CHEM330

Physical chemistry of polymers

Credit hours: 1 h course + 1 h Laboratory

College of Science

Chemistry department

1443H-2022

Grades

- 1^{rst} Midterm Exam : 15 points
- 2^{nd} Midterm Exam : 15 points
- lab: 30 points
- Final Exam : 40 points

References and books

- Ger Challa “Polymer chemistry: an introduction: Ellis Horwood, 1993

- Polymer Synthesis and Characterization, Basic laboratory course, Edited by Florian Paulus, Dirk Steinhilber, Tobias Becherer 2011/2012

- Industrial Polymers, Specialty Polymers, and Their Applications, 1rt Edition, Manas Chanda, Salil K. Roy, 2008.

Course Objectives

1-Definition and classification of polymers

2-Polymers and copolymers Nomenclature

3- Structure and microstructure of polymers

4- Polymerization reactions

5- Techniques of polymerization

6- Techniques used to determine the average molecular weights

7- Thermal properties of polymers

1. Generalities

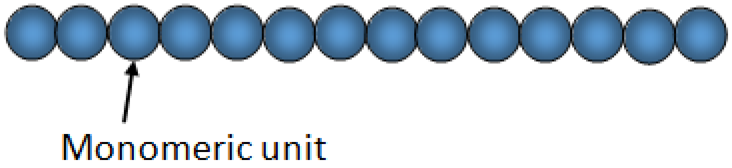
1.1Definition and classification of polymers

A polymer is one or several sequences of several molecules of the same type called “monomeric units” linked by covalent or coordination bonds.

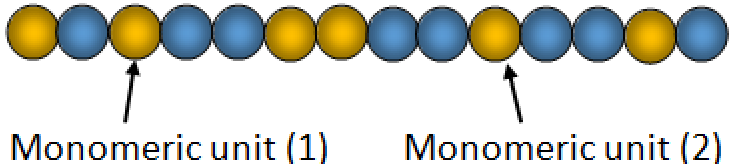
“All polymers are macromolecules but not all macromolecules are polymers, because a macromolecule does not necessarily include repetitive units”

There are two types of polymer, depending on the nature of the monomeric units.

- ❑ Homogeneous also called “homopolymer” in which all the monomeric units are similar



- ❑ Heterogeneous called “copolymer” in which the monomeric units are different



Examples: Homogeneous polymers

Polyethylene (PE), Poly(methyl methacrylate)(PMMA), poly(dimethyl siloxane)(PDMS), polystyrene (PS)…

The parenthesis (…): We must put the name of the monomer in parentheses only if is composed of two or more words

For example:
Polyethylene: "ethylene" is only in one word
Poly(methyl methacrylate): "methyl methacrylate" is composed of two words methyl and methacrylate

Examples: Heterogeneous polymers

Poly(ethylene-co-terephtalate) (PET), Poly(styrene-co-butadiene)(PSB)

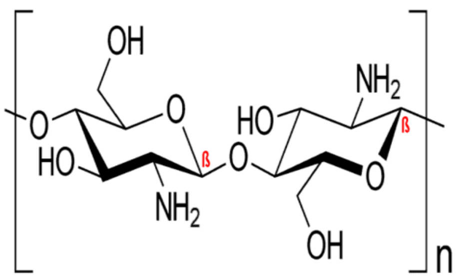
The symbol "co" indicates the two first letters of the word "copolymer" and indicates that the two units coexist in the same polymer chain.

1.2 Nature of polymer

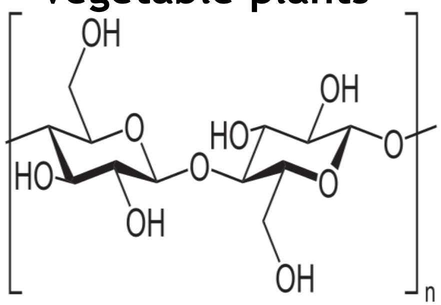
According to its origin, a polymer can be natural or synthetic

<u>1.2.1 Natural polymers:</u> These polymers are of animal origin such as **Chitosan** (shrimp shell), or plant like **cellulose**, **natural rubber** (vegetable plants)

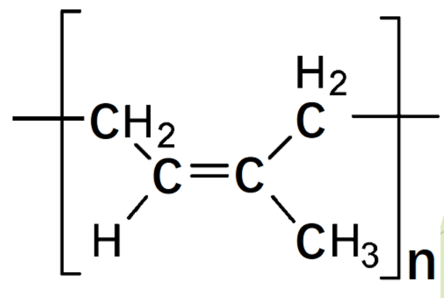
Shrimp



Vegetable plants



rubber tree



1.2.2 Synthetic polymers:

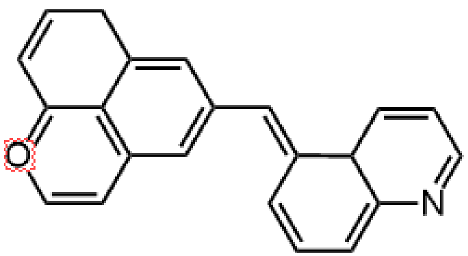
These polymers are obtained from the polymerization of monomers containing vinylic, acetylenic, di or more functional active groups and ring opening monomers containing heteroatoms.

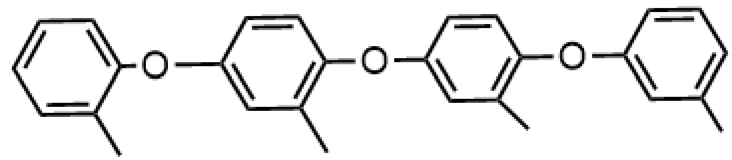
Examples:

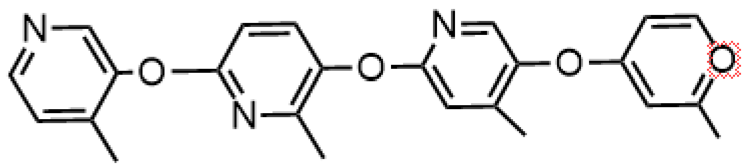
- Polymerization of vinylic monomers leads to obtain polystyrene, poly(vinyl chloride), poly(vinyl alcohol)…. etc.
- Polymerization of acetylenic monomers leads to obtain polyacetylene, poly(phenyl acetylene), poly(alkyl acetylene)… etc.
- Polymerization of monomers having di functional active groups leads to obtain poly(ethylene oxide), poly(dimethyl siloxane) oil, polyester, polyurethane … etc.
- Polymerization of monomers having tri functional active groups leads to obtain poly(dimethyl siloxane) rubber
- Polymerization by ring opening of monomers leads to obtain poly (caprolactone), ethylene oxide… etc.

Exercises

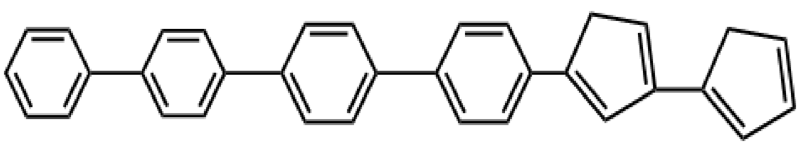
Exercise1: which among the following molecules are polymers

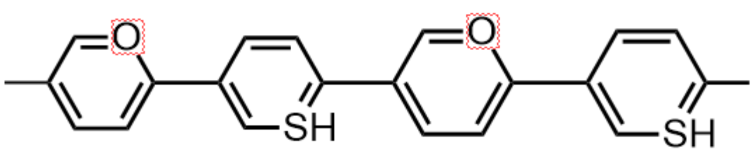


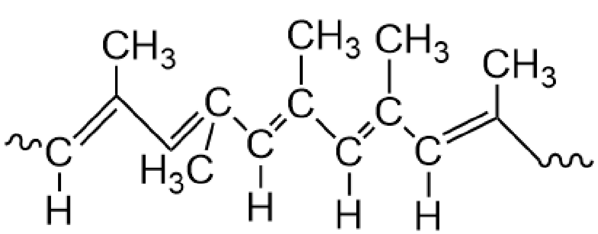


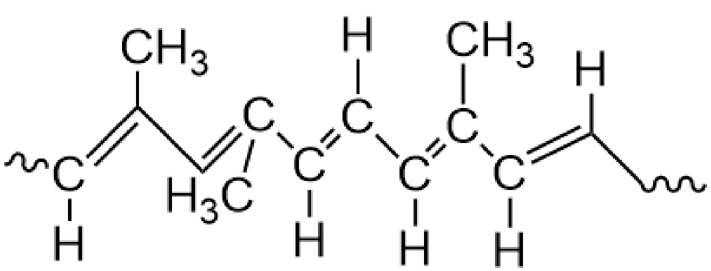


Exercise2: Which Among the following polymers, classify the homogeneous polymers and the heterogeneous polymers





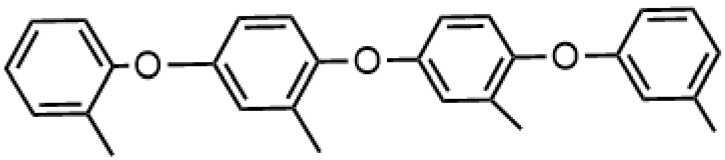


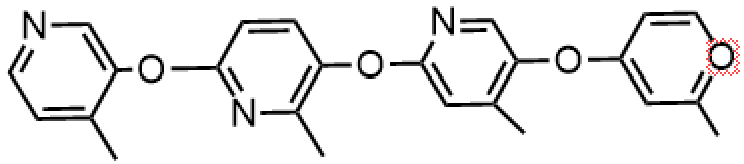


Answers

Exercise 1

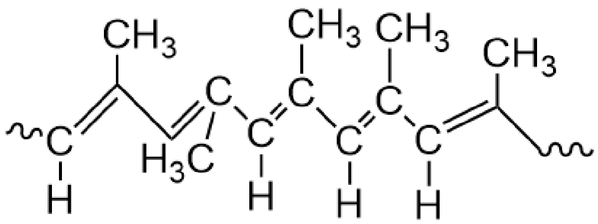
Polymers are:





Exercise 2

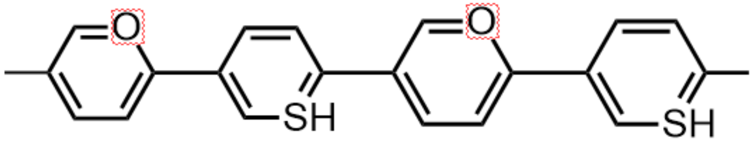
Homopolymers are:

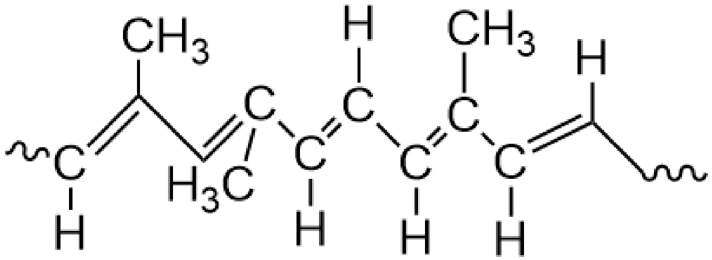


Answers

Exercise 2

Heteropolymers (copolymers)





Exercises

Exercises 3. Give two examples of natural vegetal polymer

Exercises 4. Give four examples of natural animal polymer

Exercises 5. Give three examples of synthetic polymer

Answers

Exercise 3.

- Amylopectine,
- Lignin

Exercise 4.

- Albumin,
- Collagen,
- Gelatin,
- Chondroitin

Exercise 5.

- Poly(methyl methacrylate) (Plexiglass)
- Nylon
- Acid polyacrylic

2. Structure and microstructure

2. 1 Chemical structure and microstructure

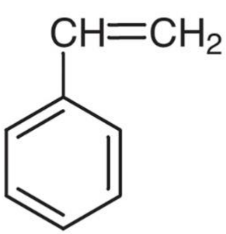
A polymer is represented by a structure well defined which is based on that of the corresponding monomer, but a polymer can have several microstructures which play a determining role in its properties.

Chemical structure of polymer

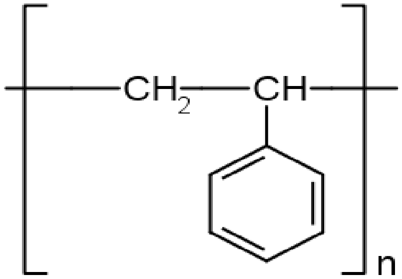
Examples:

Polystyrene its molecule is symbolized by the following structure:

styrene:



polystyrene:



- **Triple bonds such as acethylene and alkylacetylene**

$nCH{\equiv}CH$ ─ polymerization $\rightarrow$ $-[CH{=}CH]_n-$

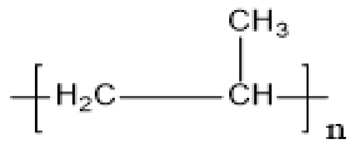
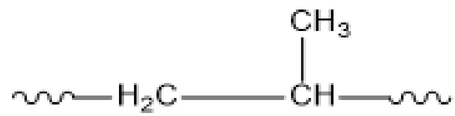
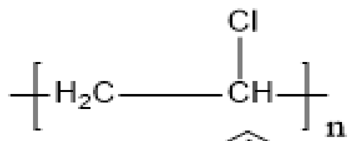
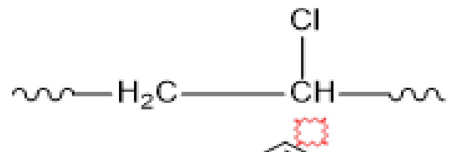
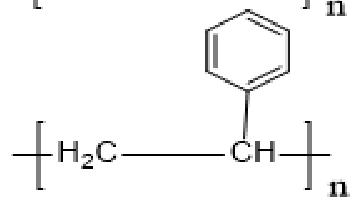
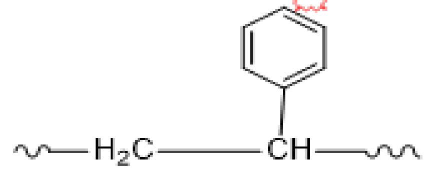
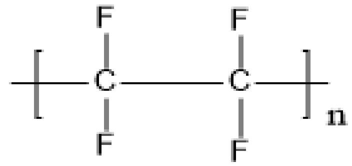
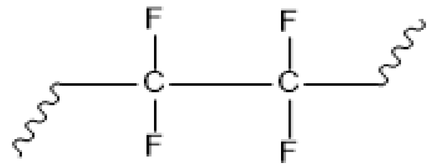
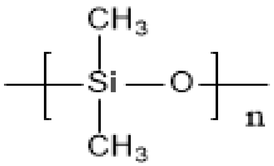
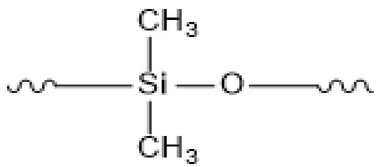
$n\ R{-}C{\equiv}CH$ - polymerization $\rightarrow$ $-[C(R){=}CH]_n-$

- **Two or more functional groups such as ethylene glycol**

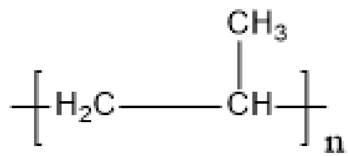
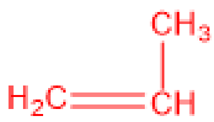
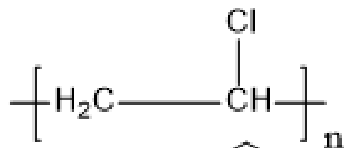
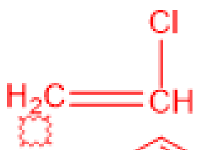
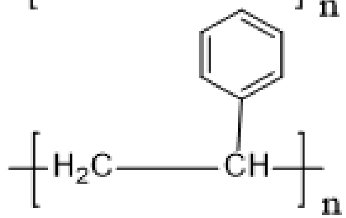
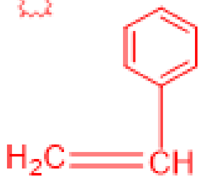
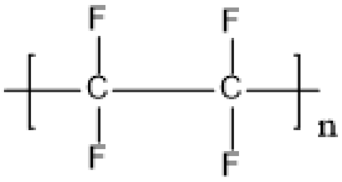
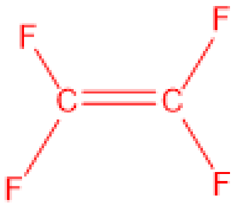
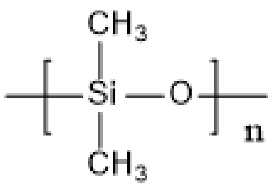
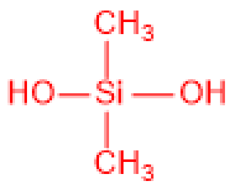
Example:

$n\ HO{-}CH_2{-}CH_2{-}OH$ ─polymerization $\rightarrow$ $-[CH_2{-}CH_2{-}O]_n-\ +\ nH_2O$

2. 3 Naming the polymers and copolymers

Name	Symbol	Structure	Structure
Poly(ethylene)	PE		
Polypropylene	PP		
Poly(vinyl chloride)	PVC		
Polystyrene	PS		
Poly(tetrafluoro ethylene)	PTFE		
Poly(dimethyl siloxane)	PDMS		

2.3Naming the polymers and copolymers

Name	Polymer structure	Name of monomer used	Monomer Structure
Polyethylene		Ethylene	
Polypropylene		Propylene	
Poly(vinyl chloride)		Vinyl chloride	
Polystyrene		Styrene or vinylbenzene	
Poly(ethylene tethafluride)		Ethylene tethafluride	
Poly(dimethyl siloxane)		Dimethylsiloxane	

Exercise 1: What is the nomenclature and the structure of the each polymer synthesized from the following monomers?

A) Acrylononitrile (CH_2=CH-CN)
B) Acrylic acid (CH_2=CH-COOH
C) Acrylamide (CH_2=CH-CO-NH_2)
D) Vinylalcohol (CH_2=CH-OH)
E) Vinylacetate (CH_2=CH-O-CO-CH_3)

Exercise 2: What is the nomenclature and the structure of the each monomer used in the synthesis of the following polymers?

A) poly(methyl methacrylate)
B) Poly(vinylpyridine)
C) Poly(2-hydroxyethylmethacrylate)
D) Poly(ethylene glycol)
E) Poly(vinylnaphtalene)

CORRECTION 1

A) Nomenclature: Polyacrylonitrile structure: -[CH2-CH(CN)]n-

B) Nomenclature: Poly(acrylic acid) structure: -[CH2-CH(COOH)]n-

C) Nomenclature: Polyacrylamide) structure: -[CH2-CH(CO-NH2)]n-

D) Nomenclature: Poly(vinyl alcohol) structure: -[CH2-CH(OH)]n-

A) Nomenclature: Poly(vinyl acetate) structure: -[CH2-CH(O-CO-CH3)]n-

CORRECTION 2

A) Nomenclature: methyl methacrylate
   Structure: $CH_2=C(CH_3)(COOCH_3)$

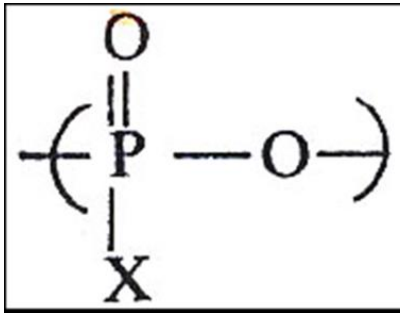
B) Nomenclature: vinylpyridine
   Structure: $CH_2=CH(C_5H_4N)$

C) Nomenclature: 2-hydroxyethylmethacrylate
   Structure: $CH_2=C(CH_3)(COO-(CH_2)_2-OH)]_n-$

D) Nomenclature: ethylene glycol
   Structure: $HO-CH_2-CH_2-OH$

E) Nomenclature: vinylnaphtalene
   Structure: $CH_2=CH-C_{10}H_8$

Inorganic polymer



poly (oxyphosphohalide)

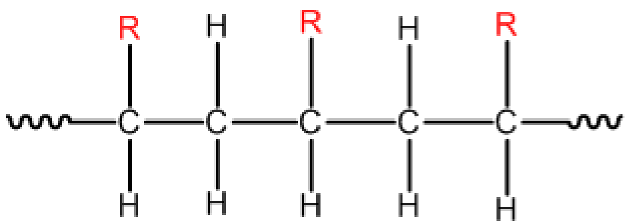
-[PH - NH]n- **Poly(phosphazene)**

2.4 Polymer microstructure (tacticity, cis/trans)

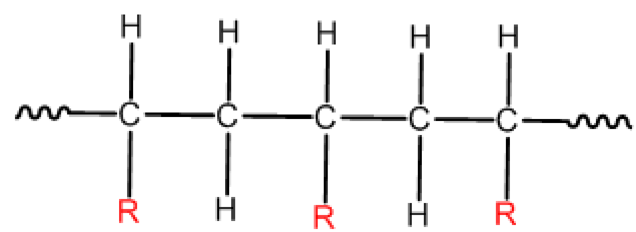
A-Tacticity of Polymers

A polymer can be present three distinct microstructures

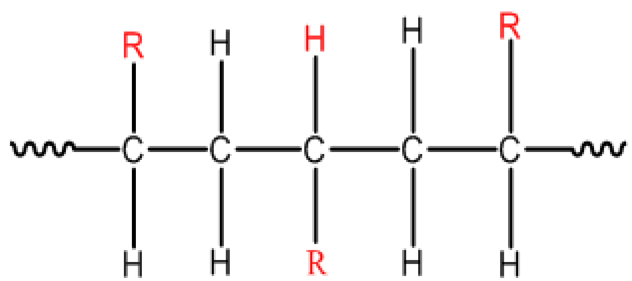
1) Isotactic



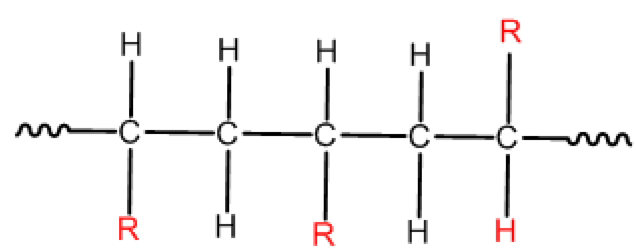
or



2) Syndiotactic



3) Atactic

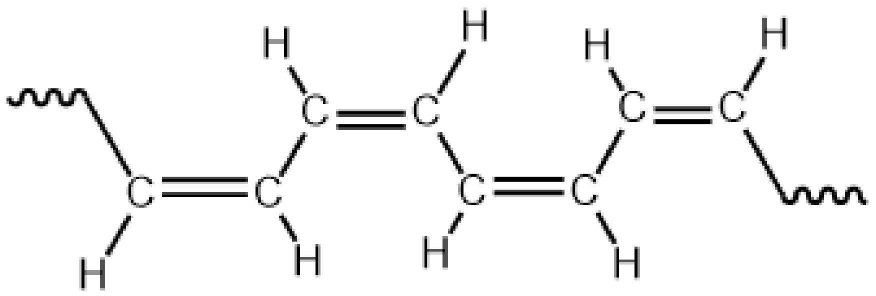


B- Isomery Cis/Trans

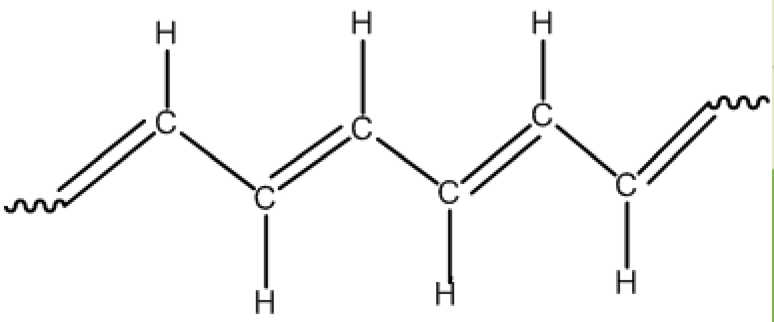
A polyconjugated polymer can be present two microstructures cis or trans with respect to the double bonds

Example

Microstructure Cis:



Microstructure Trans:



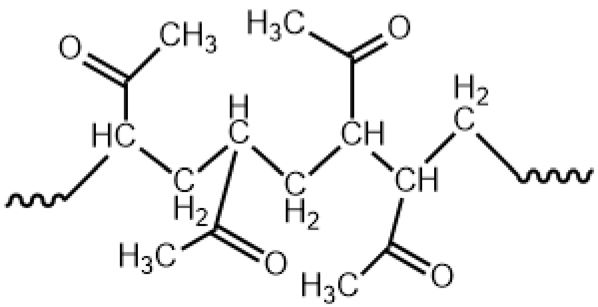
EXERCISES

Exercise 1

Among the following polymers Indicate those have a tacticity.
$-[CH_2-CH(COOH)]_n-$; $-[CH_2-CH(C_6H_5)]_n-$; $-[CH_2-CH_2]_n-$; $-[CH_2-CH_2-O-]_n-$; $-[O-C_6H_4-]_n-$

Exercise 2

What is the tacticity of the following molecule.



Exercise 3

Write the mi or the following molecules. – Poly(vinyl chloride); Poly(sodium acrylate)

Correction 1

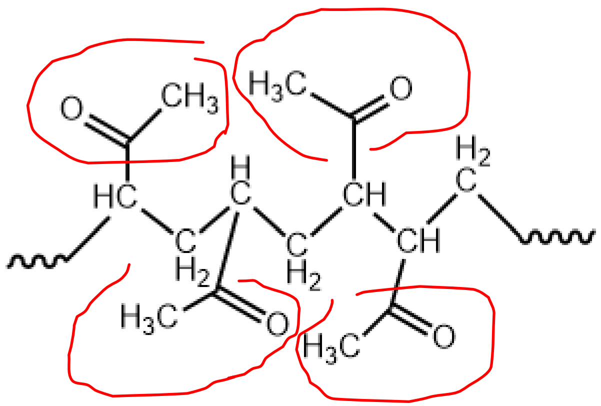
The molecules that have tacticities are:

$-[CH_2-CH(COOH)]_n-$; $-[CH2-CH(C_6H_5)]_n-$

Because these molecules have substituent : in the first one presence of carboxylic group and in the second one presence of benzyl group

Correction 2

The tacticity of this molecule is syndiotactic. Because the substitutents are distributed alternativement on both sides of the polymer chain (backbone)

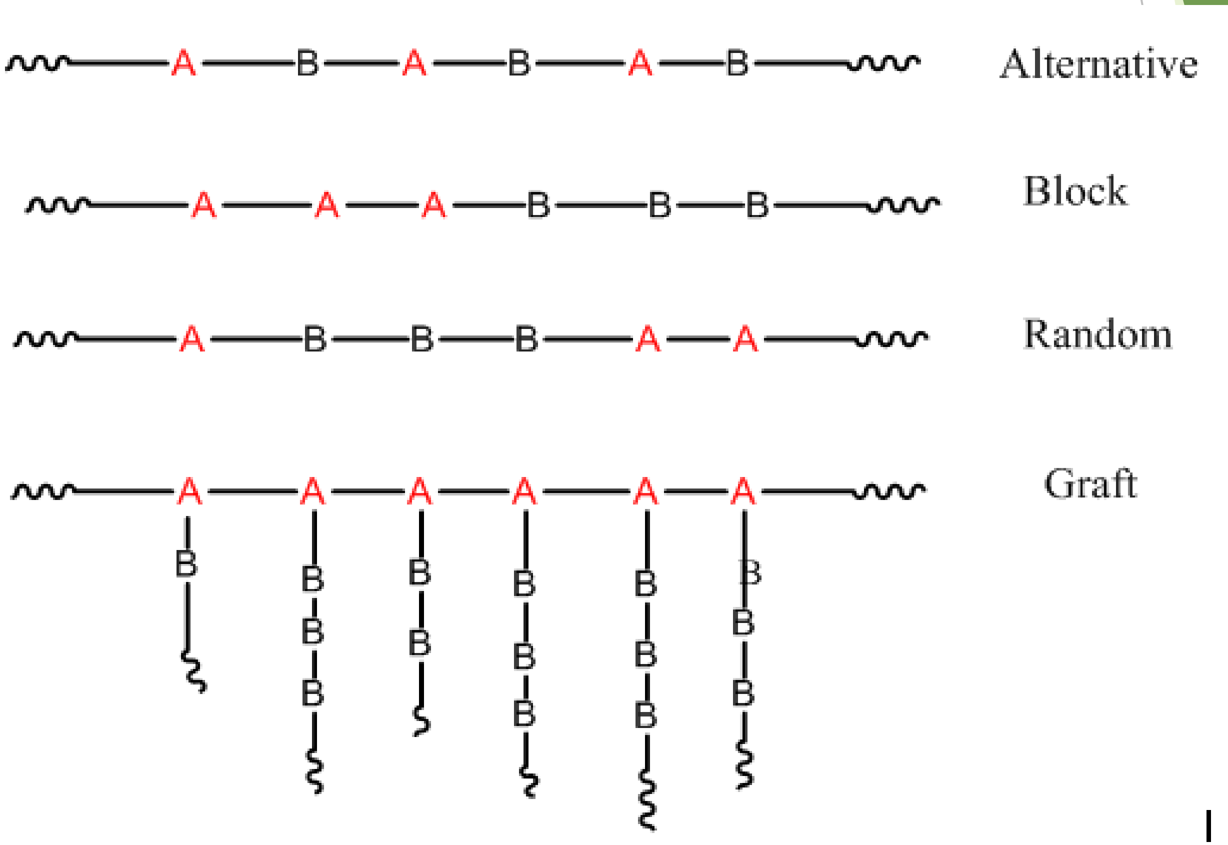


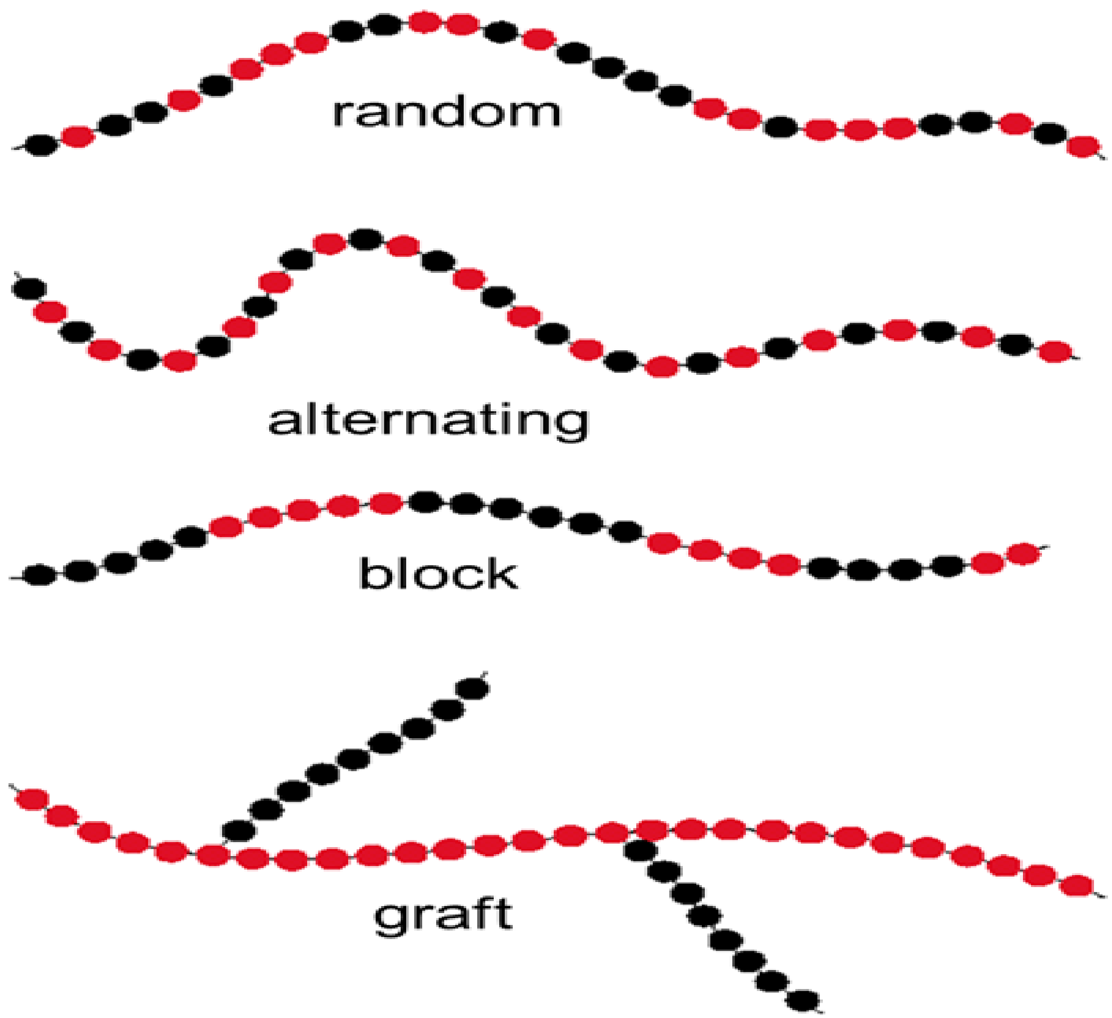
Correction 3

Copolymer structure

A copolymer also called heterogen polymer contains two or more monomeric units in its chain.

If A and B are its monomer units we can write Its structure as follow:




random
alternating
block
graft

Examples

Nomenclature: The polymerization of ethylene with vinyl alcohol give a copolymer called poly(ethylene-co-vinyl alcohol) or copoly(ethylene/vinylalcohol)
Structure: -[CH_2-CH_2]n-[CH_2-CH(OH)]m-

- If this copolymer is alternative: poly(ethylene-alt-vinyl alcohol)
- If this copolymer is sequenced: poly(ethylene-block-vinyl alcohol)
- If this copolymer is rundom: poly(ethylene-rand-vinyl alcohol)
- If this copolymer is grafted: poly(ethylene-graf-vinyl alcohol)

Exercises

Exercise1: Indicate the name and the formula of a grafted copolymer prepared from styrene and acrylic acid

Exercise2: Indicate the name and the formula of a block copolymer prepared from acrylonitrile and acrylamide

Exercise3: Indicate the name and the formula of a grafted copolymer prepared from acrylonitrile and styrene

Exercise4: Indicate the name and the formula of a random copolymer prepared from acrylonitrile and styrene

Exercise5: Indicate the name and the formula of a random terpolymer prepared from acrylonitrile, styrene and methyl methacrylate

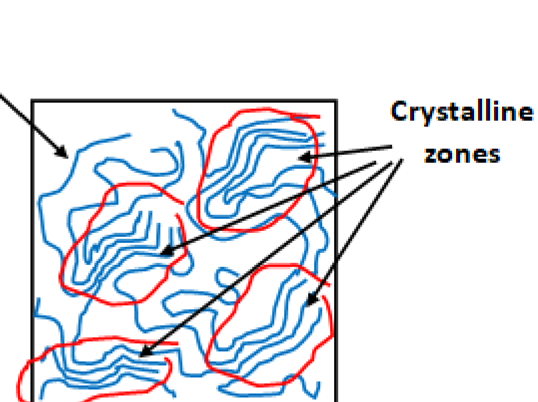
Corrections

3. Polymer crystallinity

3. Polymer crystalline and polymer amorphous

The principle of crystallinity in polymers is different from that of small molecules. Because a crystalline system in small molecules is characterized by a well-defined geometry of crystals in the crystal lattice eg NaCl the crystals have cubic shapes. But in polymers, only parts of the chain is in orderly condition with other parts of other chains. In this case the crystallinity in the polymers means that some parts of the chains are in an certain ordered state as shown in the figure above. A state is said to be amorphous when the chains are randomly arranged in the polymer matrix and do not obey any defined order.

The crystallinity of polymers can be compared to hair that is neither smooth nor crisp. There is no such thing as a 100% crystalline polymer , polymer has a semi -crystalline structure, the most crystalline does not exceed 80% and varies according to the nature and the structure and microstructure of the polymer.



3.Polymer crystalline and polymer amorphous

The more linear polymer chains, the higher their degrees of crystallinity.

For example the maximum degree of crystallinity (~ 80 %) is found in polyethylene because polyethylene does not have substituents.

Poly(methylmethacrylate) (PMMA) is amorphous, because this polymer has bulky substitutents.

Most polymers are amorphous due to the presence of very crowded substitutes. Most amorphous polymers do not have melting temperatures.

3. Polymer crystalline and polymer amorphous

Properties

A- Amorphous polymers:

1- clear
2- high elongation
3-Non specific melting temperature
4- low-moderate chemical resistance

3. Polymer crystalline polymer and polymer amorphous

Properties

B- Semi-crystalline polymers

1- cloudy opaque

2- low elongation

3- specific melting temperature

4- good-to high chemical resistance

3. Polymer crystalline polymer and polymer amorphous

crystalline polymers

1-opaque

2- low elongation

3- specific melting temperature

4- good-to high chemical resistance

5- Strength

6-Higher density

7-Less Soluble

8-Less Permeable

3. Polymer crystalline polymer and polymer amorphous

Factors affected on the crystallinity

Crystalline (rigid, soluble)...... amorphous(Soft, rubbery material)

1- Rate of cooling during solidification

2-monmer complexity

3-side group

4-Copolymerization

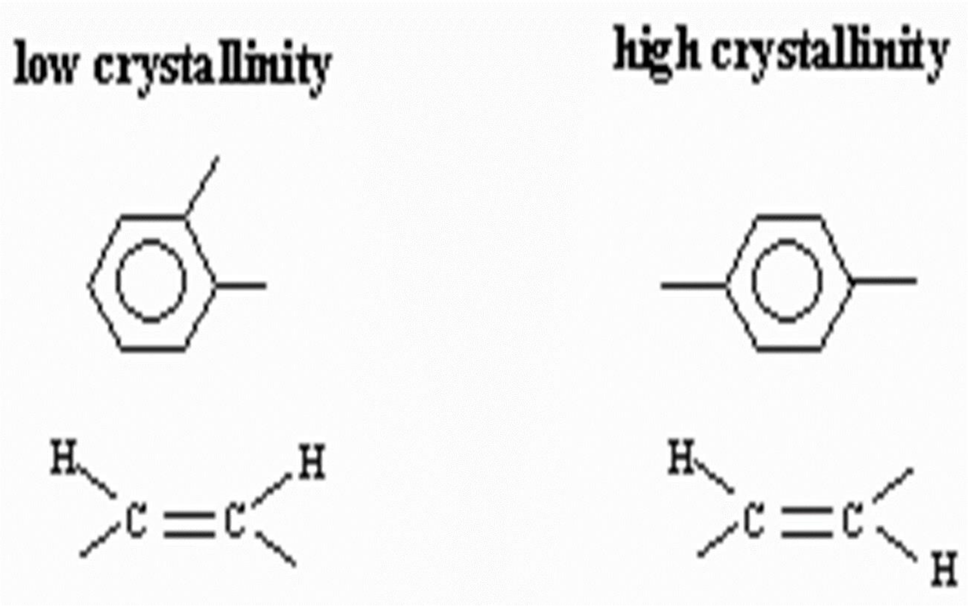
*alternating and block can crystallize more easily as compared to random and graft

3. Polymer crystalline polymer and polymer amorphous

Factors affected on the crystallinity

5-Chain flexibility

Ether, imine, double bonds in cis form, C-O and C-N



3. Polymer crystalline polymer and polymer amorphous

Factors affected on the crystallinity

6- chine structure

- Linear polymers crystallize relatively easily
- Branches inhibit crystallization,
- Network polymers almost completely amorphous
- Crosslinked polymers can be both crystalline and amorphous

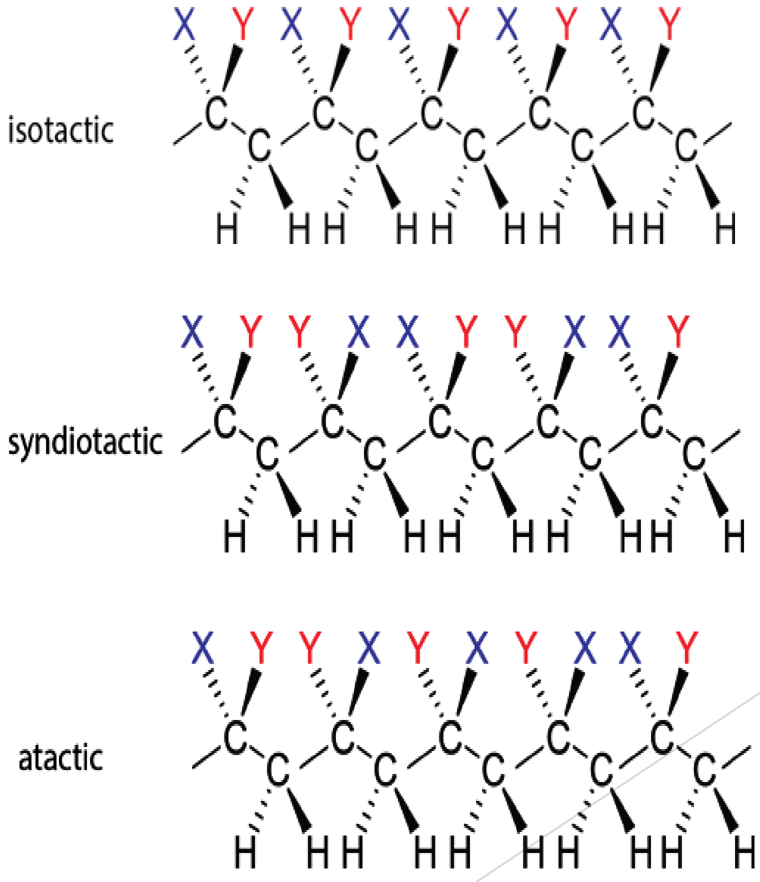
3. Polymer crystalline polymer and polymer amorphous

Factors affected on the crystallinity

7- Isomerism

*Isotactic and syndiotactic polymers crystallize relatively easily

*atactic difficult to crystallize



3. Polymer crystalline polymer and polymer amorphous

Measuring Crystallinity

A-Density measurements

B-X-ray diffraction e.g. powder (XRD)

C-Differential scanning calorimeter (DSC)

4. Polymerization and copolymerization monomers

Principal polymerization reactions

Polyaddition	Polycondensation	Ring opening
Vinylic, ethylenic and acetylenic monomers	Monomers having two or more functional groups	Monomers cyclic heteroatomic

4.1 Polyaddition reactions

Polyadditions

- Free radical polymerization
  - Chemical polymerization
  - Physical polymerization
- Ionic polymerization
  - Anionic polymerization
  - Cationic polymerization
- Coordination polymerization
  - Ziegler-Natta polymerization
  - Metathesis polymerization

4.1.1 Free radical Polymerization

Monomer used: Vinylic monomers having as substituent an attractor atom or group of atoms such as : $CH_2=CH-X$ with X = Halogene, carboxylic, amine, amide, phenyl, …etc.

Chemical initiator used: Chemical substance capable to generate free radical such as: peroxide, azoisobutyronitrile (AIBN), potassium persulfate (KPS)… etc.

Physical initiator used: heat and radiation (UV, Gamma, Alpha, …etc.)

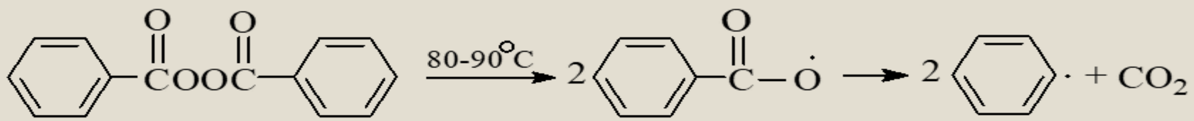
A-Steps of polymerization

Steps of polymerization

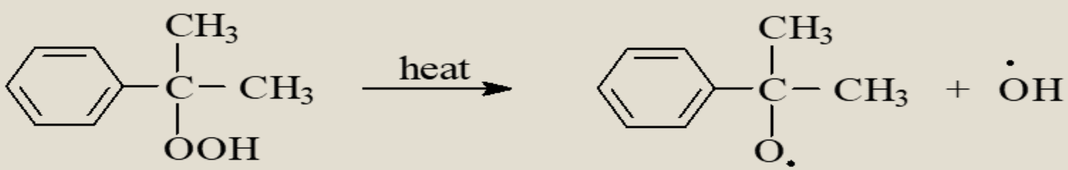
Initiation → **Propagation** → **Termination**

Initiation	Propagation	Termination
Formation of the active center	Progression of chains or chains growth	Maturation of the polymer chains
A-M*	**A-M-M-M-M***	**A-M-M-M-M-M**

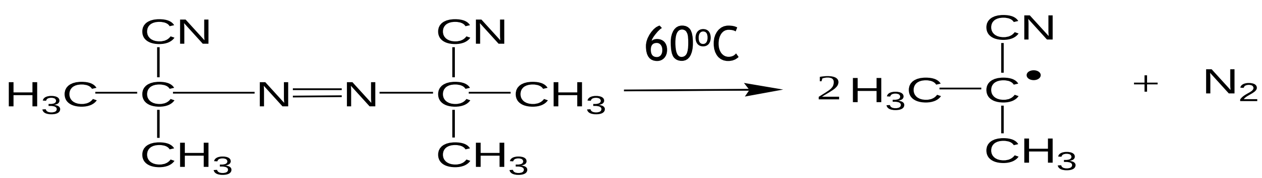
A-1.Initiators and free radical formation



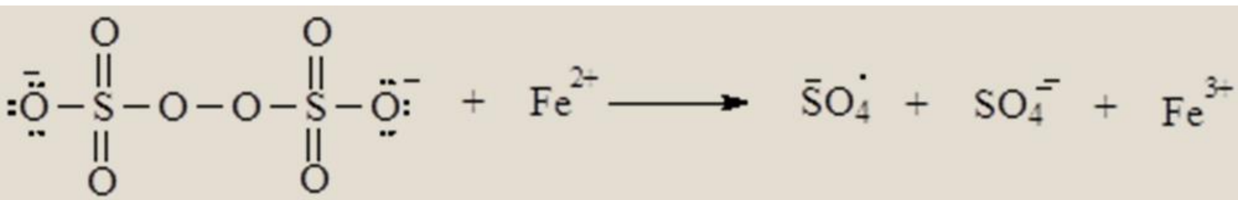
Benzoyl peroxide

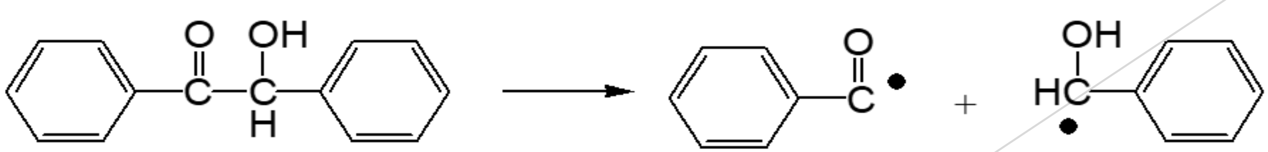


Cumen hydroperoxide



Azo bis isobutyronitrile
(AIBN)





2-Hydroxy-1,2-diphenyl-ethanone

❑ Initiation (formation of the active center):

Initiators and free radical formation

If A_2 is the chemical initiator and M the monomer

$$A_2 \xrightarrow{\Delta} 2\,A^* \qquad A^*\text{: Free radical}$$

$$A^* + M \longrightarrow A\text{-}M^* \qquad A\text{-}M^*\text{: Active center}$$

For example:

A_2 : diacyl peroxid : $C_6H_5\text{-CO-O-O-CO-}C_6H_5$

M: Acid acrylic: $CH_2\text{=CH-COOH}$

$$C_6H_5\text{-CO-O-O-CO-}C_6H_5 \longrightarrow 2\,C_6H_5\text{-CO-O}^*$$

$$C_6H_5\text{-CO-O}^* + CH_2\text{=CH-COOH} \longrightarrow C_6H_5\text{-CO-O-}CH_2\text{-CH}^*\text{(COOH)}$$

(Active center)

❑ Propagation (Chains progression)

(Macroradical formation)

$$C_6H_5\text{-}CO\text{-}O\ \text{-}CH_2\text{-}CH^*(COOH) \quad + \quad n\ (CH_2{=}CHCOOH)$$

$$\downarrow$$

$$C_6H_5\text{-}CO\text{-}O\ \text{-}[CH_2\text{-}CH^*COOH]_n\text{-}\ CH_2\text{-}CH^*COOH$$

(Macroradical)

❑ Termination

This step can be achieved by different reactions

A- Transfer to the impurity according to the following reactions:

presence of impurity (I) in the reaction mixture

C_6H_5-CO-O -[CH_2-CH*COOH]n- CH_2-CH*COOH + I
(Macroradical)

↓

C_6H_5-CO-O -[CH_2-CH*COOH]n- CH_2-CHCOOH + I*

↓

I* + m (CH_2=CH-COOH) → I-CH_2-CH*COOH]n- CH_2-CH*COOH

B) Transfer to the solvent (S)

C_6H_5-CO-O –[CH_2-CH*COOH]n- CH_2-CH*COOH + S

(Macroradical)

↓

C_6H_5-CO-O –[CH_2-CH*COOH]n- CH_2-CHCOOH + S*

(Mature chain)

↓

S* + m (CH_2=CH-COOH) → S-CH_2-CH*COOH]n- CH_2-CH*COOH

(Macroradical)

This termination type can occur in the hologened solvent such as chloroform.

C) Transfer to the Monomer (M)

$$C_6H_5\text{-CO-O -}[CH_2\text{-CHCOOH}]_n\text{- } CH_2\text{-CH*COOH} + M$$

(Macroradical)

$$\downarrow$$

$$C_6H_5\text{-CO-O -}[CH_2\text{-CHCOOH}]n\text{- } CH_2\text{-CHCOOH} + M^*$$

(Mature chain)

$$\downarrow$$

$$M^* + m\,(CH_2\text{=CH-COOH}) \longrightarrow M\text{-}CH_2\text{-CH*COOH}]n\text{- } CH_2\text{-CH*COOH}$$

D) Termination by combination of two macroradical

C_6H_5-CO-O -[CH_2-CHCOOH]n- CH_2-CH*COOH

(Macroradical)

+

C_6H_5-CO-O -[CH_2-CHCOOH]n- CH_2-CH*COOH

(Macroradical)

↓

C_6H_5-CO-O -[CH_2-CH*COOH]n- CH_2-CHCOOH
|
C_6H_5-CO-O -[CH_2-CH*COOH]n- CH_2-CHCOOH

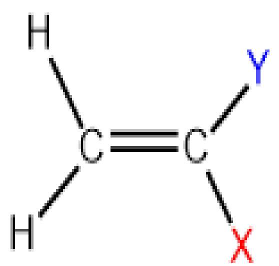
Usually this type of termination leads to long polymer chains

4.1.2 Anionic polymerization

Initiators: **Strong base such as : NaOH, KOH, KNH_2, Carbanion such as Butyl lithium ($Li^+C_4H_9^-$), sodium ethanolate ($NaOC_2H_5$) …etc.**

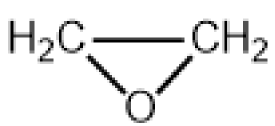
Monomers: **vinylic monomers having attractor atoms or group of atoms and other molecules such as ethylene epoxide.**

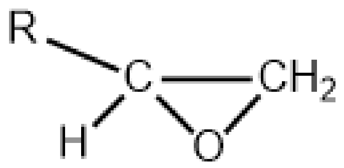
Vinylic monomers



X: Halogene; COOH, COOR, $CONH_2$, HCO, OH, .Phenyl ...etc

Y: H or CH_3



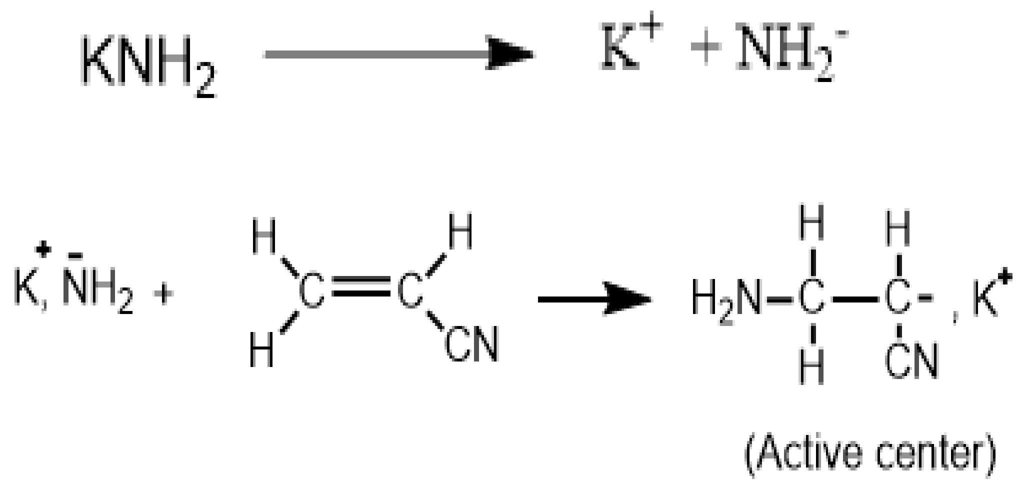


❑ Initiation (Active center formation)

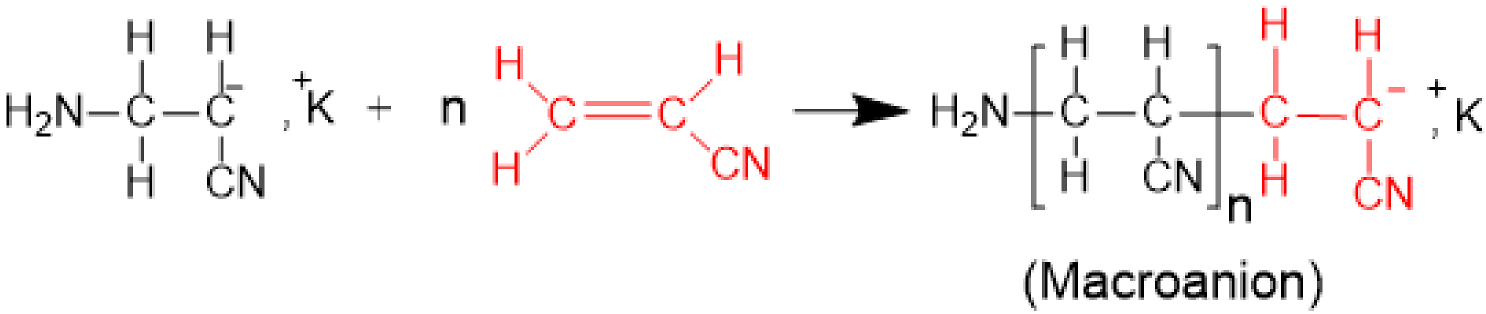
<u>Example</u>:

Initiator= KNH_2 (Potassium amide)

Monomer = $H_2C{=}CH{-}CN$ (Acrylonitrile)

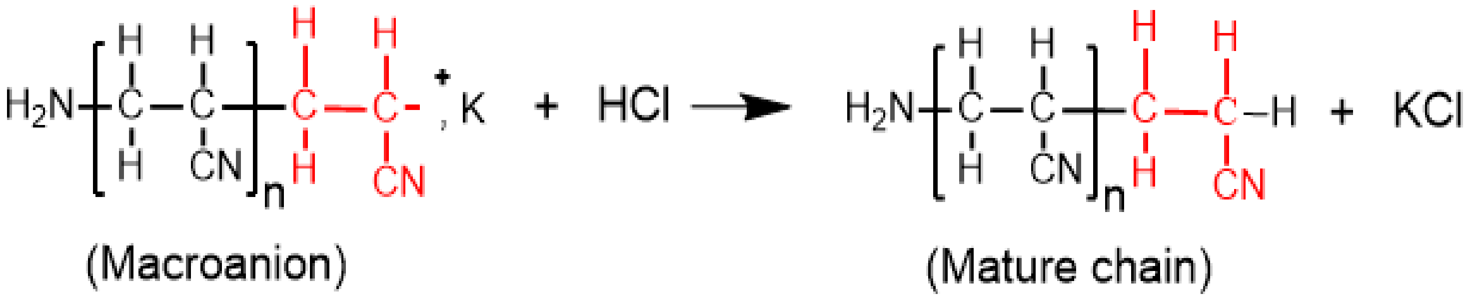


❑ Propagation (Chain growth)



❑ Termination (Chain maturation)

In most cases the termination is achieved by adding small amounts of mineral acid such as HCl, HNO3, … etc.



4.1.3 Cationic polymerization

Initiators: Strong acid such as: HCl, H_2SO_4, HNO_3, Carbocation (Iodate tertiobutylate$(CH_3)_3I$), Lewis acids, … etc.

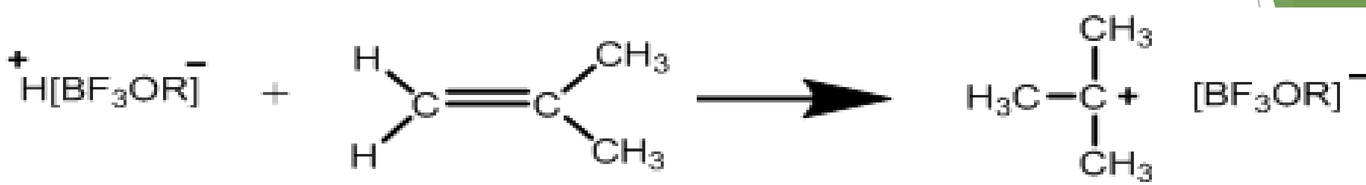
Monomers: Vinyl monomers, epoxide, two conjugated double bonds

❑ Initiation (active center formation)

For example : BF_3 as initiator and traces of H_2O or ROH as co-initiator
$CH_2{=}C(CH_3)_2$ as monomer

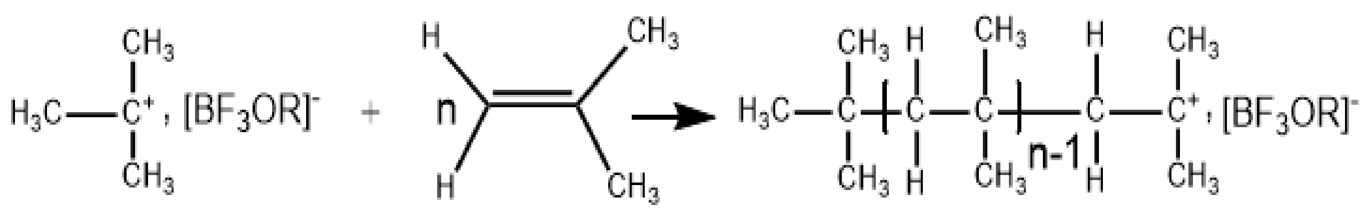
$$BF_3 + H_2O \rightleftharpoons {}^{-}BF_3O^{+}H_2 \rightleftharpoons [BF_3\,OH]^{-}H^{+}$$

Initiation



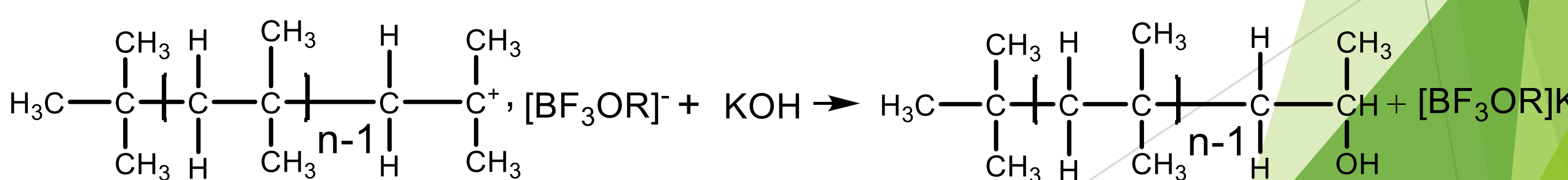
(Active center)

Propagation (chain growth)



Termination (chain maturation)

In most cases the termination is achieved by adding small amounts of mineral base



$$BF_3 + ROH \rightleftharpoons \overset{+}{H}[BF_3\overset{-}{O}R]$$

(Lewis acid) (Protonic acid complex)

Factors affecting the rate of ionic polymerization (anionic and cationic)

A- Effect of the temperature of polymerization

B- Effect of the solvent

C- Effect of the counter ion of the catalyst

D- Effect of the monomer structure

HW1:Compare between ionic and cationic polymerization

4.1.4 Coordination polymerization

Initiators = complex formed from a catalyst + co-catalyst system

Catalyst: Transition element + halogen ligand

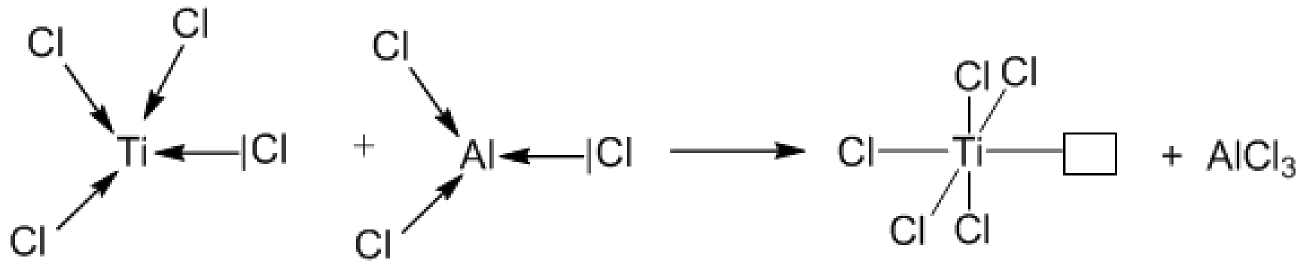
Examples: $TiCl_4$, $TiCl_3$, VCl_3, $CoCl_2$, … etc

Co-catalyst: Aluminum chloride ($AlCl_3$), Alkyl Aluminum Al(Butyl)$_3$, Aluminum chloride ($AlCl_3$)… etc.

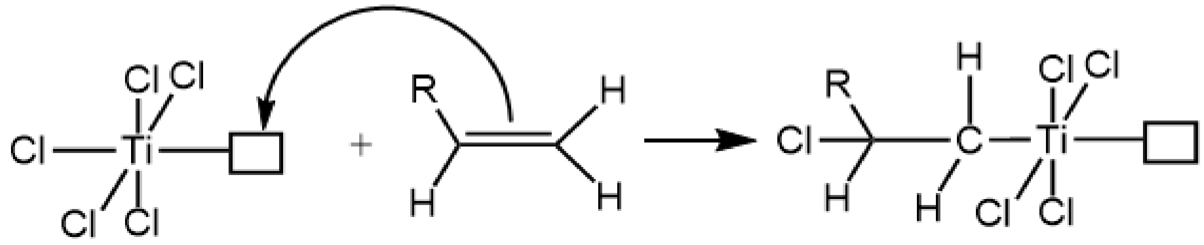
Monomers:

All vinylic, ethylenic and acetylenic monomers do not weigh attracting atoms such as oxygen, nitrogen, sulfur, phosphate. Monomers with fully carbon aromatic rings polymerize by these catalysts such as styrene and phenyl acetylene.

Complex formation

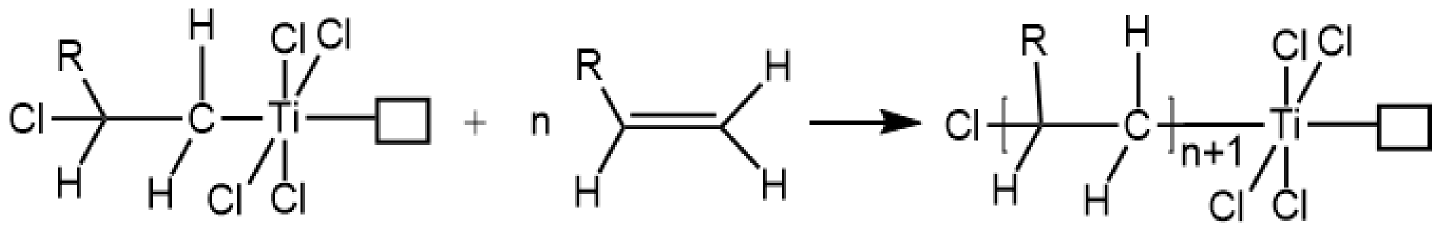


❑ Initiation (active center formation)



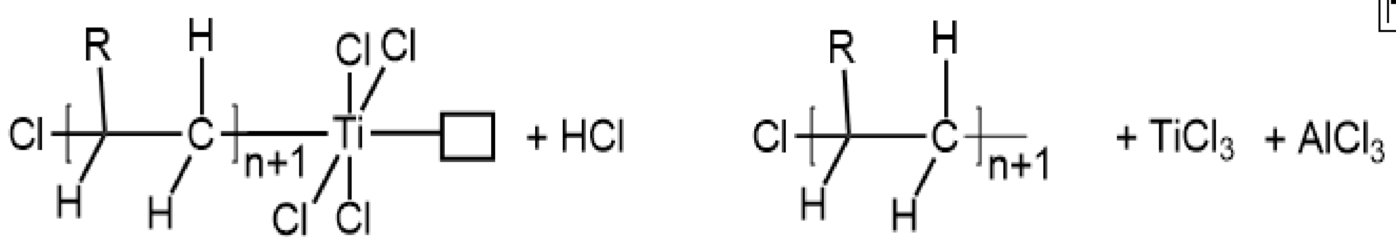
(Active center)

❑ Propagation (chain growth)



❑ Termination (Chain maturation)

In most cases the termination is achieved by adding small amounts of mineral base of minral acid



Polyaddition/Exercises

Exercise 1: Among the following initiators, which of them can polymerize acrylic acid through radical polymerization route.

NaOH; HCl; $AlCl_4$; Ph-CO-O-CO-Ph; Et-ONa; $TiCl_4$

Exercise 2: Among the following initiators, which of them can polymerize acrylic acid through anionic polymerization route.

NaOH; HCl; $AlCl_4$; Ph-CO-O-CO-Ph; Et-ONa; $TiCl_4$

Exercise3: Among the following initiators, which of them can polymerize acrylic acid through cationic polymerization route.

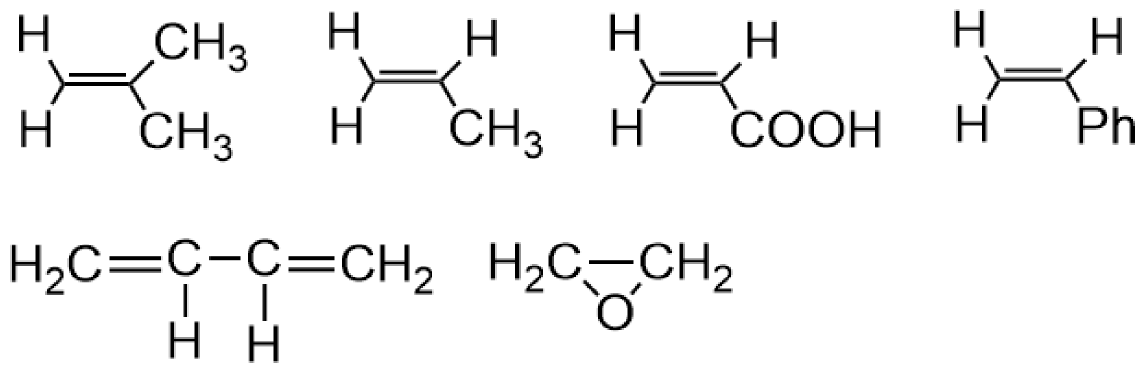
NaOH; HCl; $AlCl_4$; Ph-CO-O-CO-Ph; Et-ONa; $TiCl_4$

Exercise 4: Among the following initiators, which of them can polymerize propylene through coordination polymerization (Ziegler-Natta) route.

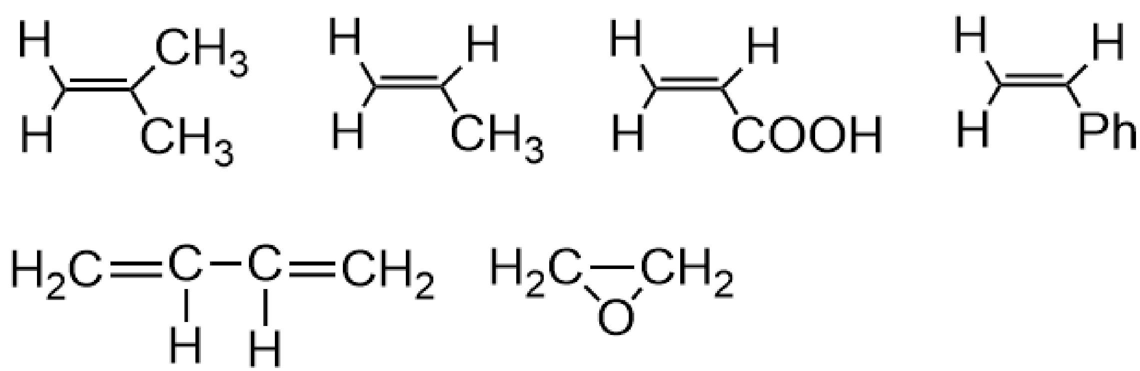
NaOH; HCl; $AlCl_4$; Ph-CO-O-CO-Ph; Et-ONa; $TiCl_4$; $TiCl_4/AlCl_3$; $NaCl/AlCl_3$; Et-Na/$AlCl_4$

Polyaddition/Exercises

Exercise5: Among the following monomers indicate which of them can be polymerized through a radical polymerization way?



Exercise6: Among the following monomers indicate which of them can be polymerized through a anionic polymerization way?



Polyaddition/Exercises

Exercise 9. **In general, the increase in the temperature of the polymerization leads to:**

A) Increase the polymerization rate

B) decrease the polymerization rate

C) Increase the molecular weight of resulted polymer

C) decrease the molecular weight of resulted polymer

D) Increase the yield of polymerization

E) decrease the yield of polymerization

Polyaddition/Exercises

Exercise 10- What is the effect of polar solvent on the polymerization of styrene

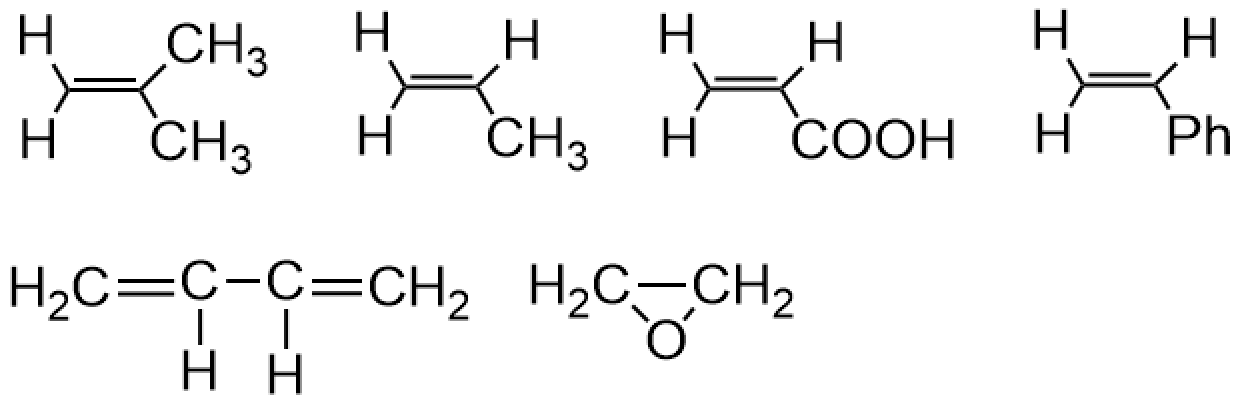
Exercise 11- What is the effect of non-polar solvent on the polymerization of acrylic acid

Exercise 12- What is the effect of the contre ion on the cationic polymerization of styrene

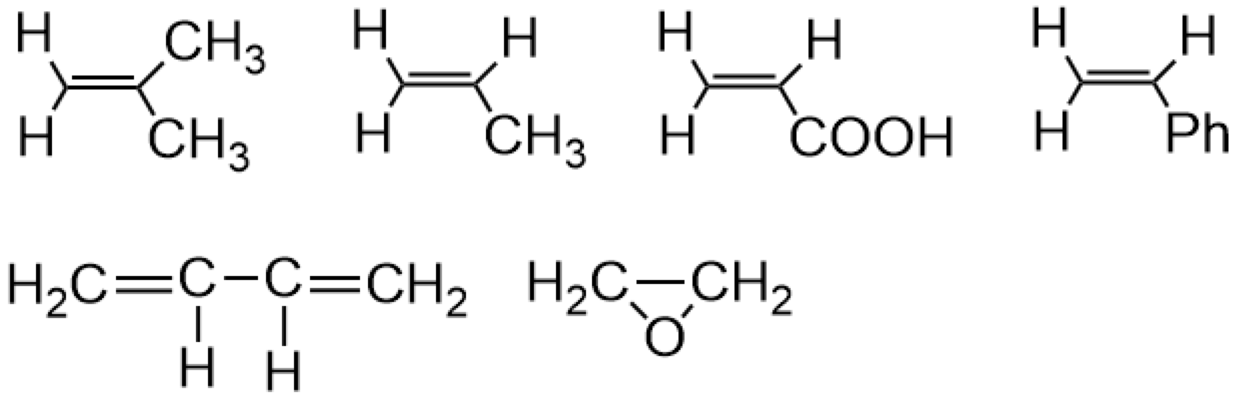
Exercise 13- What is the effect of the monomer structure on the polymerization of styrene

Polyaddition/Exercises

Exercise7: Among the following monomers indicate which of them can be polymerized through a ziegler-Natta (coordination) polymerization way?



Exercise8: Among the following monomers indicate which of them can be polymerized through a cationic polymerization way?

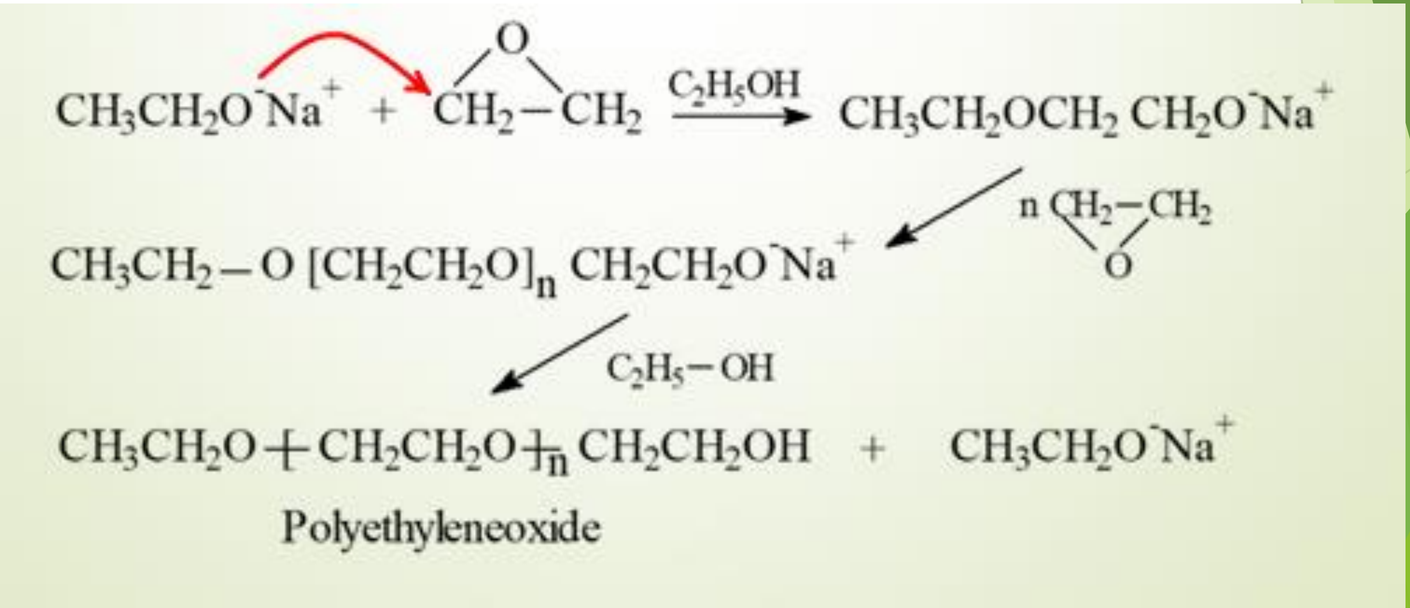


4.2 Ring Opening Polymerization

Ring Opening Polymerization can be realized by anionic or cationic catalysts

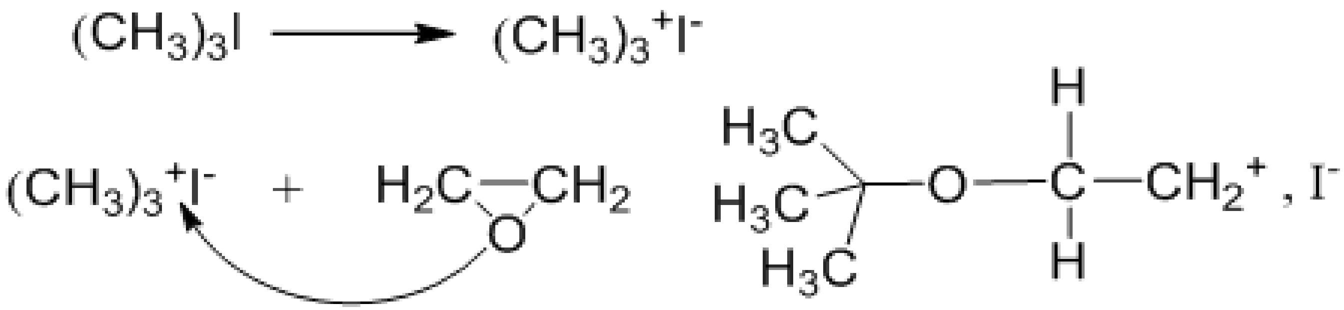
Anionic catalysts:
Exemples: Sodium ethanolate; sodium amide; NaOH; carbanion.

Monomers:
Examples: Cycle heteroatomic such as: ethylene epoxide, caprolacton, valerolactone.

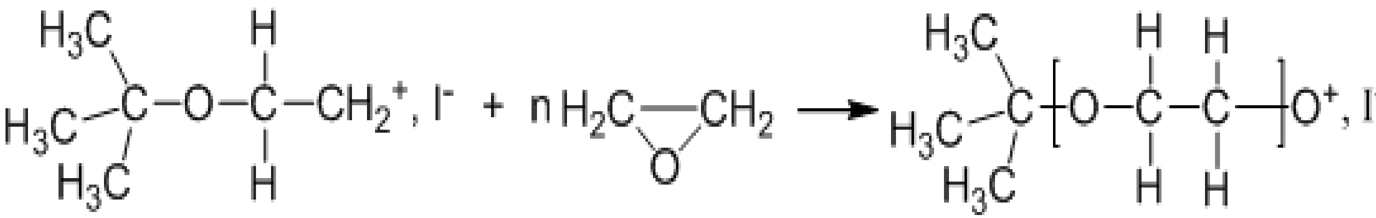


Cationic catalysts: Terbutyl iodate [$(CH_3)_3I$]
Monomer: ethylene glycol

❑ Initiation



❑ Propagation



❑ Termination

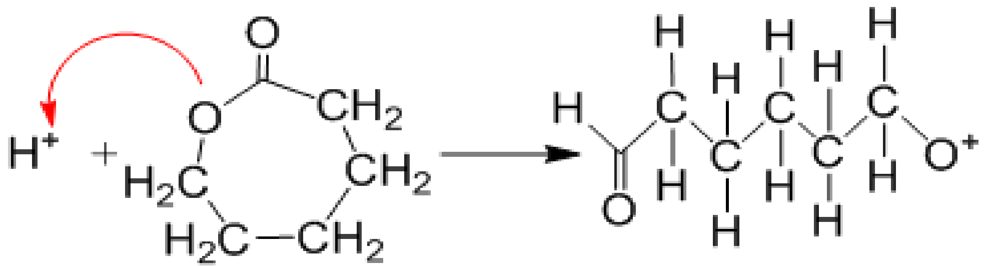
Living polymer

Cationic catalyst: H_2SO_4

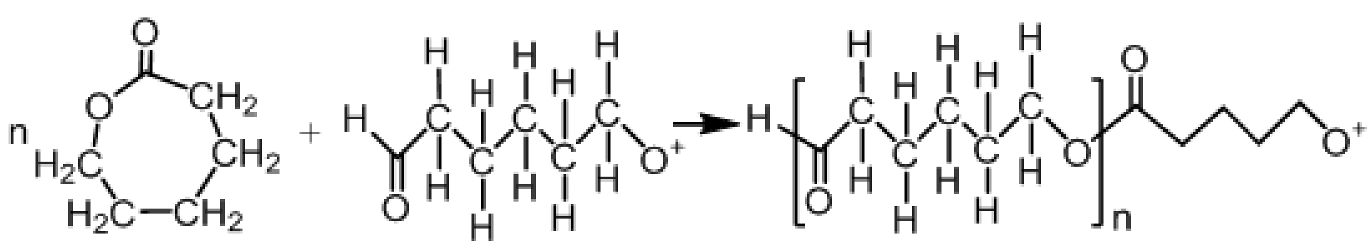
Monomer: ε-caprolactone

- Initiation

$$H_2SO_4 \longrightarrow HSO_4^- + H^+$$

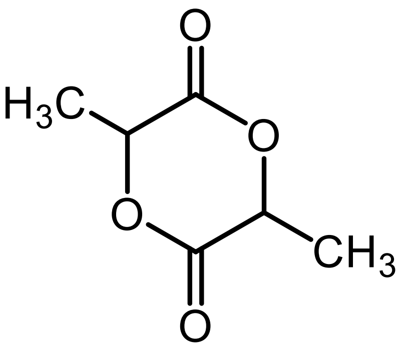


- Propagation

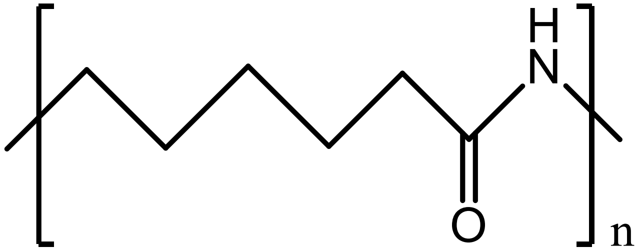


- Termination: leads to living polymers

Exercise 1: Write a ring polymerization of L-lactide



Exercise 2: Write the structure of the monomer that used to obtain the following polymer



4.3. Polycondensation reaction

Monomers: Molecules having two or more functional active groups.

Homogen such as:
Ethylene glycol ($HO-(CH_2)_2-OH$); dicarboxylic acid ($HOOC-(CH_2)_n-COOH$; dialkylamine ($H_2N-(CH_2)_n-NH_2$)

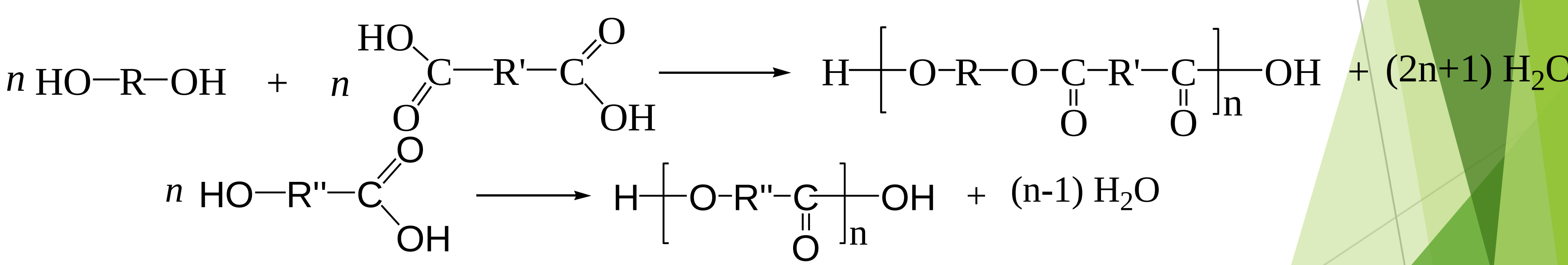
Heterogen such as: $HO-(CH_2)_2-COOH$; $HO-(CH_2)_n-NH_2$; $HCO_2-(CH_2)_n-NH_2$

Catalysts:
Strong acid: H_2SO_4; HCl; HNO_3
Strong base: $NaOH$, $NaOC_2H_5$; NH_2Na,

4.3 Polycondensation/Reactions

Step-growth Polymerization): Polymerization of monomers containing two functional groups propagates from both of the advancing chain to give a linear polymer and elimination of small molecules such as water, HCl...
On the other hand, the monomers containing three or four functional groups propagates on the three or four ends of the chain in progression giving a crosslinked polymer with elimination of small molecules such as water or HCl.

Example of linear polymer:



Produces Linear and Cross linked Polymers

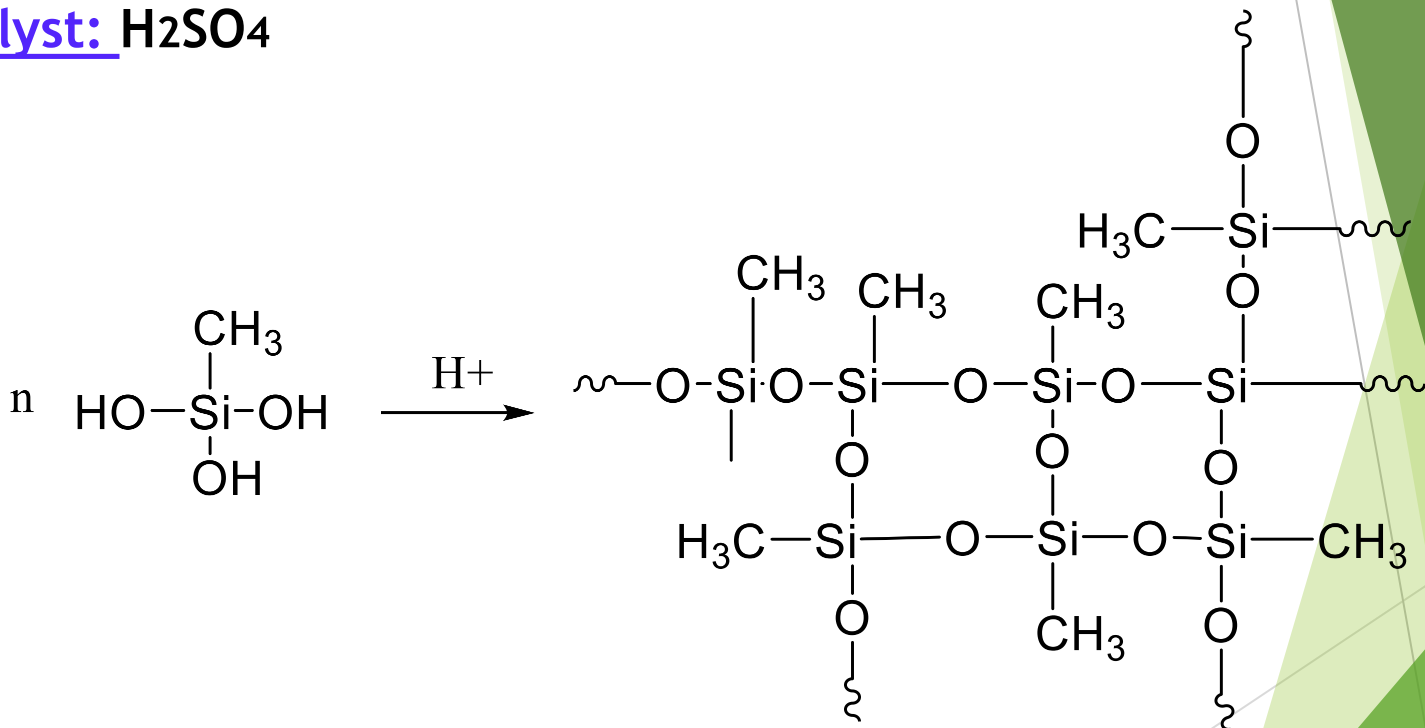
Thermoplastic

Thermoset

Example of polycondensation leading to a crosslinked polymer

Monomer: **methyltriolsiloxane**

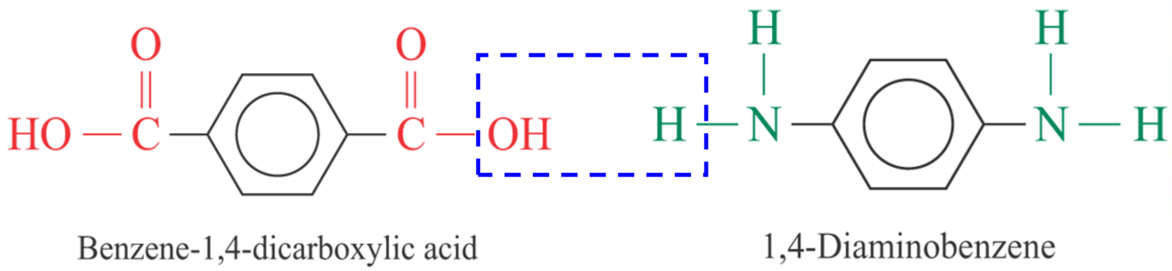
Catalyst: **H_2SO_4**



(Silicone rubber) (PDMS)

4.3 Polycondensation /properties

Kevlar



Properties

very strong material

used for reinforcing car tyres

Used to make ropes

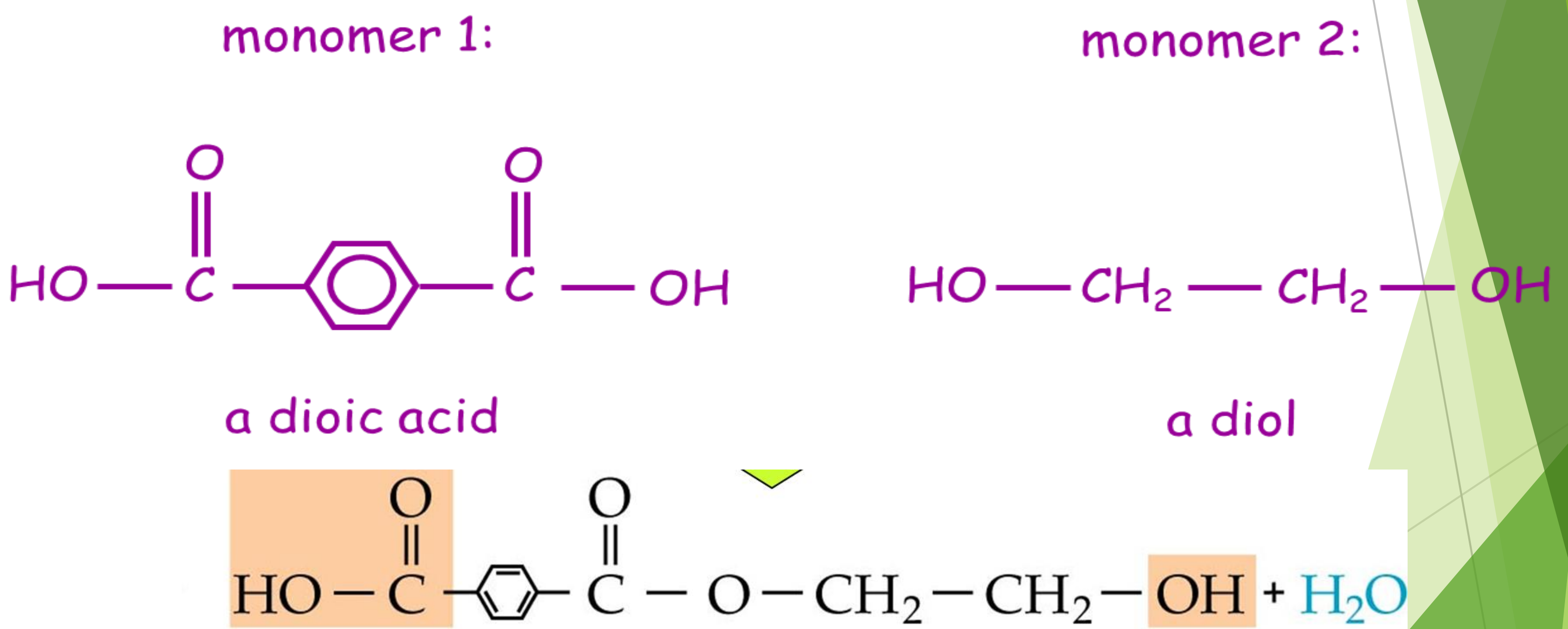
20 times as strong as steel ropes of the same weight

Used for making reinforced aircraft wings and bullet-proof vests

4.2 Polycondensation/properties

Dacron

is the DuPont trade mark for the polyester, Polyethylene terephthalate (PET, PETE, PETP) Sometimes called Terylene



Polymer chains are held together by strong dipole-dipole interaction.

4.3 Polycondensation/properties

Dacron

Strong
Tough
Smooth
Resistant to water and chemicals

4.4. Copolymerization of vinylic monomers and reactivity ratio

The polymerization reaction of vinyl monomers proceeds exactly like the homopolymerization of a monomer but it involves two or more different monomers.

Among the interests of copolymerization reaction are:

1- to improve the properties of a polymer

2- to obtain the properties of two or more homopolymers in one

3- to obtains new properties in the resulted hybrid polymer

4.4.1 Copolymerization reaction

Example:

Acrylic acid + styrene → poly(acrylic acid-co-styrene)

In a general way: nA + mB → poly(A-co-B)

In the copolymerization reaction not all A monomers always react with B monomers. This depends on the reactivity of each monomer with respect to the other.

For example: if we start from a mixture containing 50 mol% of A and 50 mol % of B, this does not necessarily give a copolymer containing 50 of A and 50 of B.

To have an idea of the composition of the copolymer resulting from a copolymerization reaction between two monomers A and B, it is then necessary to know the reactivity ratio of these two monomeric entities.

4.4.2 Reactivity ratio

The reactivity ratio is determined from the kinetic reactions of A and B during the copolymerization reaction

The kinetics of copolymerization of monomer A with B in the presence of the initiator radical Am* are written as follows:

$$\mathrm{Am}^{*} + \mathrm{A} \rightarrow \mathrm{Am\text{-}A}^{*} \begin{cases} \xrightarrow{k_{AA}} \mathrm{A} \rightarrow \mathrm{Am\text{-}A\text{-}A}^{*} \\ \xrightarrow{k_{AB}} \mathrm{B} \rightarrow \mathrm{Am\text{-}A\text{-}B}^{*} \end{cases}$$

$$\mathrm{Am}^{*} + \mathrm{B} \rightarrow \mathrm{Am\text{-}B}^{*} \begin{cases} \xrightarrow{k_{BA}} \mathrm{A} \rightarrow \mathrm{Am\text{-}B\text{-}A}^{*} \\ \xrightarrow{k_{BB}} \mathrm{B} \rightarrow \mathrm{Am\text{-}B\text{-}B}^{*} \end{cases}$$

In this case two kinetics reactions can be generated:

$\frac{dA}{dt}$= k_{AA}(**Am-A***)(**A**) +k_{AB}(**Am-A***)(**B**)

$\frac{dB}{dt}$= k_{BB}(**Am-B***)(**B**) +k_{BA}(**Am-B***)(**A**)

Dividing the first equation by the second

$$\frac{dA}{dB} = \frac{k_{AA}[Am - A^*][A] + k_{AB}[Am - A^*][B]}{K_{BB}[Am - B^*][B] + k_{BA}[Am - B^*][A]}$$

By replacing $\frac{k_{AA}}{k_{AB}}$ by R_A, $\frac{K_{BB}}{K_{BA}}$ by R_B , the mole fraction of A in the feed $\frac{[A]}{[A]+[B]}$ by f_A and the mole fraction of A in the copolymer $\frac{\mathbf{d}[A]}{\mathbf{d}[A]+\mathbf{d}[B]}$ by F_A f_A + f_B =1 and F_A+F_B=1

The reactivity ratio equation

$$\frac{dA}{dB} = \frac{k_{AA}[Am - A^*][A] + k_{AB}[Am - A^*][B]}{K_{BB}[Am - B^*][B] + k_{BA}[Am - B^*][A]}$$

can be written as follows:

$$F_A = \frac{R_A \times f_A^2 + f_A f_B}{R_A f_A^2 + 2 f_A f_B + R_B f_B^2}$$

5 cases can arise:

If **R_A ~ R_B** $>$ 1 → Block copolymer

If **R_A ~ R_B = 1** → Random copolymer

If **R_A = R_B = 0** → Alternating copolymer

If **R_A** $\sim$ **R_B >> 1** → Mixture of two homopolymers

If **R_A < 1 and R_B < 1** → Azeotrope system (feed composition = copolymer composition)

From this equation, knowing the reactivity ratios R_A and R_B, we can evaluate the composition of co-monomers in the copolymer.

In general the reactivation ratios are given in the tables.
For examples

Monomer A	Monomer B	RA	RB
Styrene	Butadiene	1.0	1.0
Styrene	Vinyl acetate	0.55	0.35
butadiene	Methyl methacrylate	0.98	1.05
Acrylonitrile	Butadiene	0.02	0.05
Vinyl acetate	Methylacrylate	0.71	0. 34
Vinyl chloride	Vinylidene chloride	2. 30	3.56

Exercises

Exercise 1. Using the data of the previous table indicate the dstribution in co-comonomers in poly(Styrene-co-butadiene).

Exercise 2. Using the data of the previous table indicate the dstribution in co-comonomers in poly(Sthyrene-co-vinyl acetate).

Exercise 3. Using the data of the previous table indicate the dstribution in co-comonomers in poly(Butadiene-co-methyl methacrylate).

Exercise 4. Using the data of the previous table indicate the dstribution in co-comonomers in poly(Acrylonitrile-co-butadiene).

Exercise 5. Using the data of the previous table indicate the dstribution in co-comonomers in poly(Vinyl acetate-co-methyl acrylate).

Exercise 6. Using the data of the previous table indicate the dstribution in co-comonomers in poly(Vinyl chloride-co- vinylidene chloride).

Corrections

Answer 1. Randum copolymer

Answer 2. Azeotropic system

Answer 3. Randum copolymer

Answer 4. Alternating copolymer

Answer 5. Azeotropic system

Answer 6. Block copolymer

5. Polymerization techniques

There are 6 ways to polymerize a monomer

1. *Bulk polymerization*
2. *Polymerization in solution*
3. *Polymerization by precipitation*
4. *Polymerization in suspension*
5. *Polymerization in emulsion*
6. Polymerization in Interface

5.1 Bulk polymerization

*need initiator and monomer only

*do not require a solvent, so the monomer must be in a liquid state, such as styrene

The polymer resulted is pure dissolved in the residual monomer (non reacted). The polymer is isolation by precipitation or by solvent evaporation.

5.2 Polymerization in Solution

*This polymerization requires the presence of a solvent that dissolves the monomer, initiator, and the resulting polymer.
*The resulting polymer is obtained by precipitating in non solvent or by solvent evaporation.

Advantages/desadvantages

Advantages

*easy way
*don't need complicated devices
*High yield and molecular mass

Desadvantages

*None economic(need solvent)

5.3 Polymerization by precipitation

*This polymerization requires the presence of a solvent that dissolves the monomer and initiator but the resulting polymer does not dissolve and is therefore easy to remove.

Advantages/desadvantages

Advantages

* Easy way
* Obtaining low molecular mass
* Don't need complicated devices

Desadvantages

None economic (need solvent)

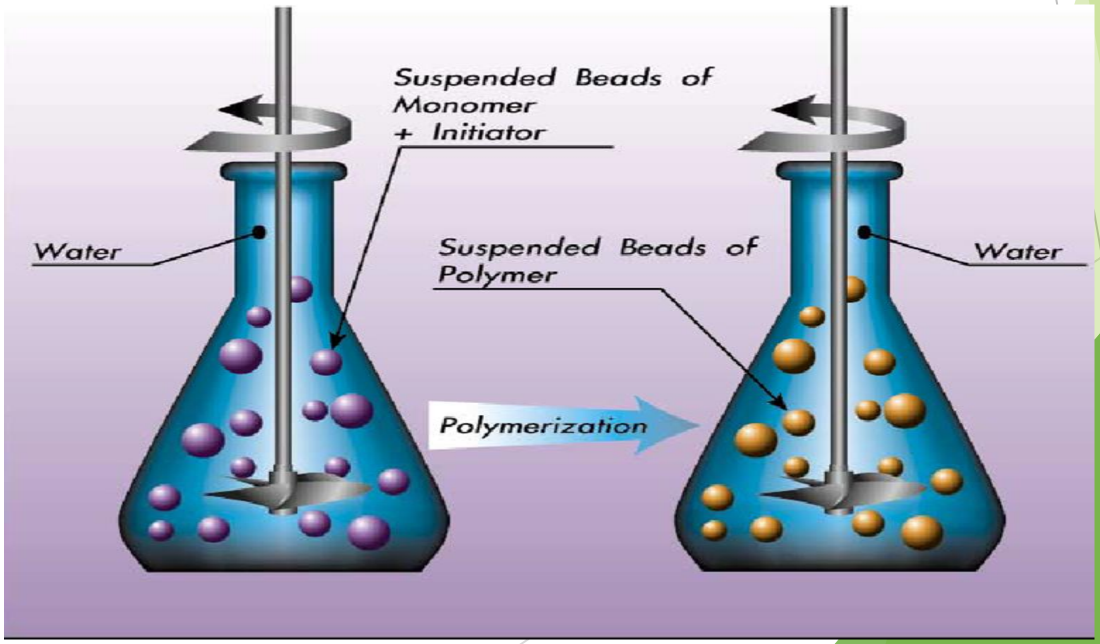
7.4 Polymerization in suspension

- This process need monomer, initiator and water

Initiator must be soluble in monomer, however both are insoluble in water.

-Initiator dissolved in monomer is in the form of a droplet in suspended in water.

-The resulting polymer is solid and insoluble in water.



5.4 Polymerization in suspension

Advantages/desadvantages

Advantages

1- The presence of water, which leads to the absorption of heat

2- The size of the polymer particles can be controlled by the suspension factor

Desadvantages

The resulting polymer is impure due to the presence of a suspension agent and is therefore not used in food applications

5.4 Polymerization in emulsion

This process needs monomer, initiator, water and surfactant (soap)

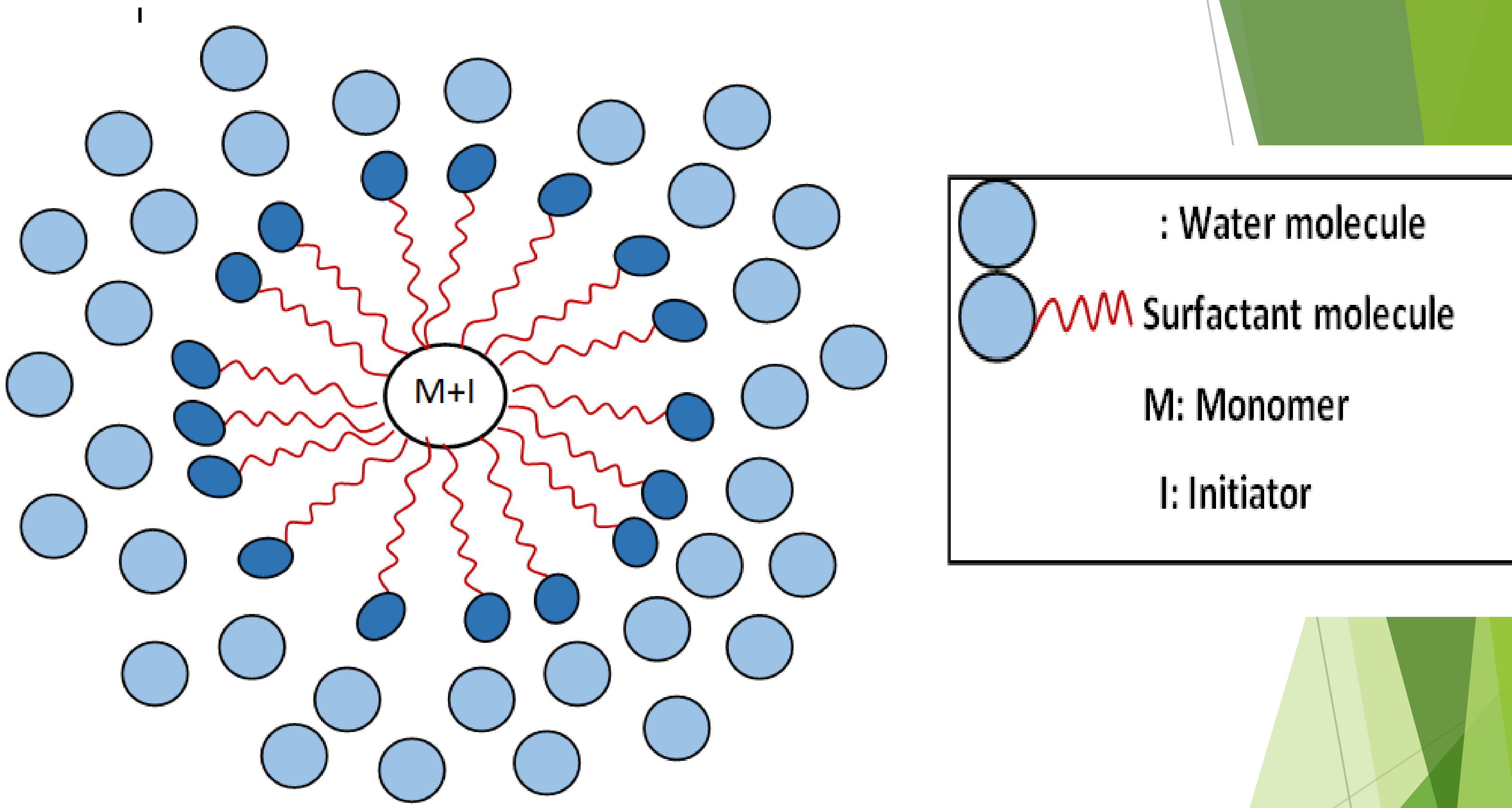
There are two types of emulsion : microemulsion rich in water (W/O) and emulsion rich in organic (O/W).

Conditions:

-This process only applies when the monomer is organic insoluble in water.

- The emulsion must be rich in water (W/O).

Micelles formation



In this case, the monomer and initiator will be surrounded by water molecules. The polymerization reaction will take place in the center of the micelle and when the polymer reaches maturity it precipitates immediately by difference in density (polymer / water).

5.4 Polymerization in interface

This process needs two monomers and water

*Two monomers, one soluble in an organic solvent and the other in water

*The polymer is formed at the interface

Such as nylon 6.6

6. Determination of molecular wights of polymers and copolymers

6. 1 Notion of molecular weight in the polymers (statistical calculation)

In a same polymer, the chains do not have the same lengths (the same masses) and this comes from the step of termination , in particular the transfer reactions. For this reason we use the term " average molecular mass" noted $\bar{M}_X$

, so there is a distribution of molecular weights. There are several ways based on statistical formula used to define an average molecular weight.

Number average molecular weight ($\bar{M}n$): $\bar{M}n = \frac{\sum Ni \times Mi}{\sum Ni}$

Ni: number of macromolecules i having a mass Mi

Weight average molecular weight ($\bar{M}w$): $\bar{M}w = \frac{\sum Ni \times M_i^2}{\sum Ni \times M_i}$

Z average molecular weight ($\bar{M}z$): $\bar{M}z = \frac{\sum Ni \times M_i^3}{\sum Ni \times M_i^2}$

Viscosity average molecular weight ($\bar{M}v$): $\bar{M}v = \left[\frac{\sum Ni \times M_i^{\alpha+1}}{\sum Ni \times M_i^2}\right]^{\frac{1}{\alpha}}$

$\bar{M}w \leq \bar{M}v \leq \bar{M}n$

When $\alpha = 1$ $\bar{M}w = \bar{M}v$ and when $\alpha = 1$ $\bar{M}v \leq \bar{M}n$

6.1Polydispersity index

The polydispersity index noted "I " is a parameter that gives an idea of the distribution of molecular masses in a sample of a polymer:

$$I = \frac{\bar{M}w}{\bar{M}n}$$

If the value of I = 1 ⟶ the polymer is "monodisperse" (all molecule chains have the same weight)

When the value of I > 1 ⟶ the polymer is "polydisperse" (all molecule chains have different weights)

"The greater the value of I, the greater the distribution of molecular masses in the polymer sample"

Importance of the molecular weight in the polymer

- 1- increase tensile strength
- 2- increase viscosity
- 3- increase chemical resistance
- 4- increase impact resistance
- 5- increase strength
- 6- decrease elongation
- 7- decrease creep
- 8-decrease melt flow

Exercises

Exercise 1: A polymer sample contains 9 moles of chains have molecular of 30,000 g/mol and 5 moles of chains have molecular weight of 50,000 g/mol. calculate $\bar{M}n$, $\bar{M}w$ and $\bar{M}z$

Exercise 2: A polymer sample contains 10^5 moles of chains have molecular weight 10^4 g/mol and 10^6 moles of chains have molecular weight 10^3 g/mol. Calculate the viscosimetric average molecular weight. given that a = 1.34.

Exercise 3: A polymer sample, synthesized by radical polymerization route, contains 10^5 moles of chains with molecular weight 10^4 g/mol and 10^6 moles of chains with molecular weight 10^3 g/mol. Calculate the number average molecular weight , the weight average molecular weight and the polydispersity index. What do you think about the distribution of molecular weight of this sample (polydisperse or monodisperse).

Exercise 4: A sample of polystyrene has the following information:
2 chain (DP= 1000), 3 chain (DP= 100), 6 chain (DP = 20) and 7 chain (DP= 40), Calculate $\bar{M}n$, $\bar{M}w$ and I

Exercises/Solutions

Exercise 1:

$$\overline{M}_n = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} = \frac{(9 \times 30{,}000) + (5 \times 50{,}000)}{(9+5)} = 37{,}000 \text{ g/mol}$$

$$\overline{M}_w = \frac{9(30{,}000)^2 + 5(50{,}000)^2}{9(30{,}000) + 5(50{,}000)} = 40{,}000 \quad \text{g/mol}$$

$$\overline{M}_z = \frac{9(30{,}000)^3 + 5(50{,}000)^3}{9(30{,}000)^2 + 5(50{,}000)^2} = 42{,}136 \quad \text{g/mol}$$

6. 2 Experimental methods used to determine the molecular masses of polymers

A- Methods based on the colligatives properties of solutions

These methods permit to determine the number average molecular weight $\bar{M}n$,

- *Freezing point depression*
- *Boiling point elevation*
- *Osmotic pressure*

B- Methods based on the light scattering and ultracentrifugation techniques.

These methods permit to determine the weight average molecular weight $\bar{M}w$

C- Methods based on the viscosity of polymeric solutions measurements. This method permit to determine the viscosimetry average molecular weight $\bar{M}v$

D- This method based on the retention volume of polymeric solution measured by the size exclusion chromatography method (SEC) also called "gel permeation chromatography" permit to determine the $\bar{M}z$

6. 2.1 Determination of molecular weight by freezing point depression

This method is used when the polymeric solution is infinitely diluted according to the Raoult's Law and only for polymers having low molecular mass

$$\frac{\Delta T_f}{C} = \frac{RT^2}{\rho \times \Delta H_f \times M_n} + A_2 C$$

ΔT_f : freezing-point depression,
C : the concentration
R : gas constant
T : freezing point
ΔHf: the latent heats of fusion
A_2 is called second coficient of **Virial** and measures the interaction between polymer and solvent.

6. 2.2 Determination of molecular weight by boiling point elevation

This method is used when the polymeric solution is infinitely diluted according to the Raoult's Law and only for polymers having low molecular mass

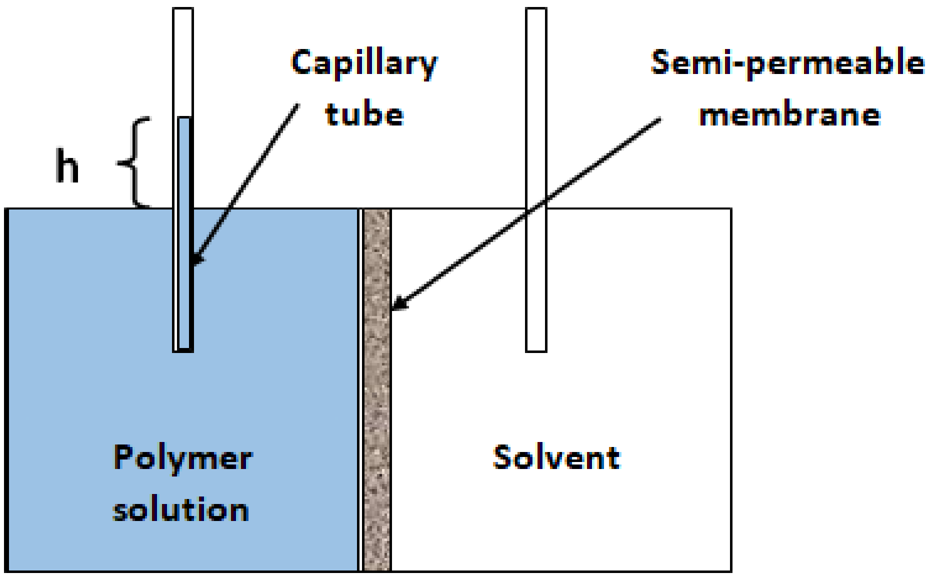
$$\frac{\Delta T_b}{C} = \frac{RT^2}{\rho \times \Delta H_v \times M_n} + A_2 C$$

ΔT_b : Boiling point depression,
C : the concentration
R : gas constant
T : freezing point
ΔHv: vaporization heats
A_2 is called second coficient of **Virial** and measures the interaction between polymer and solvent.

6. 2.3 Determination of molecular weight by Osmometry method

This method is used when the polymeric solution is infinitely diluted according to the Raoult’s Law and only for polymers having low molecular mass

According to van't Hoff equation



At infinitely diluted polymeric solution $(C \longrightarrow 0)$

$$\frac{\pi}{C\ (c \to 0)} = \frac{RT}{\bar{M}n}$$

Where π is the osmotic pressure = h x σ x g

h: The height of the polymeric solution in the capillary tube

σ: density of the polymeric solution

g: the gravitational force

C: concentration of the polymeric solution

Example: calculation of molecular mass by osmometry method

The osmotic pressures of solutions of poly(vinylchloride), PVC, in cyclohexanone at 298K are given below. The pressures are expressed in terms of the heights of solution (of mass density ṗ = 0.980 g.cm^{-3}) in balance with the osmotic pressure. The concentration of this polymeric solution is 1.0 g/dm^3 and the height of the solution in the capillary tube is 0.21 cm. If the concentration of the polymeric solution is considered as infinitely diluted Determine the molar mass of the polymer.

$$M = \frac{RT}{\rho \times g} \times \frac{1}{0.21 cm g^{-1} dm^3}$$

$$M = \frac{(8.3145 JK^{-1} mol^{-1})}{(980 kgm^{-1}) \times (9.81 ms^{-2})} \times \frac{298K}{2.1 \times 10^{-3} m^4 kg^{-1}} = 1.2 \times 10^2 kg.mol^{-1}$$

M = 1200000 g/mol = 1.2 10^6 g/mol

6.2.4. Determination of molecular weights of polymers by Light scattering method

This method is used to determine any molecular weights,

but very sensitive to solid impurities. the solution must be clean and filtered carefully.

Precautions

1- The polymer solution should be completely free of impurities
2- There should be a difference between the refractive index of the solvent and the polymer

$$\tau = Hc\,\overline{M}_W$$

$$H = \frac{32}{3}\pi\,\frac{N_o^2(dn/dc)^2}{\lambda^4 N_o}$$

Rayleigh Equation:

$$\frac{Hc}{\tau} = \frac{1}{\overline{M}P(\theta)} + 2A_2C$$

Ʈ= turbidity

C : concentration

no: refractive index of the solvent

λ : wavelength of the incident light

No : Avogadro's number

dn/dc : specific refractive increment

P(□) : function of the angle,θ

A2 : second virial coefficient

6.2.5 Determination of molecular weights of polymers by viscosimetry method

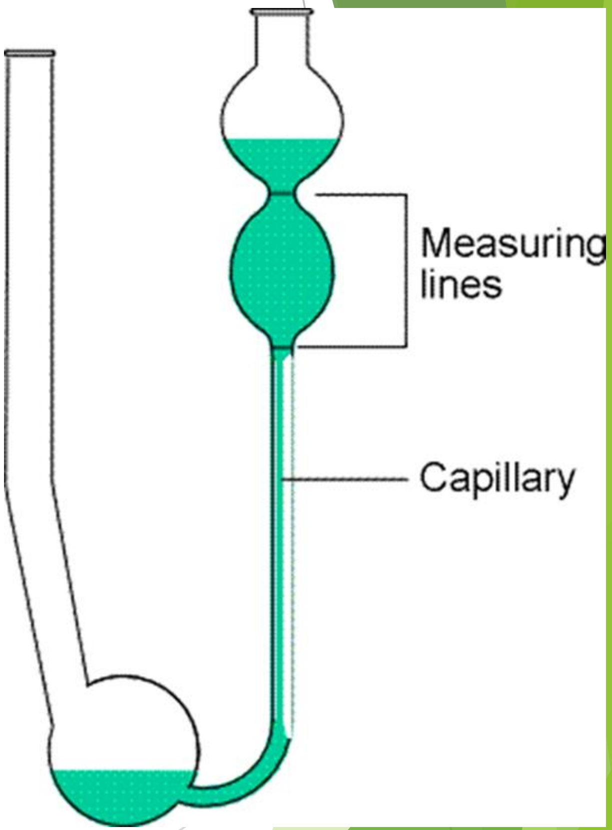
This technique is very sensitive to <u>solid impurities</u>. Any solid imurity in the capillary tube reduces the flow rate. Therefore prepared solution must be devoid of any solid impurities. <u>Filtration of the solution is necessary</u>.

Relative viscosity: $\eta_{rel} = \frac{t}{t_o}$

Specific viscosity: $\eta_{sp} = \frac{t - t_o}{t_o}$

Reduced viscosity: $\eta_{red} = \frac{\eta_{sp}}{c}$

Intrinsic viscosity: $[\eta] = \eta_{red}$ when $C \rightarrow 0$



Ubbelohde viscosimetry tube

According to the Mark Houwink and Sakurada equation

$$[\eta] = K\bar{M}_v^a$$

Where "K" and "a" are constants depending to the nature of the polymer sample, solvent and experimental temperature.

6.2.6 Determination of molecular weights of polymers by viscosimetry method

Example: **What is the average molecular weight of polystyrene is its intrinsic viscosity is 1.42 g/dm^3 and the constants "a" and "k" are 0.88 and 1.5 10^{-3}, respectively.**

$$[\eta] = K M_v^a$$

$$\mathrm{Ln}[\eta] = LnK + aLn\bar{M}n \qquad \frac{Ln[\eta] - LnK}{a} = Ln\bar{M}$$

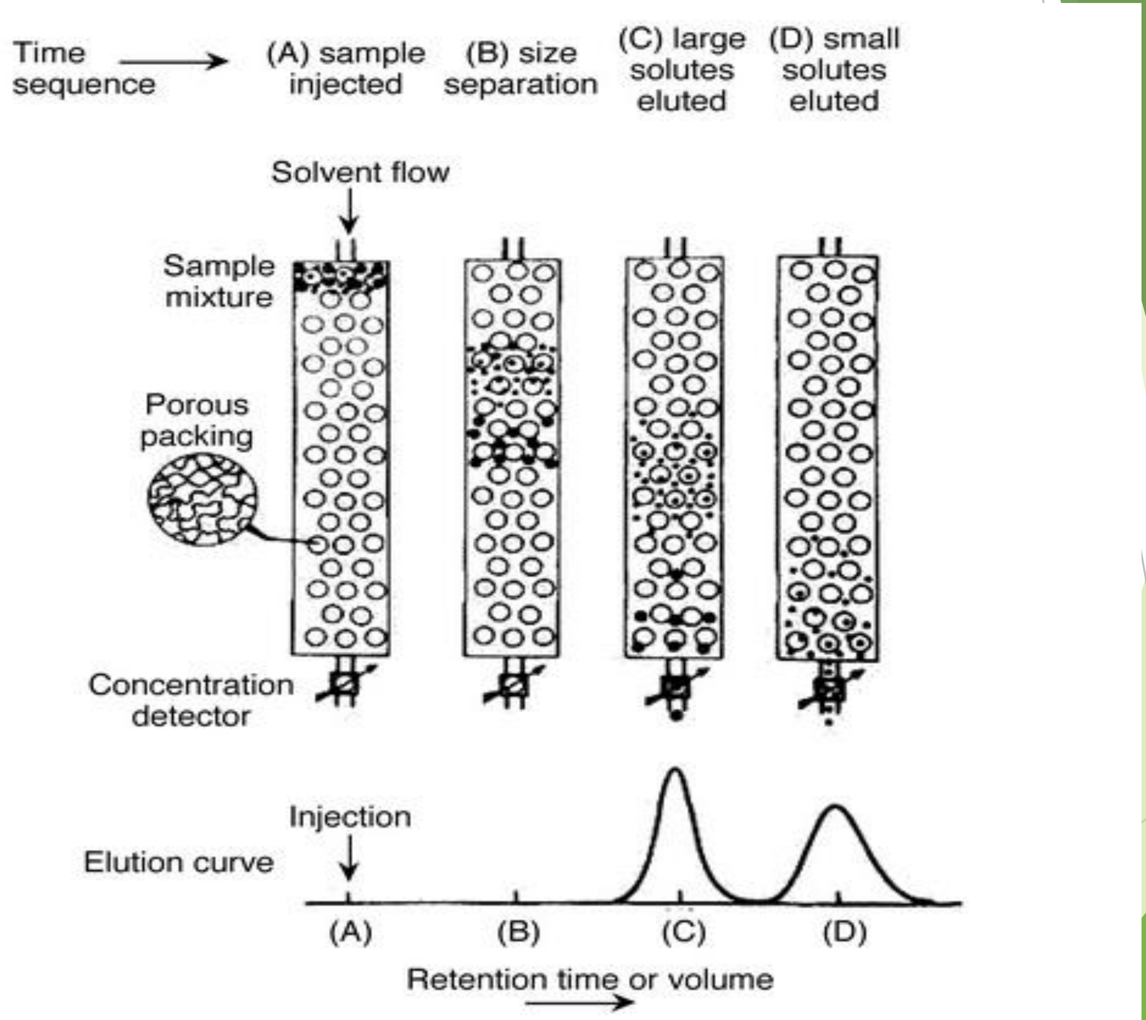
$$\bar{M}n = e^{\frac{Ln[\eta] - LnK}{a}}$$

$$\bar{M}n = e^{\frac{Ln1.42 - Ln1.510^{-3}}{0.88}}$$

$$\bar{M}n = 2286 \ g/mol$$

6.2.7 Determination of molecular weights of polymers by size exclusion Chromatography (SEC)

This technique is also called gel permeation chromatography (GPC)



HW2:What is the difference between separating organic materials and polymers by column chromatography?

Determination of average molecular weight by size exclusion chromatography (SEC) or gel permeation chromatography (GPC)

Example: **Determine the average molecular weight of poly(methyl methacrylate) by SEC technique. Given that the retention volume (Vm) is 15 mL and the standard polystyrene has an average molecular weight equal to 10^5 g/mol gives a retention volume of 14.32 mL.**

Solution:

The molecular mass of a polymer is inversely proportional to its volume of retention

$$\bar{M}w = \frac{K}{Vm}$$

$$\bar{M}w = \frac{K}{Vm}$$

$$10^5 = \frac{K}{14.32} \qquad K = 1{,}43210^5$$

$$\bar{M}w = \frac{1.43210^5}{15} = 9570 \text{ g/mol}$$

7. Degree of polymerization

The average degree of polymerization ($\overline{Dp}$ or $\overline{Xn}$ X) is defined as the number of repeating monomer units in the polymers

.

$$\overline{DP} = \frac{\text{Polymer molecular weight } (M_n)}{\text{Monomer molecular weight}}$$

Dp

Example:

If the molecular mass of a polytetrafluoroethylene is 120,000 g/mol and the molar mass of its monomer is 100 g/mol its degree of polymerization is:

120,000/100 = 1200 units

EXERCISES

Exercise 1: Calculate the degree of polymerization of nylon 6,6 if the mass of its repeated unit is: 226.32 g/mol. and the molecular mass of this polymer is 23,000 g/mol

Exercise 2: Calculate the average molecular weight of a poly(dimethylsiloxane) if the molar mass of its monomer is 74 g/mol and the polymerization degree is 2367.

Exercise 3: What is the molar mass of the monomer used to obtain a polymer with an average molar mass of 10^5 g/mol and a polymerization degree of 232.

Correction1

$$\overline{DP} = \frac{Polymer\ molecular\ weight\ (M_n)}{Monomer\ molecular\ weight}$$

With a molar mass of polymer= 23,000 g/mol

And molar mass of monomer = 226.32 g/mol

$$\overline{Dp} = \frac{23000\ g/mol}{226.32\ g/mol} = 10\ \text{units}$$

Correction 2

$$\overline{DP} = \frac{\text{Polymer molecular weight } (M_n)}{\text{Monomer molecular weight}}$$

$$Mn\ (Polymer) = Dp \times M(monomer)$$

$$Mn\ (Polymer) = 2367 \times 74 = 175158\ g/mol \approx$$

175200 g/mol

Correction 3

$$\overline{DP} = \frac{\text{Polymer molecular weight } (M_n)}{\text{Monomer molecular weight}}$$

$$M(Monomer) = \frac{\bar{M}n(polymer)}{\overline{Dp}}$$

$$M(Monomer) = \frac{10^5}{\overline{232}} = 431\ g/mol$$

Degree of polymerization

High degree of polymerization are known as polymers having high number of monomeric units ,while those having comparatively low degree of polymerization (low number of monomeric units) are known as oligomers (Dimers, trimers, and tetramers) several thousands.

Examples:

Dimers: $-[O-CH_2-CH2]_2-$; $-[CH_2-CH-Cl]_2-$; $-[Si(CH_3)_2O]_2-$
Polymerization degree is 2 (polymer having 2 monomeric units)

Trimers: $-[O-CH_2-CH_2]_3-$; $-[CH_2-CH-Cl]_3-$; $-[Si(CH_3)_2O]_3-$
Polymerization degree is 3 (polymer having 3 monomeric units)

Tetramers: $-[O-CH_2-CH_2]_4-$; $-[CH_2-CH-Cl]_4-$; $-[Si(CH_3)_2O]_4-$
Polymerization degree is 4 (polymer having 4 monomeric units)

Suplementary informations on the polymers

OLIGOMER VERSUS POLYMER

OLIGOMER	POLYMER
An oligomer is a complex molecule that is made out of a few monomer units	A polymer is a macromolecule made out of a large number of small units called monomers
The process of formation is called oligomerization	The process of formation is called polymerization
Oligomerization uses a very less number of monomers	Polymerization uses a very large number of monomers
The mass is comparatively low	The mass is comparatively high

Visit www.pediaa.com

8. Thermal properties of polymers

The thermal properties of polymers are different from those of small molecules. Polymers have neither vaporization temperature nor heat of vaporization as in the case of small organic molecules. Sometimes do not have fusion nor crystallization temperature as in the case of poly(vinyl chloride) because this polymer burns before its fusion.

*Simple molecule has 100% crystalline

*Polymers partially crystalline (amorphous and crystalline parts)

By heating the small molecules, their state changes from fusion towards vaporization and this transition is called "First order transition"

By heating the polymers, their state changes from the solid state called "<u>glassy state</u>" to the <u>soft state</u> and this transition is called the "second order transition".

8.1 Glass transition temperature (Tg)

The glass transition temperature in the polymer is the limit temperature called “Tg” localized between its glass state and its soft state.

When the chains of the polymer absorb a certain energy (second transition energy) the chains begin to slide against each other due to the breaking of certain physical bonds such as van der Waals, hydrogen bond, newton etc.

8.2 Melting temperature (Tm)

When the chains of the polymer absorb a certain energy (first transition energy) all the chains slide against each other due to the breaking of physical bonds such as van der Waals, hydrogen bond, newton etc.

8.3 Crystallization temperature Tc

During the cooling of the polymer from the fusion state to a certain temperature called crystallization temperature the polymer releases the energy which it absorbed during the fusion causing the immobility of the chains due to the development of the interchain forces again.

8.4 Temperature of degradation Td

At temperatures higher than that of fusion, the polymer degrades according to a radical mechanism. The products that generate the degradation are:

1- Radical reactions between related chains giving cross-linking polymer.

2- Radical reactions accompanied by chain scission resulting in the formation of chain fragments.

3- Elimination reactions leading to the evaporation of small molecules such as H_2O, CO_2, ethylene, benzene, etc.

4- Sometimes among the products of thermal decomposition of the polymer we find the regeneration of the monomer.

8.5 Transition phenomenon

Structure- thermal properties relationship

Factors affecting Tg

There are 7 factors affect on Tg value

1-chain flexibility

2- interchain attractive forces

3- side group

4- Cross linking

5-crystallinity

6- plasctization

7- molecular weight

1-chain flexibility

1- Long chain aliphatic

2- Ether and ester linkage

Flexibility ↑ ⟶ Tg ↓

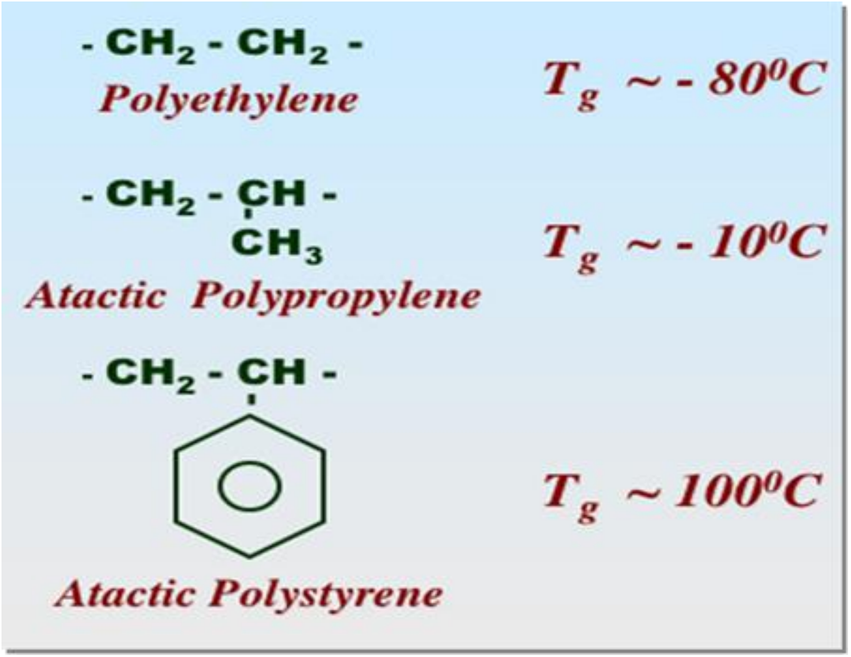
2- interchain attractive forces

With increasing increases Tg   Tg of PVC (87) > Tg of PE (-120)

3- side group

With increasing size of side group increases Tg

Tg of PS (100) > PE (-120)



4-Crosslinking

Crosslinking leads to increasing of Tg (HW such as)

5- Crystallinity

With increasing crystallinity % decrease Tg

6- Plasctization

Decrease Tg

7- Molecular weight

Increase Tg

Tg of PP (0) > Tg of PE (-120)

8.6 Determination of the thermal parameters

There are different techniques used to determine the differents thermal parameters.

1- The differential scanning calorimetry (DSC)

2- The thermogravimetry analysis (TGA)

3- The inverse gas chromatography (IGC)

4- The thermal dynamic mechanical Analysis (TDMA)

We mention in this program only the most commonly techniques used such as the DSC and theTGA.

1- <u>DSC Analysis</u>

This technique is based on the measurement of the heat released or absorbed by the polymer during its heating. Since the heat capacity (Cp (glass)) of the glass state is different from that of the soft state (Cp(solft)), during the transition from one state to another the materials keep the temperature constant. during this time they absorb or release energy called transition energy.

Before the glass transition the heating enthalpy is:

$\Delta H_1 = C_p(glass)(T_g - T_1)$

After the glass transition the heating enthalpy is:

$\Delta H_2 = C_p(soft)(T_2 - T_g)$

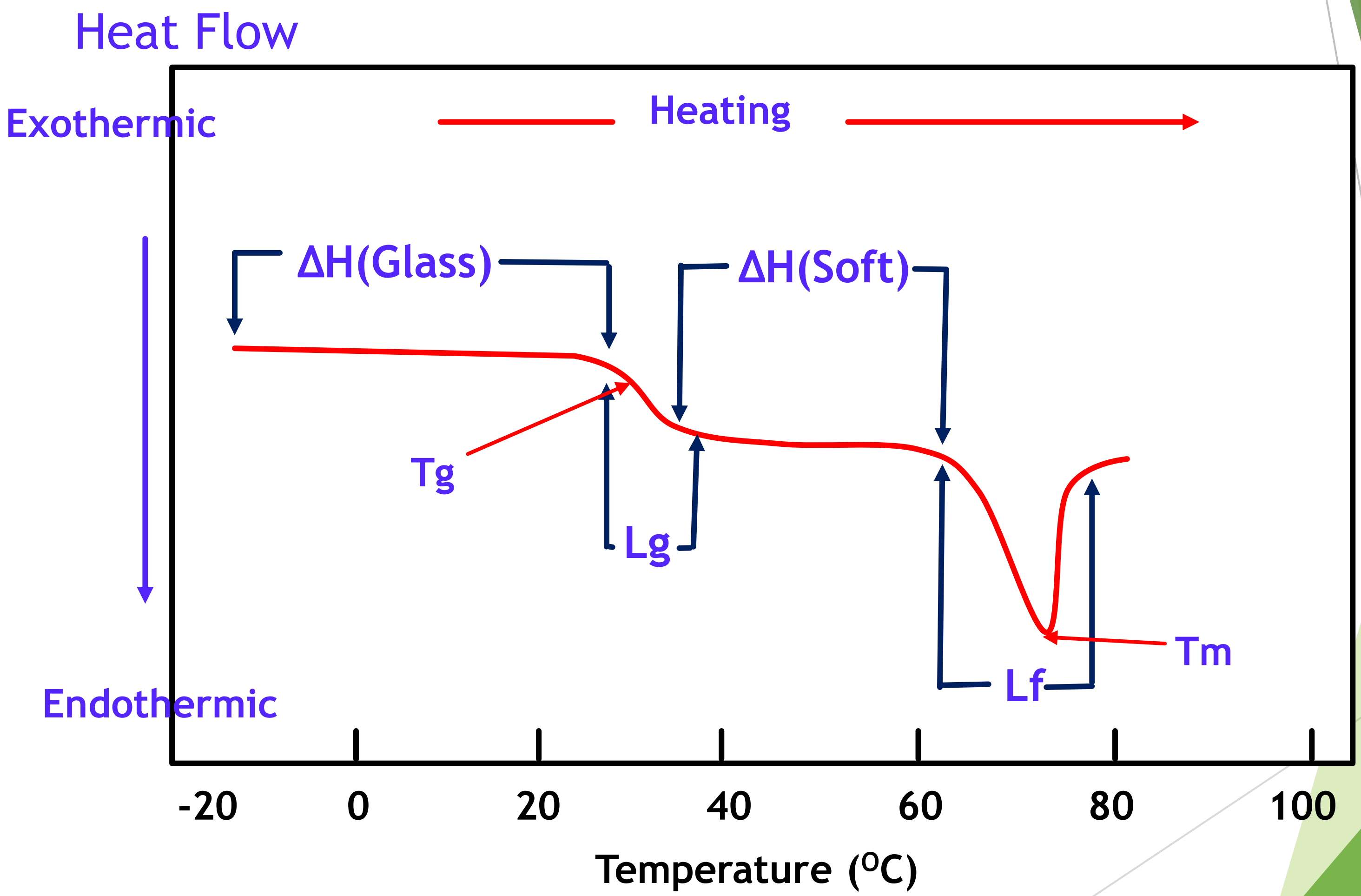
During the glass transition the enthalpy absorbed is the **latent heat of glass transition (Lg)** and during fusion the enthalpy absorbed is **the latent heat of fusion (Lf)**. These two parameters are practically **independent of temperature**.

The total heat (ΔH_T) required to heat the polymer from start to finish is equal to:

$$\Delta H_T = C_p(glass)(T_g - T_1) + L_g + C_p(soft)(T_2 - T_g) + L_f$$

The variation of the heating enthalpy as a function of temperature is represented by as following curbe called "**DSC thermogram**":

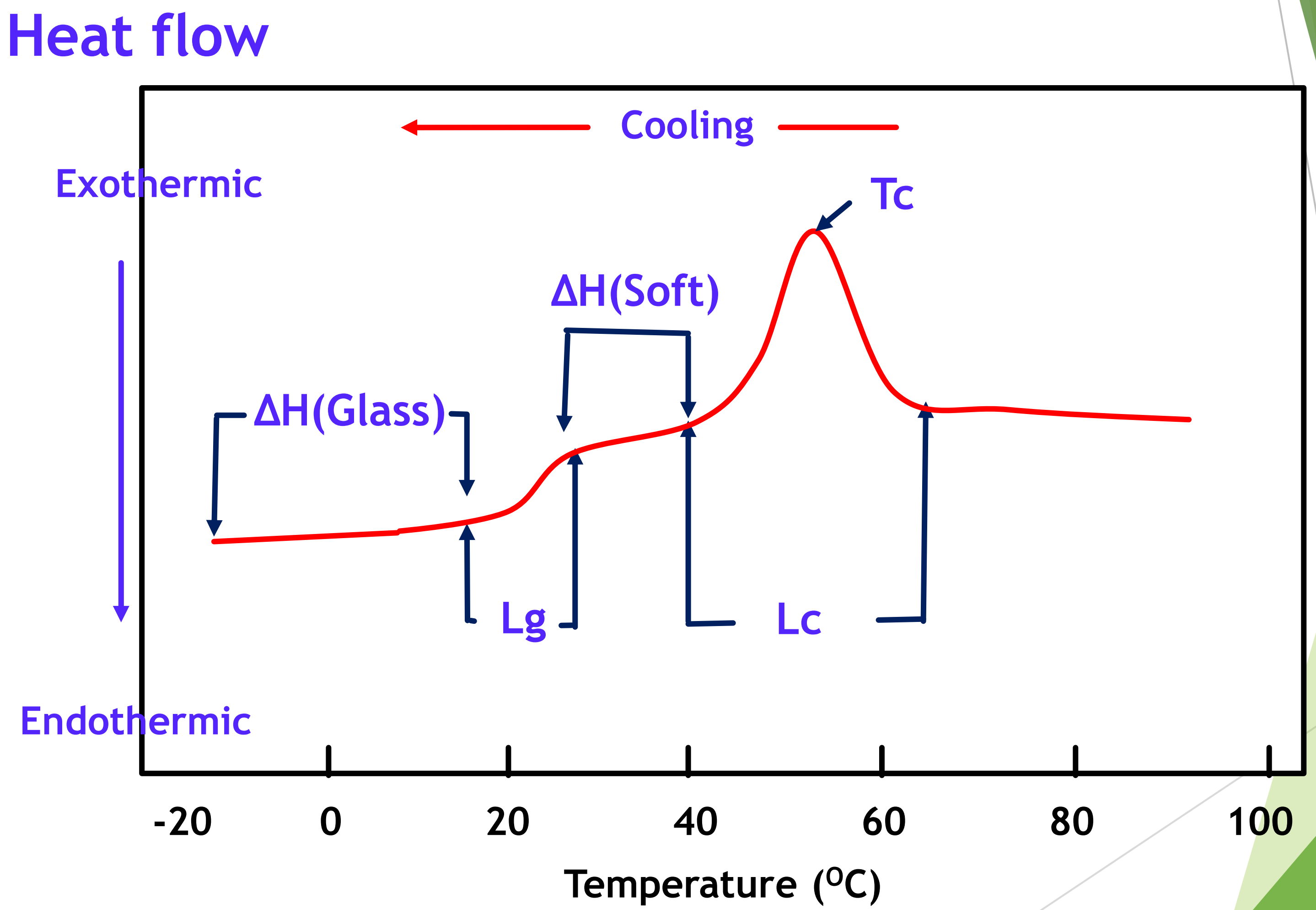
DSC Thermogram (Heating mode)



During the cooling, the polymer passes from the liquid state where it is at high temperature through the crystalline state, then through the soft state and finally it will end up in the glass state (solid).

During this step, the polymer first releases the heat that was absorbed during fusion which is called the heat of crystallization (ΔH (crystallization) then the soft state and puts back the heat of the glass transition to pass to the glass state as shown in the DSC diagram below. Noting in this case all energy are exothermic.

Thermogram DSC (Cooling mode)

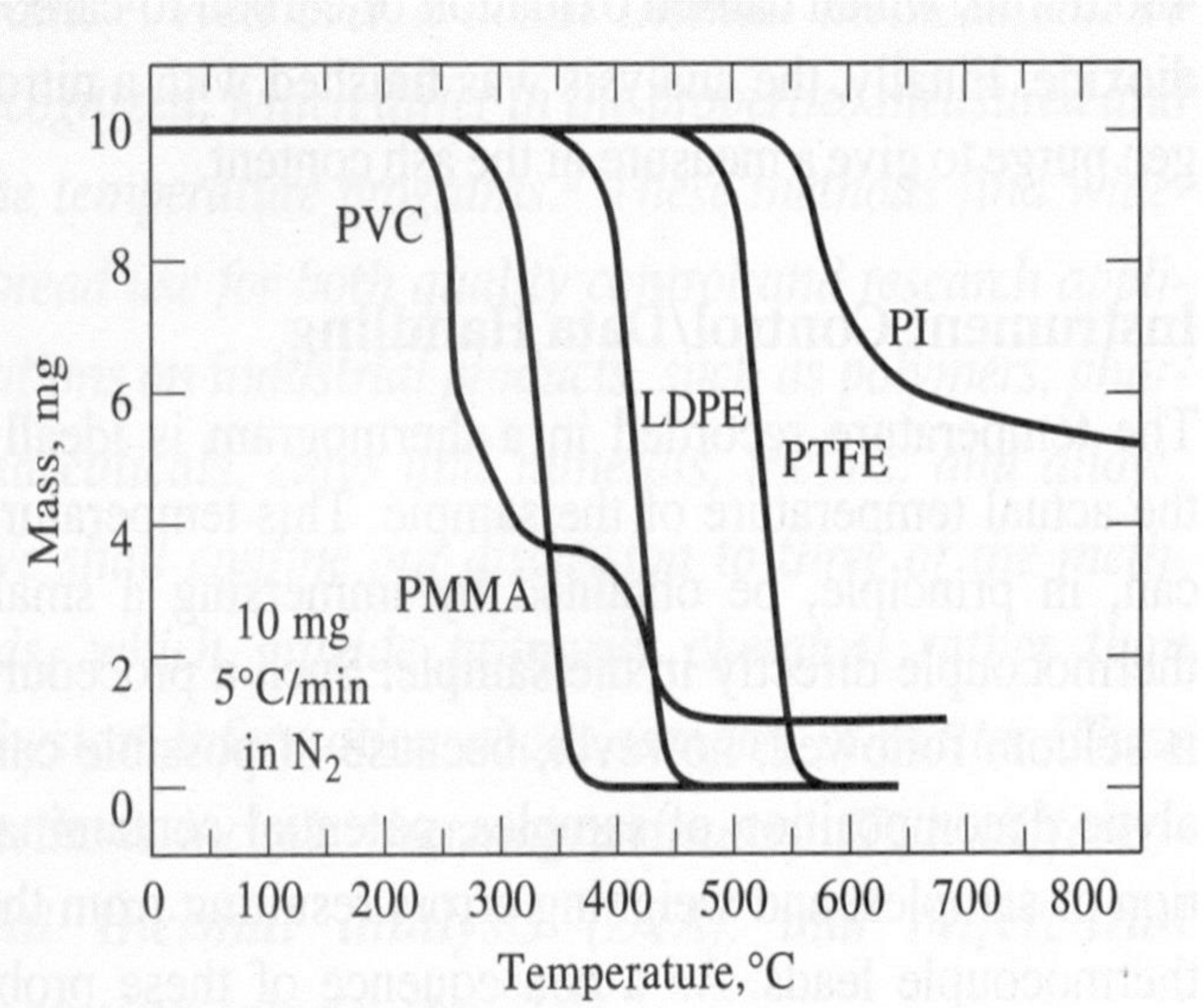


2-Thermogravimetry Analysis (TGA)

This technique measures the weight loss of the polymer sample during the period of its thermal degradation using a microbalance incorporated into the analysis system.

This analysis generates a curve indicating the weight loss of the polymer sample versus temperature called "TGA thermogram".

The first break in this thermogram indicates the limit of the thermal stability of the polymer. In the Figure, different TGA thermograms attributed to the degradation of poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), low density polyethylene (LDPE), poly(ethylene terephthalate) (PTFE) and polyisoprene (PI).
These thermograms shows the thermal stability (TS) of each polymer. TS(PVC) = 220 ^{o}C; TS(PMMA) = 260^{o}C; TS(LDPE)= 340^{o}C; TS(PTFE) = 450 ^{o}C and TS(PI) = 520^{o}C.



PVC
PMMA
LDPE
PTFE
PI
10 mg
5°C/min
in N_2
Mass, mg
Temperature, °C
0
2
4
6
8
10
0
100
200
300
400
500
600
700
800

9-Solubility of polymer

Solution(solvent +polymer)

types of solvents:

1- good solvent

2- bad solvent

3- Edge solvent(theta solvent)

The factors affecting on the solubility of polymers

1- polarity

2- Mwt ↑ Solubility ↓

3- Cross linking ↑ S ↓

4- Crystalinity ↑ S ↓