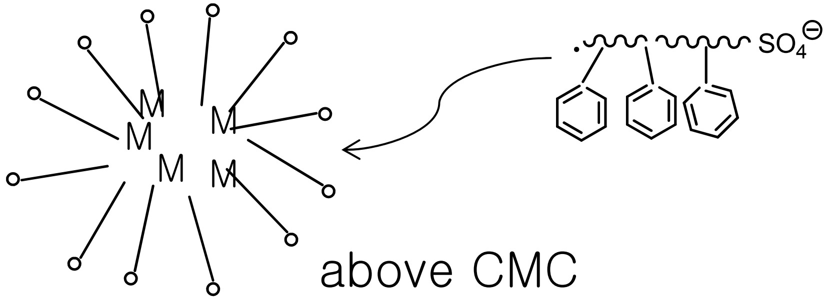
three types of domains in the water:

i) monomer droplets
ii) inactive micelles in which polymerization is not occurring,
iii) polymer particles: active micelles in which polymerization is occurring

Two mechanisms for particle nucleation (i.e., formation of polymer particles)

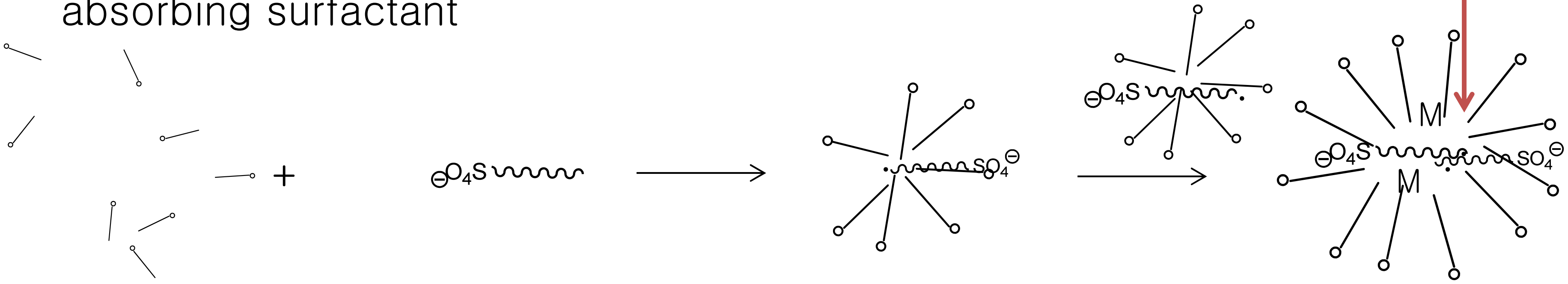
1. micellar particle nucleation (heterogeneous particle nucleation)

oligomeric radicals (formed in solution of DP of 1–5) from the aqueous phase enter the micelles.



2. Homogeneous particle nucleation

solution–polymerized oligomeric radicals precipated, then stabilized by absorbing surfactant



Coupling;
No radcial left

4-1b-3 Progress of Polymerization

Three intervals (I, II, III) based on the particle number (*N*) and the existence of monomer droplets

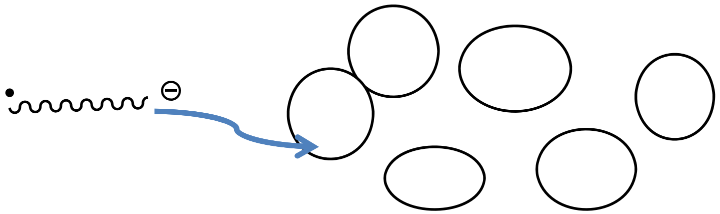
1. intervals I : particle formation

N and particle size increases with time with absorbing more and more surfactant.
Shortest of the three intervals (2-15% conversion)

Particle size distribution

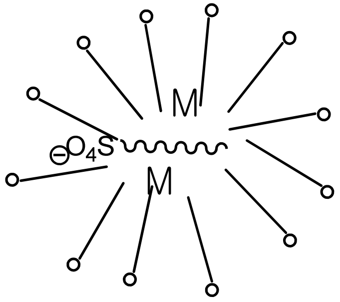
-In the beginning; large distribution because the particles are formed either by i) micellar particle nucleation or ii) by homogeneous particle nucleation
They forms particles with very different sizes

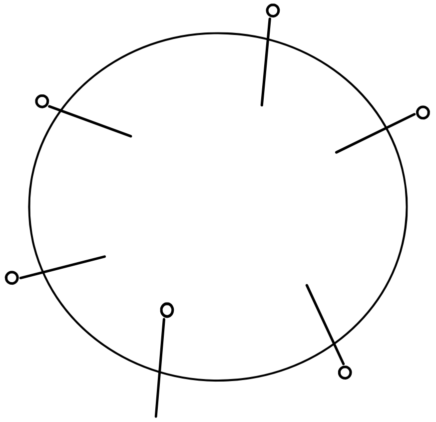
-By the end of interval I : uniform size distribution
almost all of the surfactant in the system absorbed by the polymer particles.
Then all the propagating chains in water enter into the polymer particle



2. intervals II : particle growth starts after the particle formation stops
then *N* remains the same, particle size increases

Now there are only particles and monomer droplets





Size	50 – 300 nm	1 – 10 μm
Monomer concentration	~5 moles/L 50% monomer	~10 moles/L bulk

In 50 nm particle on average 100 dead polymers, ½ radicals (0 or 1 radical)

– Polymerization proceeds in the polymer particles as the monomer concentration in the particles maintained at the equilibrium

Ex) The volume fraction of monomer ϕ_m : 0.2, 0.3, 0.5, 0.6, 0.71, and 0.85 for ethylene, vinyl chloride, butadiene, styrene, methyl methacrylate, and vinyl acetate, respectively

The polymerization rate either is constant (behavior D) or increases slightly with time (E, gel or Trommsdorff effect) during interval II in Fig. 4–2

The transition from interval II to interval III occurs at lower conversions
the water solubility of the monomer ↑
extent of swelling of the polymer particles by monomer increases ↑
ϕ_m ↑

Ex) vinyl acetate at 15%, methyl methacrylate at 25%, styrene and butadiene at 40 50%, vinyl chloride at 70–80% conversion

Interval III starts when all the monomer droplets are consumed!

3. intervals III

- *N* remains the same, the monomer concentration decreases with time

- In this phase, particles can contain more than two radicals

- The final polymer particles, spherical in shape (diameters of 50–300 nm) obtained

Interval	Conversion (%)	micelle	Monomer droplet	Particle number	Particle size
I	0- 12	o	o	↑	↑
II	10 - 40	x	o	constant	↑
III	40 -	x	x	constant	Roughly constant

4–2 QUANTITATIVE ASPECTS

4–2a Rate of Polymerization

At the start of polymerization

concentration of micelles : 10^{21} L^{-1}

the formation of radicals is 10^{16} $L^{-1}s^{-1}$

then on average a radical diffuses into a micelle every 10^5 s

Intervals II and III

A radical enters a polymer particle on an average of every 10 s
where N is typically 10^{17} L^{-1}

radical propagates rate inside the micelle or polymer particle,

$$r_p = k_p[\mathbf{M}]$$

The monomer concentration : 50–85% by volume (typically 5 M)
[M] varies only weakly with the size of the polymer particles.

[M·] : there are one or zero radicals in the particles

the radical concentration in a polymer particle is 10^{-6} M or higher
- much larger than in the normal radical polymerization, 10^{-8} M

radical lifetime : a few thousandths of a second. (much shorter)

polymer particle will have either one or zero radicals because a second radical into the polymer particle results in immediate bimolecular termination. The particle is then dormant until another (the third) radical arrives.

Compartmentalization (or segregation)
- higher molecular weight can be achieved than in solution polymerization because a propagating radical in a polymer particle is isolated

where N' : concentration of micelles + particles,
$\bar{\boldsymbol{n}}$: average number of radicals per micelle plus particle
N_A : Avogadro number.

the polymerization rate

$N'\bar{n}$ is zero at the start of interval I, since $\bar{n} = 0$.

N' decreases, $\bar{n}$ increases, and the product $N'\bar{n}$ increases with time during interval I.

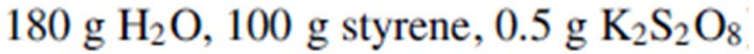
At the start of interval II, *N'* has reached its steady state value *N*.
– In intervals II and III where only polymer particles exist (no micelles)

Case 2: $\bar{n} = 0.5$: normal emulsion polymerization in interval II

i) Desorption is negligible
ii) Particle size is not very large
iii) Initiation rate is not very large
iv) Negligible termination in the aqueous phase

Case 1: $\bar{n} < 0.5$. desorption + termination in the aqueous phase

Case 3: $\bar{n} > 0.5$. When particle size is very large ex) Interval III emulsion polymerizations of styrene with potassium laurate at 60 °C.


180 g H_2O, 100 g styrene, 0.5 g $K_2S_2O_8$

emulsifier 0.0035 (plot 1), 0.007 (plot 2), and 0.014 (plot 3).

Emulsifier (surfactant) ↑ , N ↑ , R_p ↑

4-2b Degree of Polymerization

The rate r_i at which primary radicals enter a polymer particle

$r_i = r_t$ (rate of termination)

for case 2 termination occurs immediately on the entry of a radical into a polymer particle

Emulsifier (surfactant) ↑ , N ↑ , $\overline{X}_n$ ↑

CT decrease the MW

180 g H_2O, 100 g styrene, 0.5 g $K_2S_2O_8$

emulsifier 0.0035 (plot 1), 0.007 (plot 2), and 0.014 (plot 3).

The conditions for growing a mono disperse latex (polymer particle)
→ very complicated

i) High rate of radical generation
→ slow generation of propagating radicals makes small particles continuously

ii) High flux of radical into the particles
→ when the interval I finished earlier, the particle size can be more uniform

iii) High temperature can increase the rate of radical generation and the flux

4-2c Number of Polymer Particles

Experimental equation of *N*

$\boldsymbol{S}$: total concentration of surfactant (in micelles, solution, monomer droplets).

$\boldsymbol{a_s}$: interfacial surface area occupied by a surfactant

$a_s S$: total surface area of surfactant present in the system

μ : rate of volume increase of polymer particle (determined from r_p (radical propagates rate) and geometric considerations).

k : 0.37 – 0.53 , determined by

i) efficiencies of radical capture by micelles versus polymer particles

ii) geometric parameter of the particle (radius, surface area or volume)

4-3 OTHER CHARACTERISTICS OF EMULSION POLYMERIZATION

4-3a Initiators

Redox systems such as persulfate with ferrous ion are commonly used.

$$^{-}O_3S-O-O-SO_3^{-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{-}\bullet$$

Other redox systems include cumyl hydroperoxide or hydrogen peroxide with ferrous, sulfite (SO_3^{2-}), or bisulfite HSO_3^{-} ion.

$$H_2O_2 + Fe^{2+} \longrightarrow HO^{-} + HO\bullet + Fe^{3+}$$

$$^{-}O_3S-O-O-SO_3^{-}$$

water-soluble initiators : potassium or ammonium persulfate[$(NH_4)_2S_2O_8$], hydrogen peroxide, and 2,2'-azobis(2-amidinopropane) dihydrochloride.

Partially water-soluble peroxides : succinic acid peroxide and t-butyl hydroperoxide and azo compounds such as 4,4'-azobis(4-cyanopentanoic acid)

4-3b Surfactants

Fatty acid soaps (sodium or potassium stearate, laurate, palmitate), sulfates, and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate).

Nonionic surfactants such as poly(ethylene oxide), poly(vinyl alcohol) and hydroxyethyl cellulose are sometimes used in conjuction with anionic surfactants for improving the freeze-thaw and shear stability of the polymer or to aid in controlling particle size and size distribution.

4-3c Other Components

The quality of the water used in emulsion polymerization is important.

4-3h Other Emulsion Polymerization Systems

Inverse emulsion polymerization

- an aqueous solution of a hydrophilic monomer is emulsified in a nonpolar organic solvent such as xylene or paraffin and polymerization initiated with an oil-soluble initiator.
- used in various commercial polymerizations and copolymerizations of acrylamide as well as other water-soluble monomers.

Miniemulsion polymerization

- surfactant concentrations are generally below CMC (no micelles)
- monomer droplets in water with much smaller (30–1000 nm) than in emulsion polymerization(1–100 μm)

How ?
Water-insoluble co-stabilizers such as hexadecane and cetyl alcohol are present along with the surfactant to prevent the diffusional degradation (coagulation), referred to as Ostwald ripening.

- useful for producing high-solids-content latexes.

Microemulsion polymerization

- very much smaller monomer droplets, about 10–100 nm compared to 1–100 μm (co-surfactants are used to reduce the size)

- the surfactant concentration is above CMC (micelles are present)

- The final polymer particles are smaller (diameters of 10–50 nm).

type	Particle radius	Droplet size	initiator	Continuos phase	Discrete phase (particle)
emulsion	50-300 nm	~ 1 – 10 μm	Water-soluble	water	Initially absent, monomer-swollen polymer ptcles form
precipitation	50-300 nm	N/A	Soluble in monomer	Monomer or water	As in ordinary emulsion polymerization, but mono-mer doesnot swell polymer
suspension	≥ 1 μm	~ 1 – 10 μm	Soluble in monomer	water	Monomer + formed polymer in preexisting droplet
disersion	≥ 1 μm	N/A	Soluble in solvent	solvenr	Initially absent, monomer-swollen polymer particles form
microemulsion	10-30 nm	10-100 nm	Water-soluble	water	Monomer, co-surfactant + formed polymer
inveremulsion	100-1000 nm	~ 1 – 10 μm	Water- or monomer - soluble	monomer	Monomer, water + formed polymer
miniemulsion	30-100 nm	~ 50 – 1000 nm	Water-soluble	water	Monomer, co-surfactant + formed polymer