POLYMER SCIENCE

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Chapter 1. Basic principles

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1.2 Definitions

A. Acoording to the amount of repeating units

- monomer : one unit
- oligomer : few
- polymer : many (poly many, mer part)

telechelic polymer : polymer containing reactive end group

(tele = far, chele = claw)

telechelic oligomer : oligomer containing reactive end group

macromer(=macro monomer) : monomer containing long chain

1.2 Definitions

B. DP : Degree of polymerization

The total number of repeating units contained terminal group

C. The kinds of applied monomers

- One kind : Homopolymer
- Two kinds : Copolymer
- Three kinds : Terpolymer



E. Representation of polymer types



F. Representation of polymer architectures



F. Representation of polymer architectures







(f) polycatenane



(g) dendrimer

Thermoplastic : Linear or branched polymer

Thermoset : Network polymer

1.3 Polymerization Processes

A. Classification of polymers to be suggested by Carothers

Addition polymers : repeating units and monomers are same

Condensation polymers : repeating units and monomers are not equal, to be split out small molecule 1. Polyester from lactone (1.7) &

from ω -hydroxycarboxylic acid (1.8)





2. Polyamide from lactam (1.9), and from ω-aminocarboxylic acid (1.10)





3. Polyurethane from diisocyanate and dialcohol(1.11) and from diamine and bischloroformate(1.12):



4. Hydrocarbon polymer from ethylene (1.13), and from α,ω -dibromide (1.14)

$$CH_2 = CH_2 \xrightarrow{\text{initiator}} - CH_2 CH_2 - (1.13)$$

BrCH₂(CH₂)₈CH₂Br
$$\xrightarrow{2Na}$$
 $+$ CH₂CH₂ $+$ 2NaBr (1.14)

1.3 Polymerization Processes

B. Modern classification of polymerization according to polymerization mechanism

Step growth polymerization : Polymers build up stepwise



Chain growth polymerization : Addition polymerization molecular weights increase successively, one by one monomer

Ring-opening polymerization may be either step or chain reaction



1.4 Step-reaction Polymerization

A. Monomer to have difunctional group

1. One having both reactive functional groups in one molecule



2. Other having two difunctional monomers



B. Reaction : Condensation reaction using functional group

Example - Polyesterification





(*N*_o: number of molecules
N: total molecules after a given reaction period.
*N*_o - *N*: The amount reacted
P: The reaction conversion)

$$P = \frac{N_0}{N_0} \qquad Or \qquad N = N_0(1-P)$$

(**DP** is the average number of repeating units of all molecules present)

 $\overline{\text{DP}} = N_{O}/N$

$$\overline{\mathbf{DP}} = \frac{1}{1 - P}$$

For example At 98% conversion $\overrightarrow{DP} = \frac{1}{1 - 0.98}$



1.5 Chain-reaction Polymerization

A. Monomer : vinyl monomer _xCH₂=CH₂

B. Reaction : Addition reaction initiated by active species

C. Mechanism :

■ Initiation $R = + CH_2 = CH_2 \rightarrow RCH_2 CH_2$

■ Propagation $RCH_2CH_2^{\bullet} + CH_2 = CH_2 \rightarrow RCH_2CH_2CH_2CH_2$

TABLE 1.1 Comparison of Step-Reaction and
Chain-Reaction Polymerization

Chain Reaction
Growth occurs by successive addition of monomer units to limited number of growing chains DP can be very high Monomer consumed relatively slowly, but molecular weight increases rapidly Initiation and propagation mechanisms differe Usually chain-terminating step involved Polymerizaion rate increases initially as tiveinitiator units generated; remains relatively succession constant until monomer depleted

^aDP, average degree of polymerization.

1.6 Step-reaction Addition and Chain-reaction Condensation

A. Step-reaction Addition.



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1.6 Step-reaction Addition and Chain-reaction Condensation

B. Chain-reaction Condensation



A. Types of Nomenclature

a. Source name : to be based on names of corresponding monomer

Polyethylene, Poly(vinyl chloride), Poly(ethylene oxide)

b. IUPAC name : to be based on CRU, systematic name

Poly(methylene), Poly(1-chloroethylene), Poly(oxyethylene)

c. Functional group name :

Acoording to name of functional group in the polymer backbone

Polyamide, Polyester

d. Trade name : The commercial names by manufacturer Teflon, Nylon

e. Abbreviation name : PVC, PET

f. Complex and Network polymer : Phenol-formaldehyde polymer

g. Vinyl polymer : Polyolefin

1.7.1 Vinyl polymers

A. Vinyl polymers

a. **Source name** : Polystyrene, Poly(acrylic acid),

Poly(α-methyl styrene), Poly(1-pentene)

b. **IUPAC name** : Poly(1-phenylethylene), Poly(1-carboxylatoethylene)

Poly(1-methyl-1-phenylethylene), Poly(1-propylethylene)

Polystyrene

Poly(acrylic acid)





Poly(α-methylstyrene)







B. Diene monomers



Source name : 1,2-Poly(1,3-butadiene) 1,4-Poly(1,3-butadiene)

IUPAC name : Poly(1-vinylethylene) Poly(1-butene-1,4-diyl)

cf) Table 1.2

1.7.2 Vinyl copolymer

Systematic

Poly[styrene-co-(methyl methacrylate)] Poly[styrene-*alt*-(methyl methacrylate)] Polystyrene-*block*-poly(methyl methacrylate) Polystyrene-*graft*-poly(methyl methacrylate)

Concise

Copoly(styrene/methyl methacrylate) *Alt*-copoly(styrene/methyl methacrylate) *Block*-copoly(styrene/methyl methacrylate) *Graft*-copoly(styrene/methyl methacrylate)

1.7.3 Nonvinyl Polymers







1.7.4 Nonvinyl copolymers

a. Poly(ethylene terephthalate-co-ethylene isophthalate)



b. Poly[(6-aminohexanoic acid)-co-(11-aminoundecanoic acid)]

$$- \left[- NH - \left(- CH_2 \right)_5^{O} C - - NH - \left(- CH_2 \right)_{10}^{O} C - \right] - \left[- CH_2 \right]_{10}^{O} C - \left[- CH_2 \right]_{10}^{O}$$
1.7.5 End Group

нҢосң₂сң₂Ңон

α -Hydro- ω -hydroxypoly(oxyethylene)

1.7.6 Abbreviations

- **PVC** Poly(vinyl chloride)
- HDPE High-density polyethylene
- LDPE Low-density polyethylene
- **PET** Poly(ethylene terephthalate)

Туре	Abbreviation	Major Uses
Low-density polyeth	ylene LDPE	Packaging film, wire and cable insulation, toys, flexible bottles housewares, coating
High-density Polyethylene	HDPE	Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation
Polypropylene	PP	Automobile and appliance parts, furniture cordage, webbing, carpeting, film packa
Poly(vinyl chloride)	PVC	Construction, rigid pipe, flooring, wire and cable insulation, film and sheet
Polystyrene	PS	Packaging (foam and film), foam insulation appliances, housewares, toy

1) Cellulosic :

Acetate rayon, Viscose rayon

2) Noncellulosic :

Polyester, Nylon(Nylon6,6, Nylon6, etc) Olefin (PP, Copolymer(PVC 85%+PAN and others 15%; *vinyon*))

3) Acrylic :

Contain at least 80% acrylonitrile (PAN 80% + PVC and others 20%)

1.8.3 Rubber (Elastomers)

1) Natural rubber :

cis-polyisoprene

2) Synthetic rubber :

Styrene-butadiene, Polybutadiene, Ethylene-propylene(EPDM), Polychloroprene, Polyisoprene, Nitrile, Butyl, Silicone, Urethane

3) Thermoplastic elastomer :

Styrene-butadiene block copolymer (SB or SBS)

TABLE 1.7 Principal Synthetic

Fibor	0
Туре	Description
Cellulosic Acetate rayor Viscose rayo	n Cellulose acetate nRegenerated cellulose
Polvester	Principally poly(ethylene terephthalate)
Nylon	Includes nylon 66, nylon 6, and a variety of other aliphatic and
Olefin	aromatic polyamides
	Includes polypropylene and copolymers of vinyl chloride, with
Acrylic	lesser amounts of acrylonitrile, vinyl acetate, or vinylidene chloride (copolymers consisting of more than 85% vinyl chloride are called <i>vinyon</i> fibers)
	Contain at least 80% acrylonitrile; included are modacrylic
	TIDERS

comprising acrylonitrile and about 20% vinyl chloride $^{\!\!\!\!^{42}}$ or

1.9 Polymer Recycling

a. Durability of polymer property

- 1) Advantage : Good materials for use
- 2) Disadvantage : Environmental problem
- b. Treatment of waste polymer : Incinerate, Landfill, Recycling

ex) Waste Tire : Paving materials Waste PET : To make monomer (hydrolysis) To make polyol (glycolysis)

Polymers

What is a polymer?

Very Large molecules structures chain-like in nature.

Poly mer many repeat unit



Adapted from Fig. 14.2, Callister 7e.

Polymer Composition

Most polymers are hydrocarbons – i.e. made up of H and C

- Saturated hydrocarbons
 - Each carbon bonded to four other atoms





Isomerism

Isomerism

 two compounds with same chemical formula can have quite different structures/atomic arrangement

Ex: C₈H₁₈

• n-octane

• 2-methyl-4-ethyl pentane (isooctane)

Chemistry of Polymers







Note: polyethylene is just a long HC - paraffin is short polyethylene

Bulk or Commodity Polymers

Table 14.3 A Listing of Repeat Units for Polymeric Materials







Molecular Structures

· Covalent chain configurations and strength:



Direction of increasing strength

Adapted from Fig. 14.7, Callister 7e.



Range of Polymers

- Traditionally, the industry has produced two main types of synthetic polymer – plastics and rubbers.
- Plastics are (generally) rigid materials at service temperatures
- Rubbers are flexible, low modulus materials which exhibit long-range elasticity.

Range of Polymers

Plastics are further subdivided into thermoplastics and thermosets

Thermoplastics & Thermosetting polymers

- <u>Thermoplastics</u> polymers: soften when heated and harden when cooled and vice versa
- Structure Example: linear, branched:
- Polyethylene, polystyrene, PVC, Poly (ethylene terephthalate)
- <u>Thermosetting</u> polymers: permanently hard (do not soften when heated)
- Made from network polymers: covalent bond resist motion at high temperature prevent.
- Epoxies, phenolics, and some polyester resins.



Synthesis of Polymers

Synthesis of Polymers

- There are a number different methods of preparing polymers from suitable monomers, these are
 - step-growth (or condensation) polymerisation
 - addition polymerisation
 - insertion polymerisation.

Types of Polymerization

 Chain-growth polymers, also known as addition polymers, are made by chain reactions



Types of Polymerization

 Step-growth polymers, also called condensation polymers, are made by combining two molecules by removing a small molecule

$$CH_{3}O-C-\bigcirc O\\C-OCH_{3}+O\\C-OCH_{2}CH_{2}OH \xrightarrow{\Delta} O\\C-OCH_{2}CH_{2}O-C-\bigcirc O\\C-OCH_{2}CH_{2}OH \xrightarrow{\Delta} O\\C-OCH_{2}CH_{2}O-C-\bigcirc O\\C-OCH_{2}CH_{2}O-C-\bigcirc O\\C-OCH_{2}CH_{2}O-C-O\\C-OCH_{2}$$

Addition Vs. Condensation Polymerization

Polymerisation reactions can generally be written as

x-mer + y-mer (x + y)-mer

- In a reaction that leads to condensation polymers, x and y may assume any value
- i.e. chains of any size may react together as long as they are capped with the correct functional group

Types of Addition Polymerization

- Free Radical
- Cationic
- Anionic

- Usually, many low molecular weight alkenes undergo rapid polymerization reactions when treated with small amounts of a radical initiator.
- For example, the polymerization of ethylene



step 2: Propagation

$$R-CH_2CH_2 \bullet CH_2 = CH_2 - R-CH_2CH_2CH_2CH_2 \bullet$$



step 3: Termination

 $2 R - (CH_2CH_2)_n CH_2CH_2 \rightarrow R - (CH_2CH_2)_n CH_2CH_2 - CH_2CH_2(CH_2CH_2)_n R$

 $2 \text{ R}^{-}(\text{CH}_2\text{CH}_2)_{n}\text{CH}_2\text{CH}_2^{\bullet} \longrightarrow \text{R}^{-}(\text{CH}_2\text{CH}_2)_{n}\text{CH}=\text{CH}_2 + \text{R}^{-}(\text{CH}_2\text{CH}_2)_{n}\text{CH}_2\text{CH}_2$

 Ionic polymerization is more complex than free-radical polymerization

 Whereas free radical polymerization is nonspecific, the type of ionic polymerization procedure and catalysts depend on the nature of the substituent (R) on the vinyl (ethenyl) monomer.

- Cationic initiation is therefore usually limited to the polymerization of monomers where the R group is electron-donating
- This helps stabilise the delocation of the positive charge through the p orbitals of the double bond

 Anionic initiation, requires the R group to be electron withdrawing in order to promote the formation of a stable carbanion (ie, -M and -I effects help stabilise the negative charge).

Cationic

R - Electron donating

Anionic

R - Electron withdrawing

(i) Initiation can occur in one of the four following ways:



- M is a Monomer Unit.
- As these ions are associated with a counterion or gegen-ion the solvent has important effects on the polymerization procedure.
(ii) Chain Propagation depends on :

- Ion separation
- The nature of the Solvent
- Nature of the counter lon

 Involves the polymerization of monomers that have strong electron-withdrawing groups, eg, acrylonitrile, vinyl chloride, methyl methacrylate, styrene etc. The reactions can be initiated by methods (b) and (c) as shown in the sheet on ionic polymerization

• eg, for mechanism (b)



 The gegen-ion may be inorganic or organic and typical initiators include KNH2, n-BuLi, and Grignard reagents such as alkyl magnesium bromides

 If the monomer has only a weak electronwithdrawing group then a strong base initiator is required, eg, butyllithium; for strong electron-withdrawing groups only a weak base initiator is required, eg, a Grignard reagent.

- Initiation mechanism (c) requires the direct transfer of an electron from the donor to the monomer in order to form a radical anion.
- This can be achieved by using an alkali metal eg.,

$$\begin{array}{ccc} \mathsf{CH}_{3} & \mathsf{CH}_{3} \\ \mathsf{Na} + \mathsf{H}_{2}\mathsf{C} = \overset{\mathsf{C}}{\mathsf{C}} & \longrightarrow & \mathsf{Na}^{\oplus} + \cdot \begin{bmatrix} \mathsf{CH}_{3} \\ \mathsf{H}_{2}\mathsf{C} - \overset{\mathsf{C}}{\mathsf{C}} \ominus \\ \mathsf{CN} \end{bmatrix}$$

Anionic Polymerization of Styrene



Rate $v_1 = k_1 [NH_2]$ [M]

Anionic Polymerization of Styrene



Anionic Polymerization of Styrene



(i) Initiation

$$\begin{array}{c} H & R_1 \\ C = C \\ H & R_2 \end{array} \stackrel{\oplus}{\longrightarrow} \left[\begin{array}{c} H & H & R_1 \\ C = C \\ H & R_2 \end{array} \right] \stackrel{\oplus}{\longrightarrow} \left[\begin{array}{c} H & R_1 \\ C = C \\ H & R_2 \end{array} \right] \stackrel{\oplus}{\longrightarrow} \left[\begin{array}{c} H & R_1 \\ H - C - C \\ H & R_2 \end{array} \right] \left[\begin{array}{c} SMX_n \\ SMX_n \end{array} \right] \stackrel{\oplus}{\longrightarrow} \left[\begin{array}{c} H & R_1 \\ H - C - C \\ H & R_2 \end{array} \right] \left[\begin{array}{c} SMX_n \\ SMX_n \end{array} \right]$$

 (ii) PropagationChain growth takes place through the repeated addition of a monomer in a head-to-tail manner to the ion with retention of the ionic character throughout



(iii) Termination

Termination of cationic polymerization reactions are less well-defined than in freeradical processes. Two possibilities exist as follows:

(a) Unimolecular rearrangement of the ion pair



- Hydrogen abstraction occurs from the growing chain to regenerate the catalyst-co-catalyst complex.
- Covalent combination of the active centre with a catalyst-co-catalyst complex fragment may occur giving two inactive species.

 The kinetic chain is terminated and the initiator complex is reduced - a more effective route to reaction termination.

(b) Bimolecular transfer reaction with the monomer



Reformation of the monomer-initiator complex, ensuring that the kinetic chain is not terminated by the reaction.

 The kinetics of these reactions is not well understood, but they proceed very rapidly at extremely low temperatures.

Polymerization Techniques

These include:

- Bulk Polymerization
- Solution Polymerization
- Suspension Polymerization
- Emulsion Polymerization

Bulk Polymerization

Advantages:

- High yield per reactor volume
- Easy polymer recovery
- The option of casting the polymerisation mixture into final product form

Bulk Polymerization

Limitations:

- Difficulty in removing the last traces of monomer
- The problem of dissipating heat produced during the polymerization
 - In practice, heat dissipated during bulk polymerization can be improved by providing special baffles

 Definition: A polymerization process in which the monomers and the polymerization initiators are dissolved in a nonmonomeric liquid solvent at the beginning of the polymerization reaction. The liquid is usually also a solvent for the resulting polymer or copolymer.

 Heat removed during polymerization can be facilitated by conducting the polymerization in an organic solvent or water

- Solvent Requirements:
- Both the initiator and the monomer be soluble in it
- The solvent have acceptable chain transfer characteristics and suitable melting and boiling points for the conditions of the polymerization and subsequent solventremoval step.

- Solvent choice may be influenced by other factors such as flash point, cost and toxicity
- Reactors are usually stainless steel or glass lined

Disadvantages:

- small yield per reactor volume
- The requirements for a separate solvent recovery step

 Definition: A polymerization process in which the monomer, or mixture of monomers, is dispersed by mechanical agitation in a liquid phase, usually water, in which the monomer droplets are polymerized while they are dispersed by continuous agitation. Used primarily for PVC polymerization

- If the monomer is insoluble in water, bulk polymerization can be carried out in suspended droplets, i.e., monomer is mechanically dispersed.
- The water phase becomes the heat transfer medium.

- So the heat transfer is very good. In this system, the monomer must be either
 - -1) insoluble in water or
 - 2) only slightly soluble in water, so that when it polymerizes it becomes insoluble in water.

- The behavior inside the droplets is very much like the behavior of bulk polymerization
- Since the droplets are only 10 to 1000 microns in diameter, more rapid reaction rates can be tolerated (than would be the case for bulk polymerization) without boiling the monomer.

 Emulsion polymerization is a type of <u>radical</u> polymerization that usually starts with an <u>emulsion</u> incorporating water, <u>monomer</u>, and <u>surfactant</u>.

- The most common type of emulsion polymerization is an oil-in-water emulsion, in which droplets of monomer (the oil) are emulsified (with <u>surfactants</u>) in a continuous phase of water.
- Water-soluble polymers, such as certain polyvinyl alcohols or hydroxyethyl <u>celluloses</u>, can also be used to act as emulsifiers/stabilizers.



Emulsion Polymerization – Schematic

Advantages of emulsion polymerization include:

- High <u>molecular weight</u> polymers can be made at fast polymerization rates. By contrast, in bulk and solution <u>free radical polymerization</u>, there is a tradeoff between molecular weight and polymerization rate.
- The continuous water phase is an excellent <u>conductor</u> of heat and allows the heat to be removed from the system, allowing many reaction methods to increase their rate.

Advantages Continued:

- Since <u>polymer molecules</u> are contained within the particles, <u>viscosity</u> remains close to that of water and is not dependent on <u>molecular</u> <u>weight</u>.
- The final product can be used as is and does not generally need to be altered or processed.

Disadvantages of emulsion polymerization include:

- For dry (isolated) polymers, water removal is an energy-intensive process
- Emulsion polymerizations are usually designed to operate at high conversion of monomer to polymer.
 This can result in significant <u>chain transfer</u> to polymer.