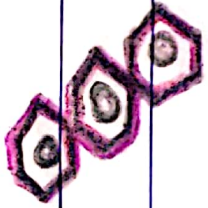
# Polymer....



Donya Salman ....

→ So you can do it
only focus......

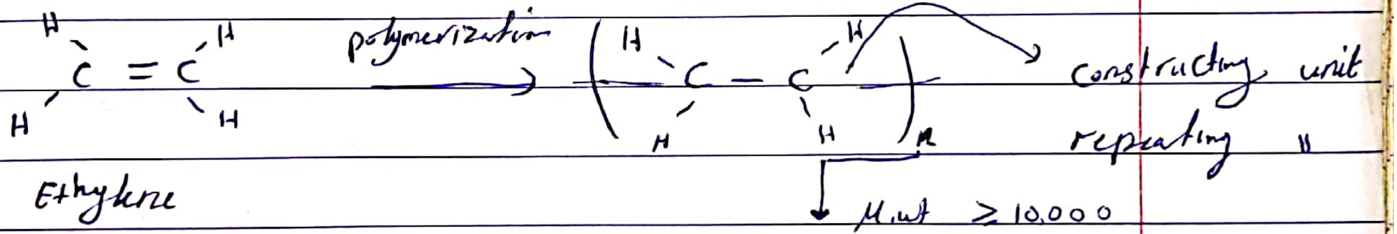
# polymer

1 Introduction
- Definition
- Types of polymers
- M.wt of polymers

2 step - Rxn polymerization

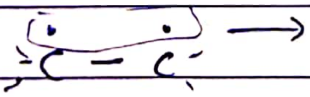
3 Chain - rxn polymerization

* poly Ethylene (PE)
* poly Ethylene Terphthalate (PET) or (PETE)



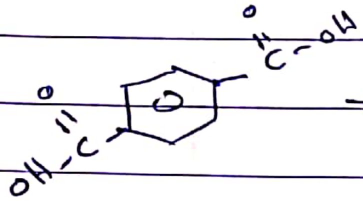
$n \geq \frac{10,1000}{28} \Rightarrow$ polymer حتى نحكي عليها

*Monomers should contains two functional group to polymerization occurs ($f = 2$)



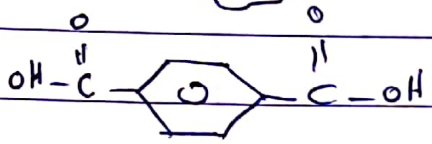
→ these two radicals ($f = 2$)

∴ So can make polymer



$+ CH_3CH_2OH \xrightarrow{poly} X$

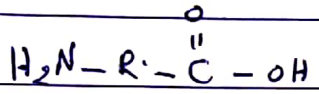
$f = 2$



$f = 2$

$+ OH CH_2 CH_2 OH \longrightarrow$ PET

ethylene glycol



$H_2N-R-\overset{O}{\overset{\|}{C}}-OH \longrightarrow f = 2 \longrightarrow$ so making polymer

$\boxed{4}$ Co-polymers

# # Chap. 1

## Introduction

Polymer ( Multi = متعدد )

Monomer ( $\xrightarrow{\text{polymerization}}$ ) polymer

A $\longrightarrow$ AAA

A + B $\longrightarrow$ AAABBB .....

co-polymer ABABAB ...

or $[AB]_n$

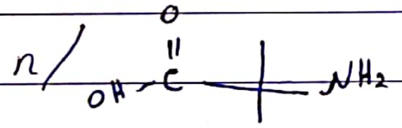
$\left.\right\}$ M.wt ≥ 10,000 (g/mol) (dalton)

M.wt < 10,1000 → oligomer

monomer $\longrightarrow$ Polymer

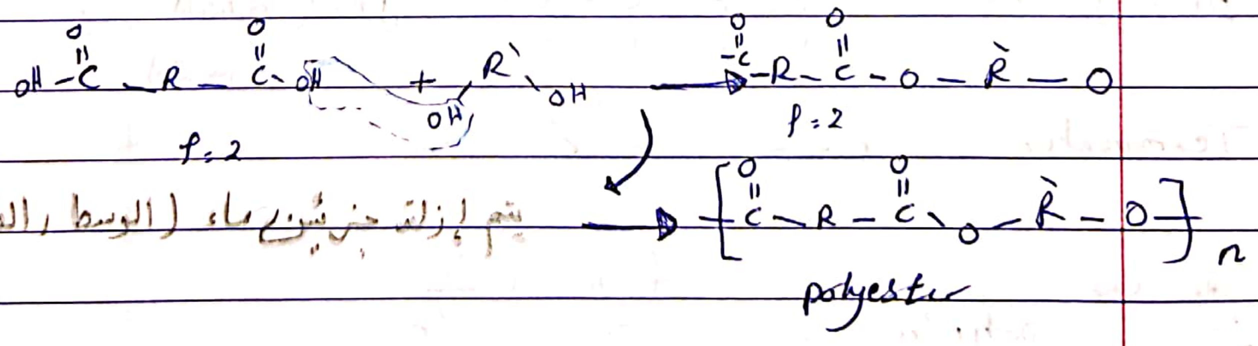
↓

must have 2 functional



$n\ HO-\overset{O}{\overset{\|}{C}}-|-NH_2 \longrightarrow$ protein (polymer)

polyester ⟸ diacid + diol ⟹ ex. is PET product



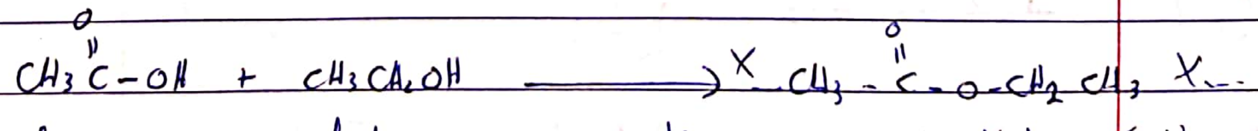
$HO-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH + R'(OH)_2 \longrightarrow -\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-O$

f = 2 f = 2

يتم إزالة جزيئين ماء (الوسط ، الطرف)

$\longrightarrow \left[\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-O\right]_n$

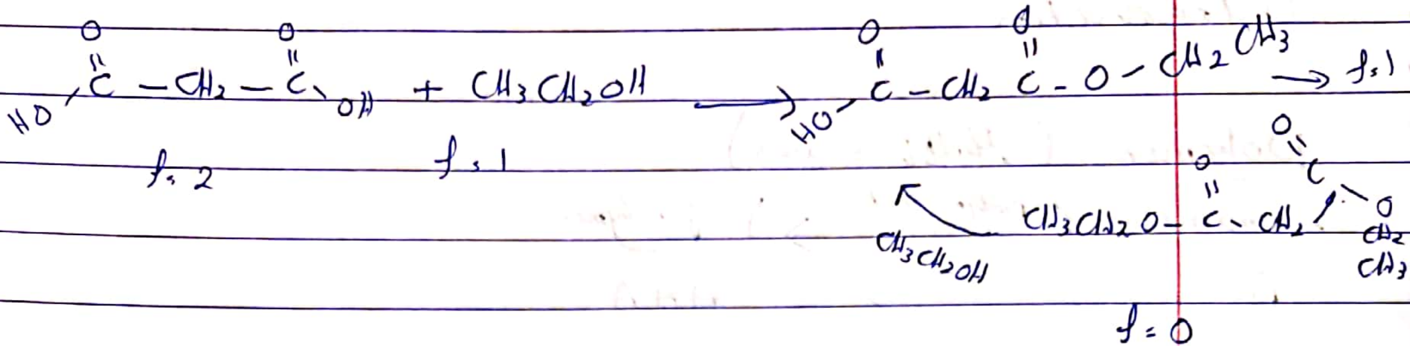
polyester



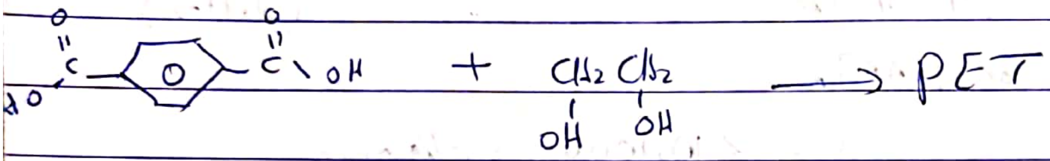
$CH_3\overset{O}{\overset{\|}{C}}-OH + CH_3CH_2OH \longrightarrow X\ CH_3-\overset{O}{\overset{\|}{C}}-O-CH_2CH_3\ X$ ...

f = 1 f = 1

لا يمكن اضافه المزيد من الجزيئات



like PET



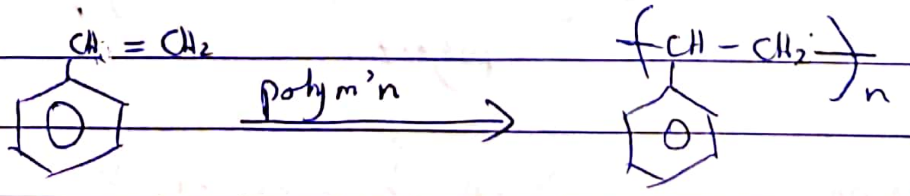
$$CH_2 = CH_2 \xrightarrow{\pi - \text{bond } (f = 1)} \left( -\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \right)_n \quad (PE)$$

Polymerization $f = 2$

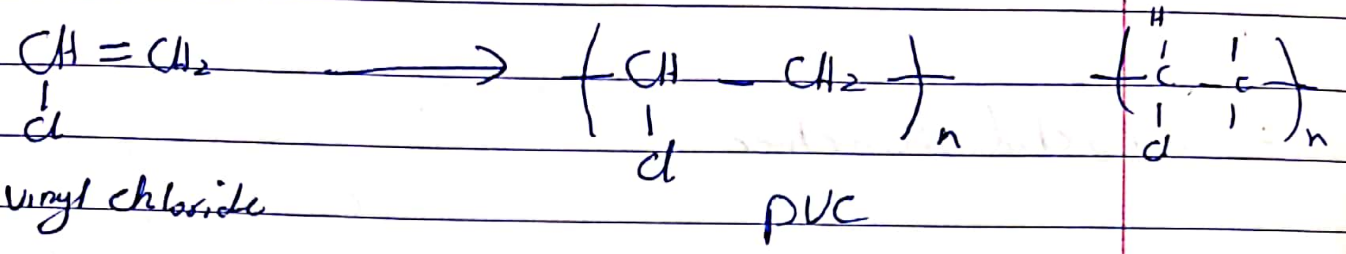
① Initiation $\Rightarrow -\dot{C}-\dot{C}-$

② propagation $\cdot C - C - C - C \cdot$ يبقى حامل (2 radicals)
التفاعل

③ Termination $\dot{C} - - - - \dot{C}$



styrene Polystyrene (PS)



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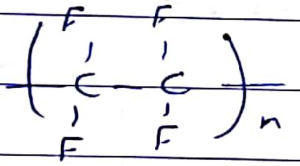
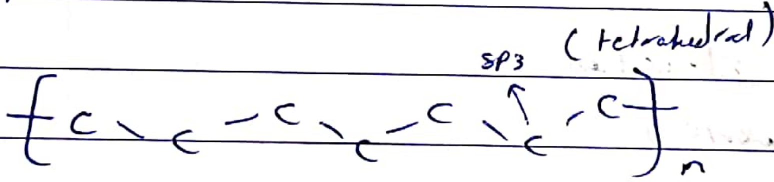
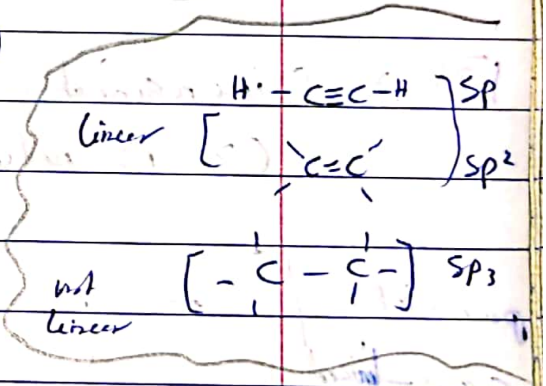
Main polymeric structure :-

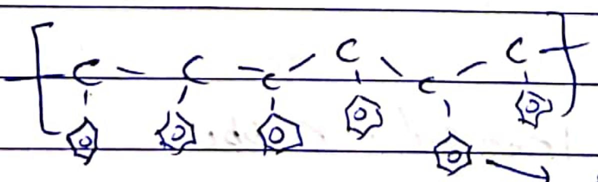
[1] linear structure : PE , PET , PS , PVC , Teflon

 ⟹ Teflon



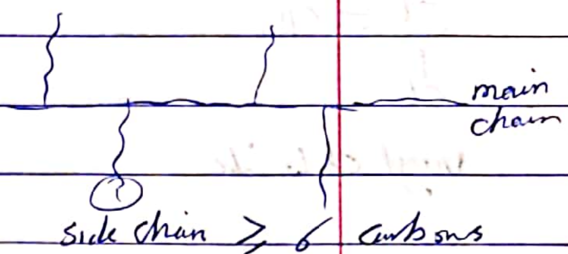


* هنا ننظر إلى البوليمر بشكل كامل، نُهمل الهيدروجين لذلك تم اعتباره خطي

 → linear

⟸ لأنّ حجم الحلقة صغير جداً بالنسبة لطول السلسلة
( Cl , Fl , $CH_3$ ---- ... ) أيضاً نفس الإشي

## 2) Branched structure

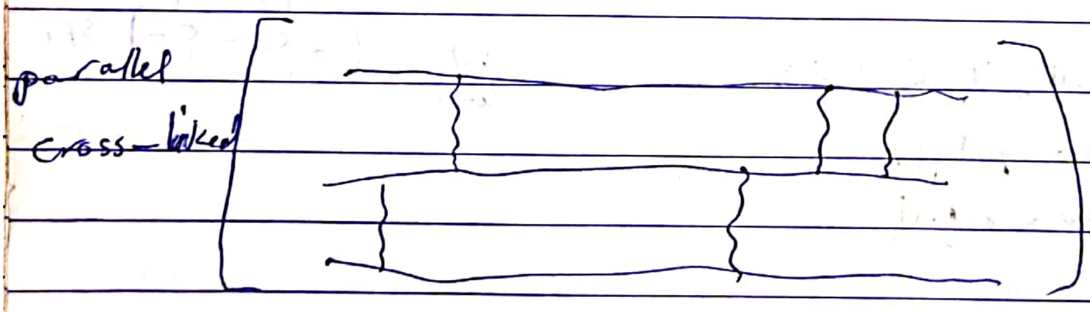


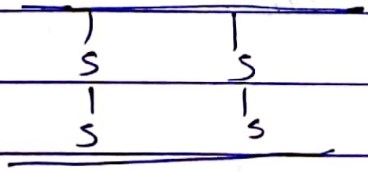
Plastics → Thermoplastic → تنصهر وتشدد بالحرارة → قابل للتدوير وإعادة التشكيل

اللدائن → Thermosets → لا تنصهر ولا تشدد بالحرارة → غير قابل للتدوير

* لا يوجد للبوليمر درجة غليان ، له درجة إنصهار

## 3) 3-Dimensional structure
(3-D network)





Volcanised - rubber
⇐ مطاط قاسي
من خلال اضافة
الكبريت

## Classification of polymers

$\| + \| + \| + \cdots \longrightarrow \left( \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} \right)_n$ , Addition polymers

diol + diacid $\longrightarrow$ polyester + $H_2O$ , Condensation rxns

تصنيف حسب التركيب

Carothers polymer → Additions polymers (PE, PS, ---)

حسب طريقة التحضير

Carothers polymer → Condensation polymers (Polyamid, poly ester, protein, Cellulose ---)

↕

حسب ميكانيكية التفاعل

Flory (Mecanism) → Chain - rxn polymers (||)

(Initiation, ———)

Flory (Mecanism) → step - rxn polymers (Condensation)

" -growth "

" -wise "

* نفس التفاعل فقط يختلف الاسم حسب العالم المصنف

## Molecular weight of polymers

monomer $\xrightarrow{\text{polym'n}}$ Polymer (matromolecules)

M.wt > 10,000

تعبر عنها average M.wt ($\overline{\overline{M.wt}}$)

100,000

401,000

601,000

يعطي أكثر من نوع

chain with different M.wt

$\overline{Mwt}$ = Dp * molar mass of CRU

Dp : Degree of polymerization in

CRU : contructing Repeating unit

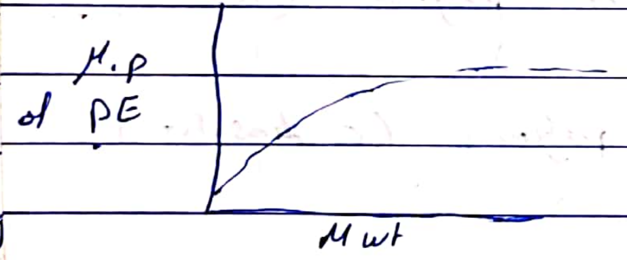
Ex :-

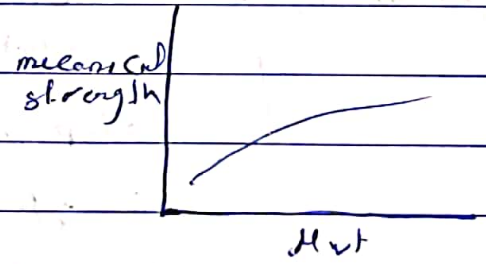
$n\ CH_2=CH_2 \longrightarrow \left( \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} \right)_n$ M.wt = 30,000

30,000 = Dp (n) * 28

$Dp = \frac{30,000}{28} = 1071$

Many properties of polymer depend on M.wt of polymers





Molecular weight calculation

Colegative properties

① Freezing point depression $\Delta T_f = mK_f$

② Boiling point elevation $\Delta T_b = mK_b$

③ vapor pressure $\Delta P = P^{\circ} X_A$

④ Osmotic pressure. $\pi = MRT$.

## $\boxed{1}$ Number Average of Molecular weight ($\bar{M}_n$)

$$\bar{M}_N = \frac{\sum_{i=1} M_i N_i}{\sum_{i=0} N_i}$$

(molecules = mole = N): no. of series

M: M.wt of each no. of series

Example: Consider polymer sample contains 5 mole of polymer having 40,000 g/mol and 15 mol having 30,000 g/mol of M.wt

$$\bar{M}_n = \frac{5(40,000) + 15(30,000)}{20}$$

$$= 32,500 \text{ g/mol}.$$

## $\boxed{2}$ Weight Average of Molecular weight ($\bar{M}_w$)

$$\bar{M}_w = \frac{\sum_{i=1}^{\infty} N_i (M_i)^2}{\sum_{i=1}^{\infty} N_i M_i}$$

$$\bar{M}_w = \frac{5(40,000)^2 + 15(30,000)^2}{15(30,020) + 5(40,000)}$$

$$= 33,076.9 \text{ g/mol}.$$

* الذي له وزنه جزيئي الكبير له مساهمه أكثر في ← average weight

Donya .....
2022 ...

①* $\bar{M}_w > \bar{M}_n \Longrightarrow$ if $\bar{M}_n = \bar{M}_w$ so chain have same length

②* poly dispersity $\frac{\bar{M}_w}{\bar{M}_n}$ always $\geq 1$

if $\frac{\bar{M}_w}{\bar{M}_n} = 1 \longrightarrow$ homogenous

$\frac{\bar{M}_w}{\bar{M}_n} < 1$ ✗ (no)

$\frac{\bar{M}_w}{\bar{M}_n} > 1$ different in chain lengths

$\bar{M}_{wt}$ & $\bar{M}_n \longrightarrow$ هي المستخدمة أكثر (because we measure poly dispersity)

**3** Z - Avarage Molecular weight ($\bar{M}_z$)

$$M_z = \frac{\sum N_i M_i^3}{\sum N_i M_i^2}$$

$M_n = 32500$ g/mol
$M_w = 33076.9$ g/mol
$M_z = 33720$ g/mol.

اللزوجة

**4** Viscosity Avarage Mw ($\bar{M}_v$)

$M_v$ depend on (Conc. & length of molecule)
(Mwt)

Donya
20/4/2022

$$M_v \overset{\alpha}{=} \left( \frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{\frac{1}{2}}$$

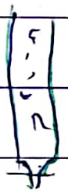
له علاقة بالمذيب الذي نقيس به اللزوجة

a: constant depend on solvent polymer (in the viscosity)

$\boxed{3} + \boxed{4} \longrightarrow$ ليست شائعة

## Molecular weight Analysis of polymers

① Gel permeation chromatography (GPC)

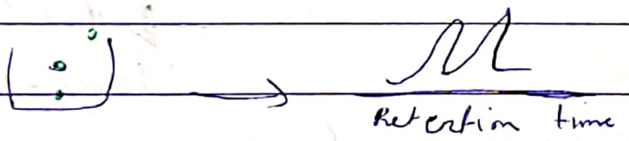


depends on size of molecule ) M.wt

large molecule → small molecules

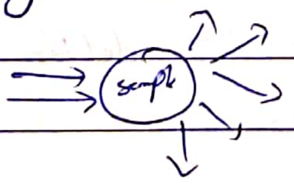
↓

يمشي أسرع



الوقت الذي تأخذه الجزيئات لتخرج....

② light scattering



Intensity of scattered light depends on

Ⓐ Concentration
Ⓑ Size of particles } M.wt + Shape
Ⓒ Polarizability الاستقطاب → صفة ليس كثيراً بالبوليمر

لمعرفة اطوال الروابط والزوايا بالمركب

شبه كريستال

③ X-ray scattering → sample must be semi crystal
wave length (0.001 nm to 0.2 nm)

two types of x-ray :
* wide angle x-ray scattering (WAXS) → orientation of crystall
* Small angle x-ray scattering (SAXS) → electron density

ē density →

④ Osometer

a) Vapor-Pressure Osometry
b) membrane Osometry

$$\pi = MRT = \frac{n}{V}RT = \frac{\frac{m}{M.wt}}{V}RT \rightarrow M.wt = (10-40)10^3$$

$(10000 - 40000)\frac{g}{mol}$

Ⓠ :-
A polymer sample has 5 macromolecules of M.wt = 10,000 da
& 20 macromolecules of M.wt = 30000 da (g/mol)
& 25 " " " = 40,000 da
& 10 " " " = 20,000 dalton
Find $\bar{M}_N$ & $\bar{M}_w$ & poly dispersity ??

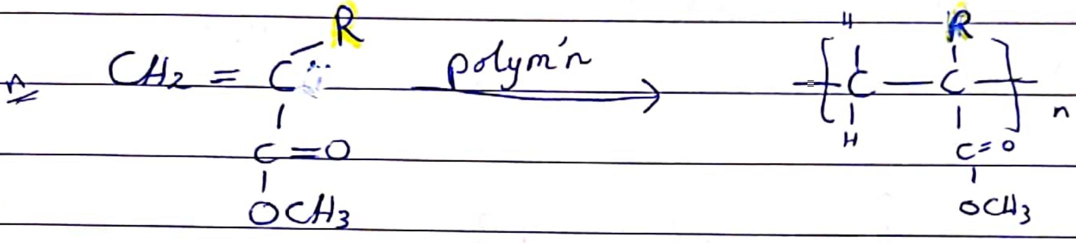
- $\bar{M}_N = 30833.33$
- $\bar{M}_w = 33783.8$
- $\text{Poly dispersity} = \frac{\bar{M}_w}{\bar{M}_n} = 1.095$

Example of polymers

⇒ Addition polymers:

1) PE 2) PP 3) PS 4) PVC 5) Teflon

6) PMMA

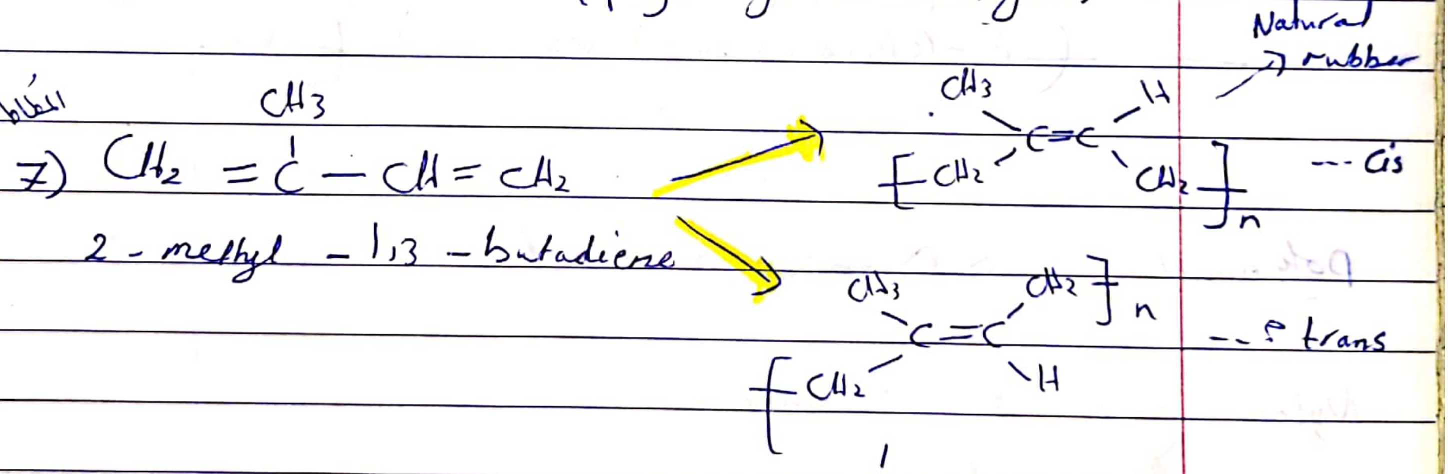


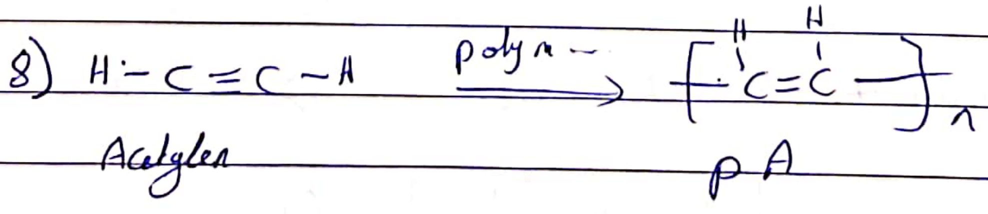
methyl methacrylate

R = H PMA (Polymethyl acrylate)

R = $CH_3$ PMMA (polymethyl methacrylate)

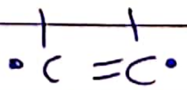
المطاط





Acetylen

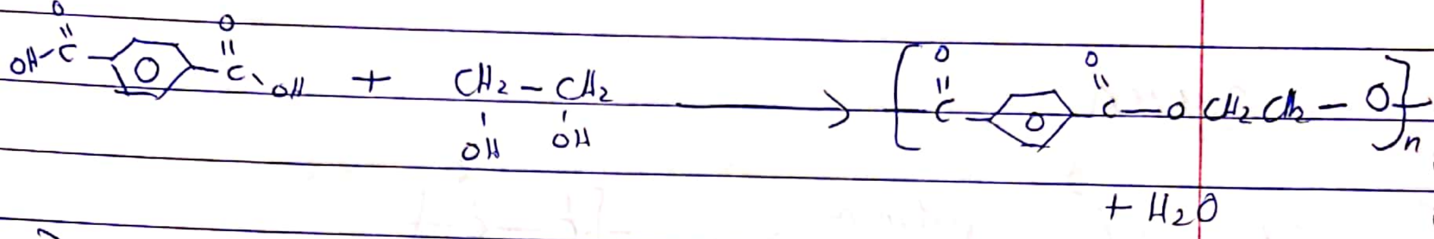
PA



f = 2

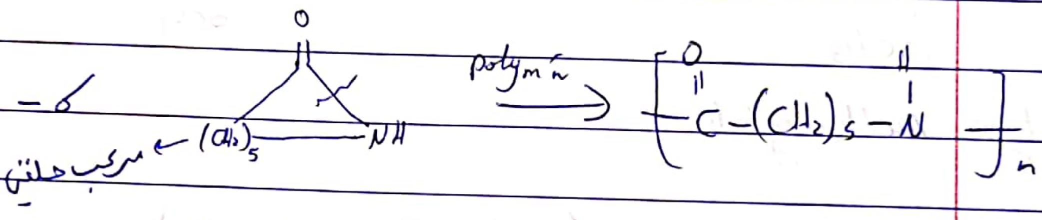
## ⟹ Condensation polymers:

1) PET or PETE



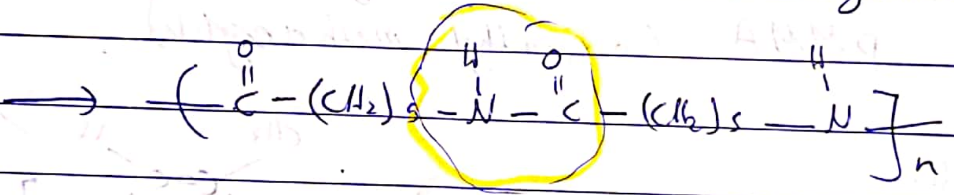
2) Polyamide

Nylon-6



Caprolactam

Nylon-6 → عدد الكربون



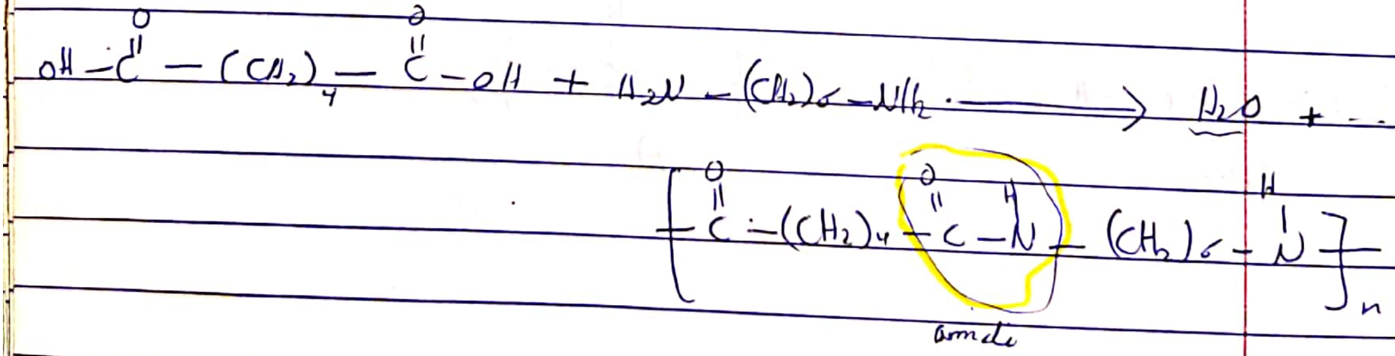
$$\longrightarrow \left(\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}}\right]_n$$

Amide

polyamide ⟶ Diamine + diacid

Nylon-6,6 ⟶ C in amine

↘ C in acid

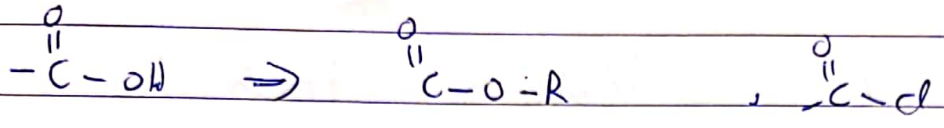


$$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + H_2N-(CH_2)_6-NH_2 \longrightarrow H_2O + \left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}\right]_n$$

amide

يستخدم في صناعة الملابس ⟸ Nylon-6,6

# Acid Derivatives



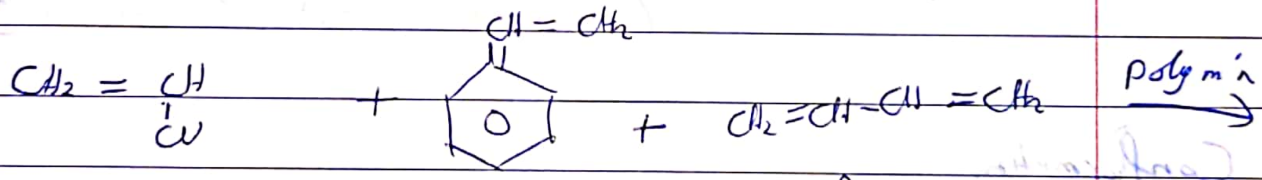
ester  Acyl chloride

more reactive than acid

--- use in produce compound تستخدم في التحضيرات

2 or more different monomer

⇒ Copolymer : 3 monomer



acrylonitrile  S  B

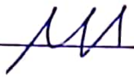
$\xrightarrow{\text{انتاج}}$ ABS

⇒ Some characteristic polymeric structure.

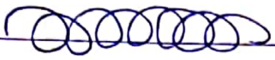
1) Configuration :- related structure which are not converted into each other unless are broken of reformed. (Cis or trans) → Butadiene → cis & trans

2) Conformation : boat ⇆ Chair
eclipsed ⇆ staggered } only heat

no bond broken or reformed

a) Zig Zag  like DNA / protein

b) folded chain  ordered

c) helix 

d) random coil 

heat
يمكن تحويل الاشكال
المنظمة الى عشوائي
بالحرارة ودون تكسير

ويمكن العكس بتقليل الحرارة ← ①
② وزيادة التركيز (تقل حركة الجزيئات)

**Conformation**
↓
Polymer --heating→ Tm (درجة انصهار)
↓ cooling
Semi Crystals ("نادرا" rare crystal)
↓ cooling
me Tg (glassy point) درجة التزجج

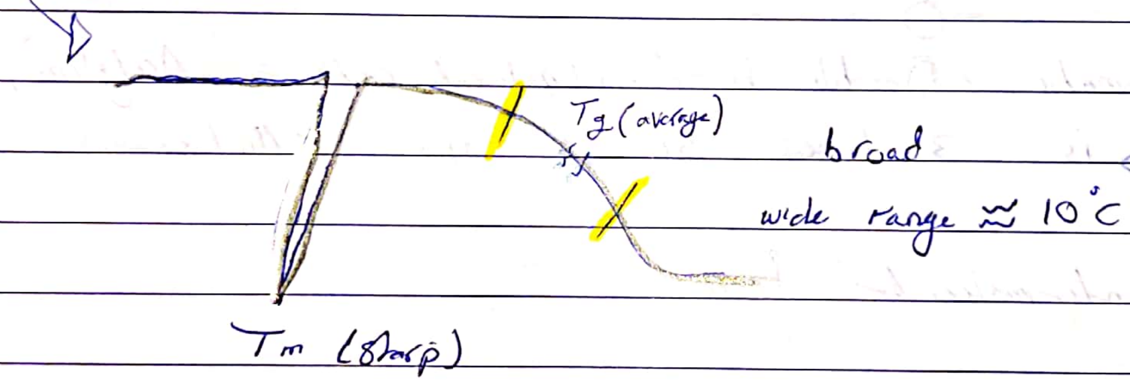
**Natural rubber**
↓
Tm = 17 °C
Tg = -73 °C } glassy, hard (قاسي) fragile brittle (هش)

Donya
25/7/2022

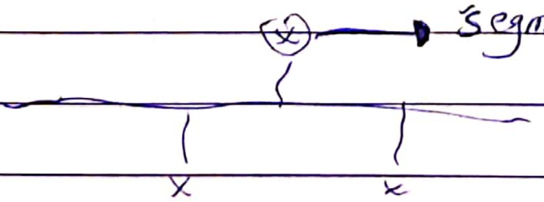
$N_2$ (l) = -180 °C ⟶ يمكننا تكسير كل المواد الموضوعة به

⇒ $T_m$ + $T_g$ are measured by :-

1) hot stage microscope
2) Differential thermal analysis (DTA) "الأكثر إستخداما"
3) differential scanning calorimetry (DSC)



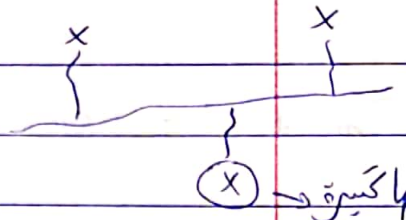
Conformation
↓
at $T_g$ the stop



⟶ segment motion is never stop
البوليمر الأقل حركة هو الأفضل
والحركة الداخلية لا يمكن إيقافها

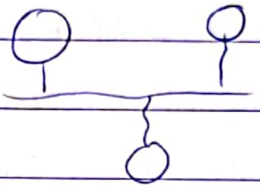
Restrict the segment motion :-

تقليل الحركة
وليس إيقافها



→ نجعلها كبيرة

**1** Bulky pendant group:



تشنج

**2** Stiffening groups in main chain

Ex: Aromatic, Double bond → (natural rubber, Acetylene)

PET → is 3 times stronger than cellulose

**3** Strong Intermolecular forces

H – bond, dipole – dipole, London force

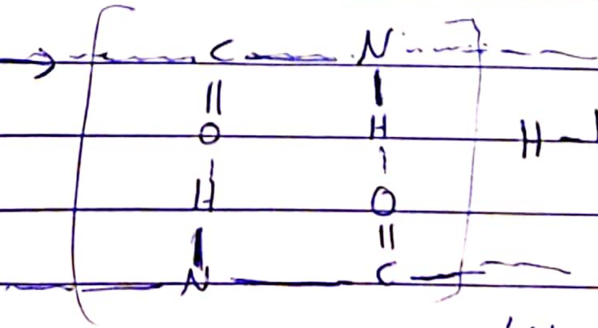
$(CH_2\ CH_2\ CH_2 \ldots)_n$

$\updownarrow\ \updownarrow\ \updownarrow$ → London force

$(CH_2\ CH_2\ CH_2 \ldots)_n$

PVC → dipole – dipole

Nylon – 6,6 →



H – bond } (H – bond) very strong

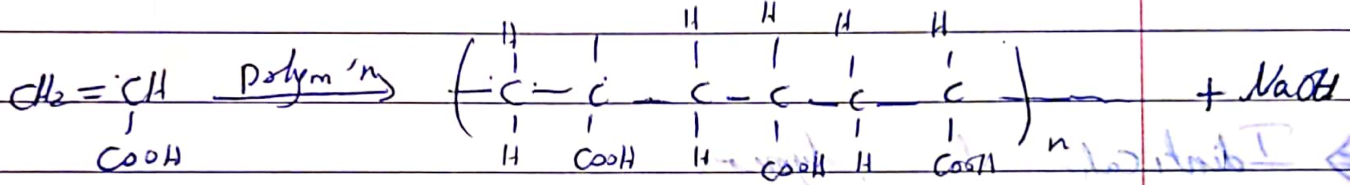
$T_m = 265\ C$

* لا يتأثر بالماء المغلي

# Bonding in polymers:

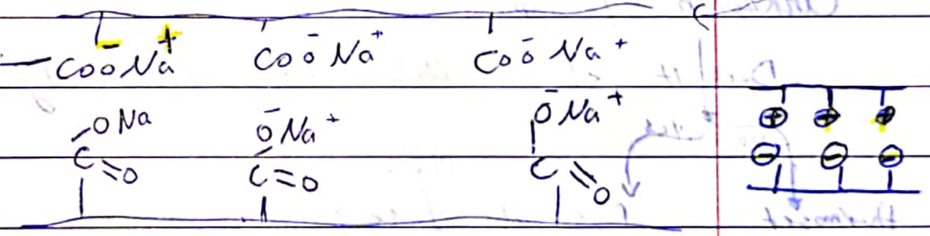
1) primary Bonding → a) Covalent bond
b) Ionic bond
c) metalic bond

Ionic bond.



$$CH_2=\underset{COOH}{\underset{|}{CH}} \xrightarrow{polym'n} \left(\underset{H}{\overset{H}{C}}-\underset{COOH}{C}-\underset{H}{\overset{H}{C}}-\underset{COOH}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{COOH}{\overset{H}{C}}\right)_n + NaOH$$

acrylic acid



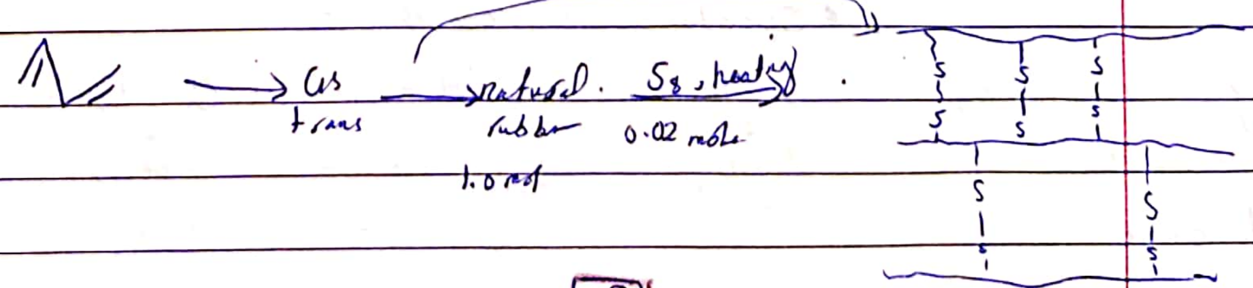
هنا بالبولمر الوحد هناك رابطة آيونية ←

2) Secondary Bonding

H-Bond, dipole-dipole, London
↓ 6-10 Kcal
↓ 2-6 Kcal
↓ 2 KCal

**4** Cross-Linking

تقسية المطاط بالكبريت
Vulcanization

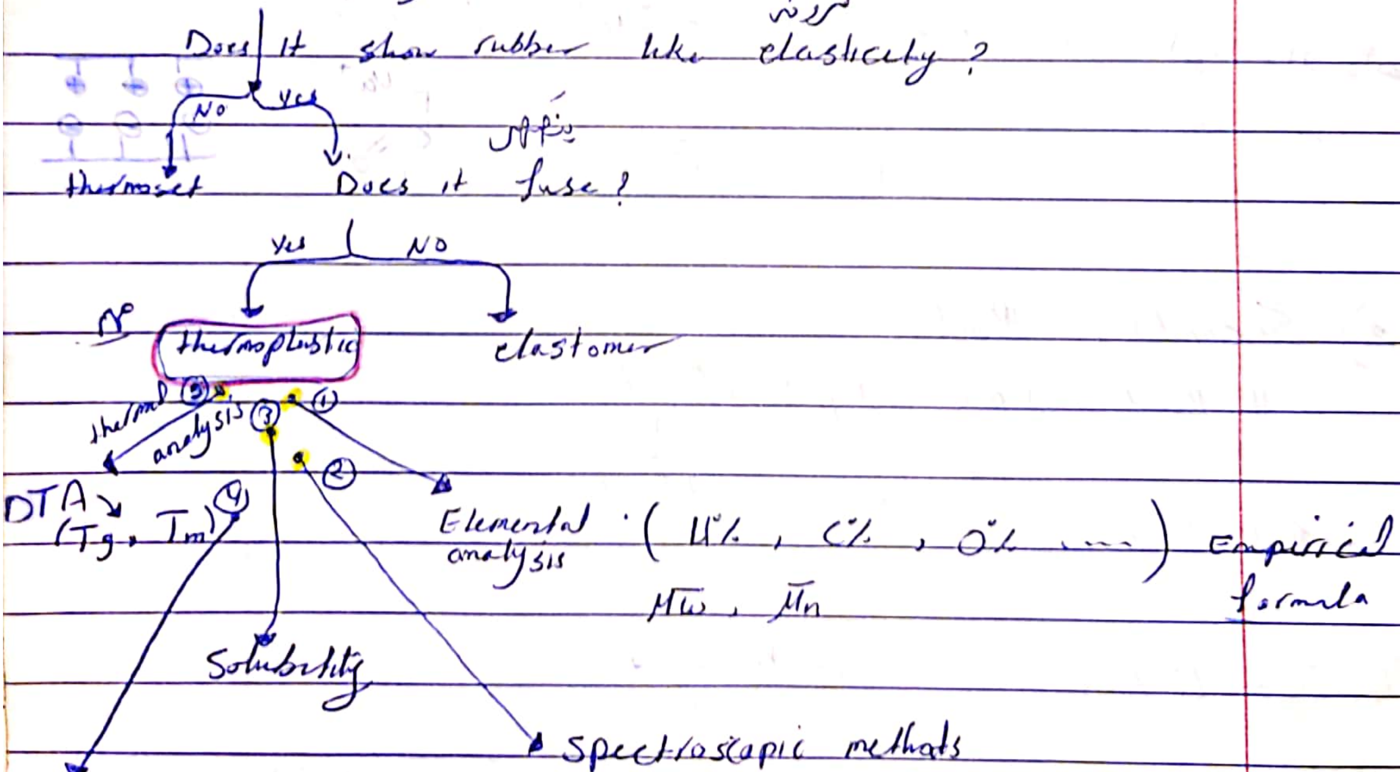


## Classification of polymer :-

1- Inorganic polymer & organic polymer
2- Natural polymer & synthetic polymer
3- Addition polymer & Condensation polymer
4- homo polymer & hetero polymer } نفس الاشي
5- homo polymer & copolymer

## ⇒ Identification of polymers

Unknown polymers



X-ray Crystallography to know exact structure

⇒ IR , UV , $^1$H - NMR , $^{13}$C - NMR

- IR ↓ functional group
- UV ↓ C=C, C=C-C=C, Conjugated system
- $^1$H - NMR ↓ لمعرفة عدد، موقع H
- $^{13}$C - NMR ↓ معرفة مكان الكربونة

⇒ Recycled polymers

≃ only Thermoplastic polymers

♳ PETE ♵ PVC

♴ HDPE ♶ LDPE

♷ PP ♸ PS

♹ others.

♴ ⇒ high Density polyethylene (Linear)
♶ ⇒ low " " (Branched) cheap

Donya Salman

# ※ Chap. 2

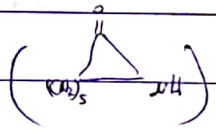
## step-Reaction polym'n (Condensation)

Method of synthesis polymer By reaction of
bi- or polyfunctional compound In step-step mechanism

monomer → dimer → trimer → tetramer —— polymer

* rxn accompanied by elimination of small molecules | $H_2O$ / HCl / ROH

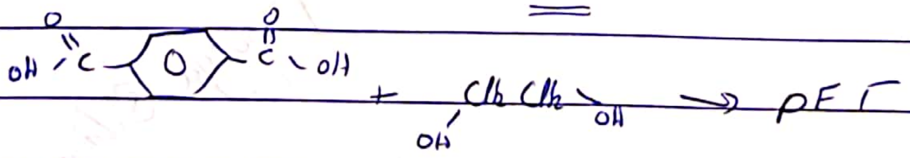
- except In Nylon-6



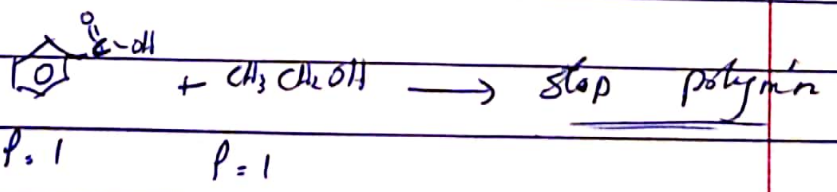
For successfull condensation polym'n

1- stochiometry: balance between Reacting molecules
Diacid + Diamine → polyamide
1 : 1

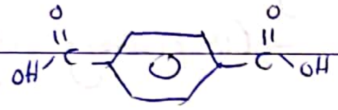
ultra
2- reactant: must be very pure & clean equipment.



possible Impurity



3 - Reaction must be selected to give high % yield of high M.wt


→ chose more reactive derivatives

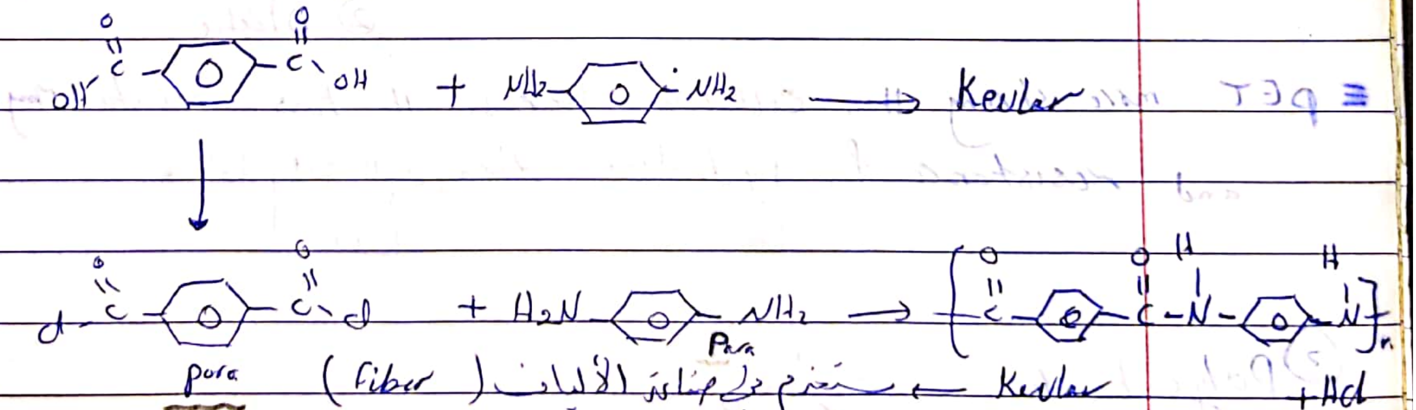
→ Instead of $R-\overset{O}{\overset{\|}{C}}-OH$ use $R-\overset{O}{\overset{\|}{C}}-Cl$

Examples of step - rxn polymers

① polyamide

Nylon - 6 , Nylon - 6,6 [Aliphatic]

Aromatic polyamides



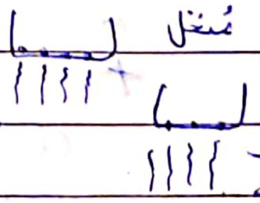
para (Fiber) يستخدم في صناعة الألياف ← Kevlar

صناعة,

* Inducing fiber by :

1) منصهر Melt spining المغزل → منصهر → مُغزل

2) Wet spining → مذاب في مذيب →


→ تنزل محلول وينفصل المذيب

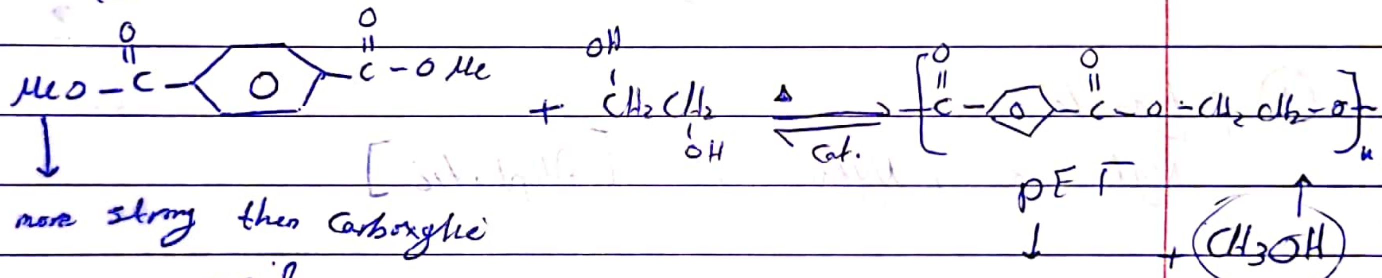
إذا كانت المونمرات meta ⇐ الناتج Nomex

meta + meta → Nomex
Para + para → Kevlar

} aromatic + H-bond
↓
stiffening
⇒ (very strong , very hard)

Nomex ⇒ يستخدم في صناعة الأشياء العالية والحماية القاسية .

② poly ester



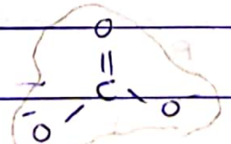
* more strong then carboxylic acid

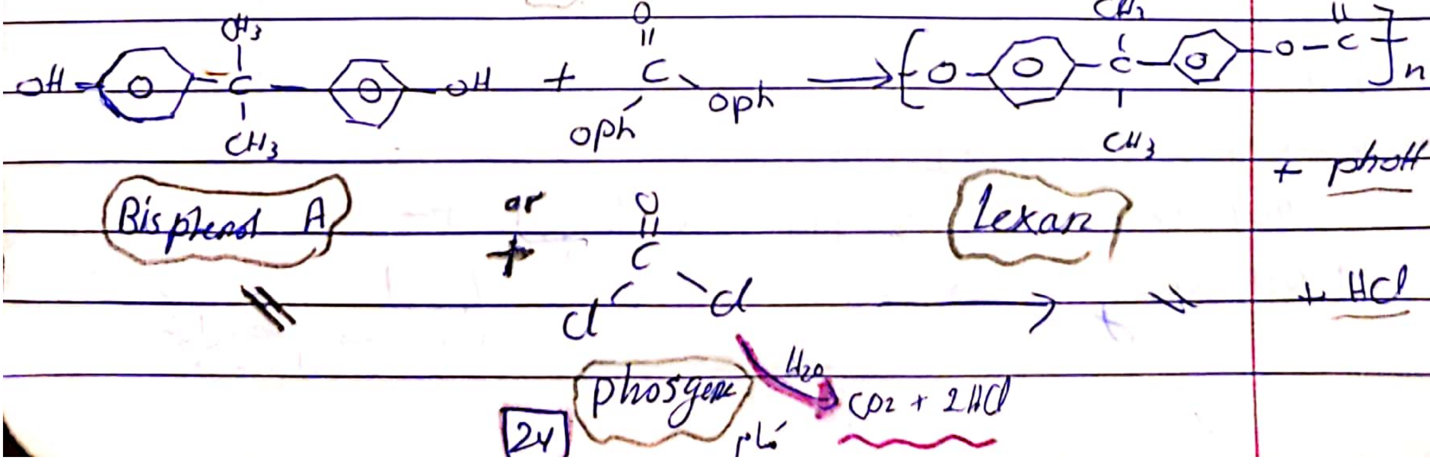
PET
↓
① fiber → النسيج والملابس
② plastic

≡ PET more strong than cellulose , because it has aromatic rings and resistance of hydrolysis

* يُقاوم التبلل و إمتصاص الماء ...

③ Polycarbonate





Hira Taher
27/7/2022

Lexan → Transparence شفاف (as glass)
strong as Stell قوي

④ poly urithane ⇐ Diol + Di iso cyanate

$$OH-(CH_2)_4-\overset{\delta-}{\ddot{O}}H + OC\equiv N-(CH_2)_6-C{=}N{=}O$$

$$+\ O{=}\overset{\delta+}{C}{=}N-(CH_2)_6-N{=}C{=}O$$

$$\longrightarrow \{O-(CH_2)_4-\underline{O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}\}_n$$

Perlon - U

✱ (ester + amide) ⇒ urithane

تُستخدم في الصناعات الإسفنجية

Naming)

| | |
|---|---|
| $CN^-$ | Syanide |
| $CNO^-$ | Syanate |
| $CNS^-$ | thiocyanate |
| $OCN^-$ | iso cyanate |
| $SCN^-$ | iso thio cyanate |

⇒ In the absence of moisture ($H_2O$)
(dry condition)

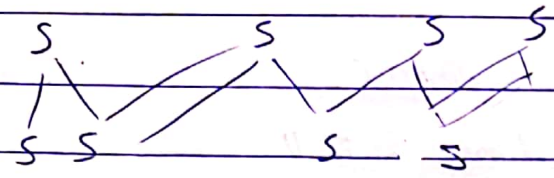
$$R-NCO + H_2O \longrightarrow RNH_2 + CO_2 \ \} \text{ decompsition}$$

⑤ poly sulfide

$$\underset{Cl}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH_2}} + Na_2S_4 \longrightarrow \{CH_2CH_2-\underset{S}{\underset{\|}{S}}-\underset{S}{\underset{\|}{S}}\}_n + 2NaCl$$

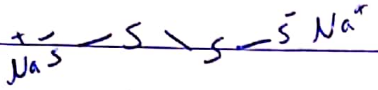
Thio Kol A ⇒ Rubber

$S_8$ →

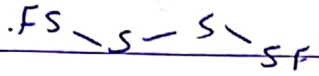


شكل تاجي

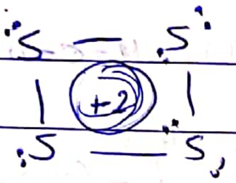
$S_4^{-2}$



$F_2S_4^{+2}$ →



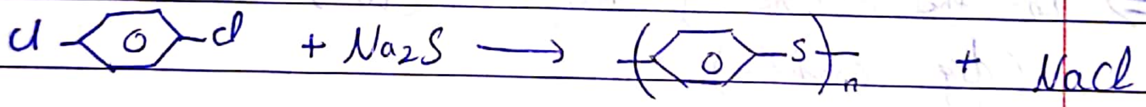
$S_4^{+2}$ →



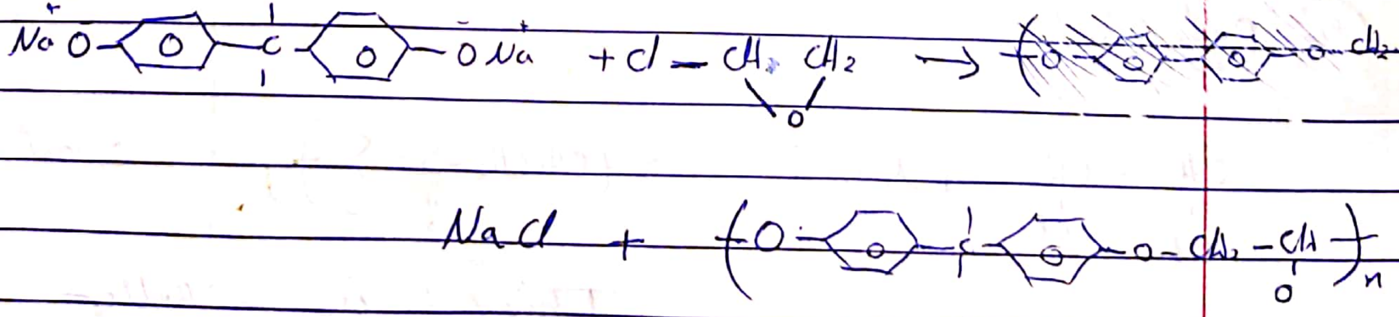
Aromatic

$S_n^{-2}$
$S_n^{+2}$ } → cyclic & open chain

⑤ example ⇒



⑥ Epoxy Resines (Adhesive) اللواصق



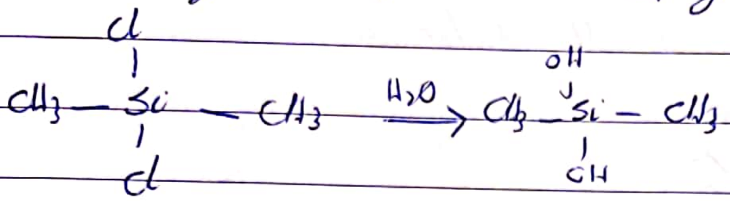
low Mwt → liquid

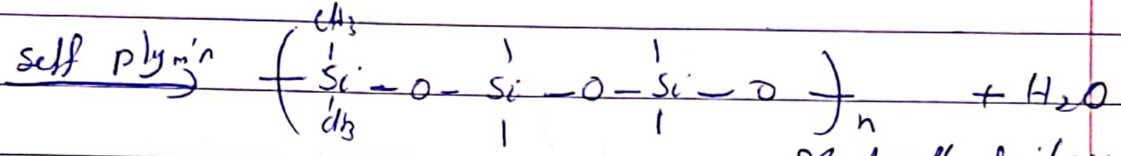
⑦ polymer of silicons (poly siloxane)

Cl–Si >> C–Cl

more active ↓ $H_2O$ SiOH

C–Cl ↓ $H_2O$ X





self plym'n

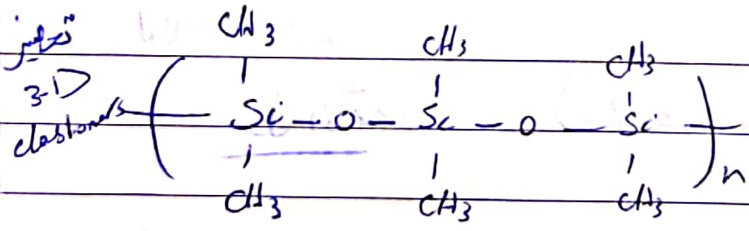
+ $H_2O$

polydimethylsiloxane

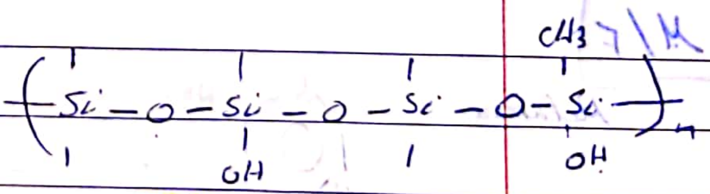
يستخدم

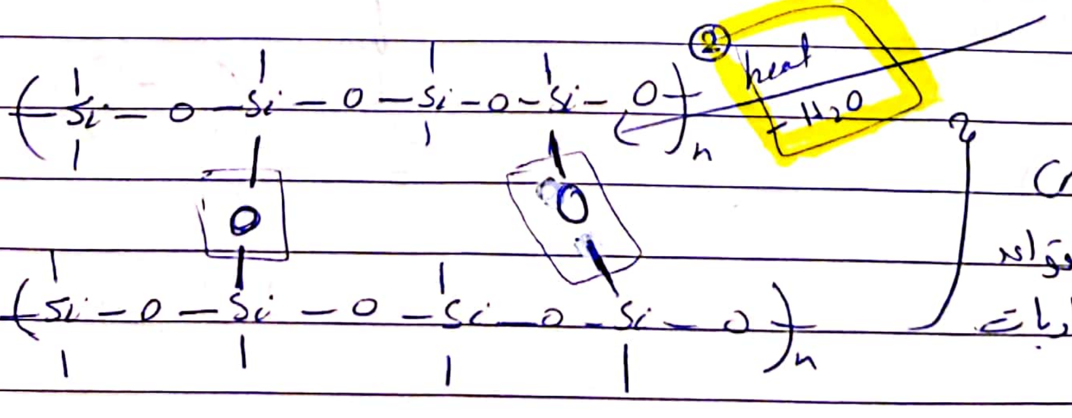
1. Oil (silicone oil)
2. grease تدهين مواد الخبز مثل المتخمر في distillation
3. Solid plastic
4. مطاط Elastomers (3-D)

تحضير 3-D elastomers



① partial hydrolysis





② heat

− $H_2O$

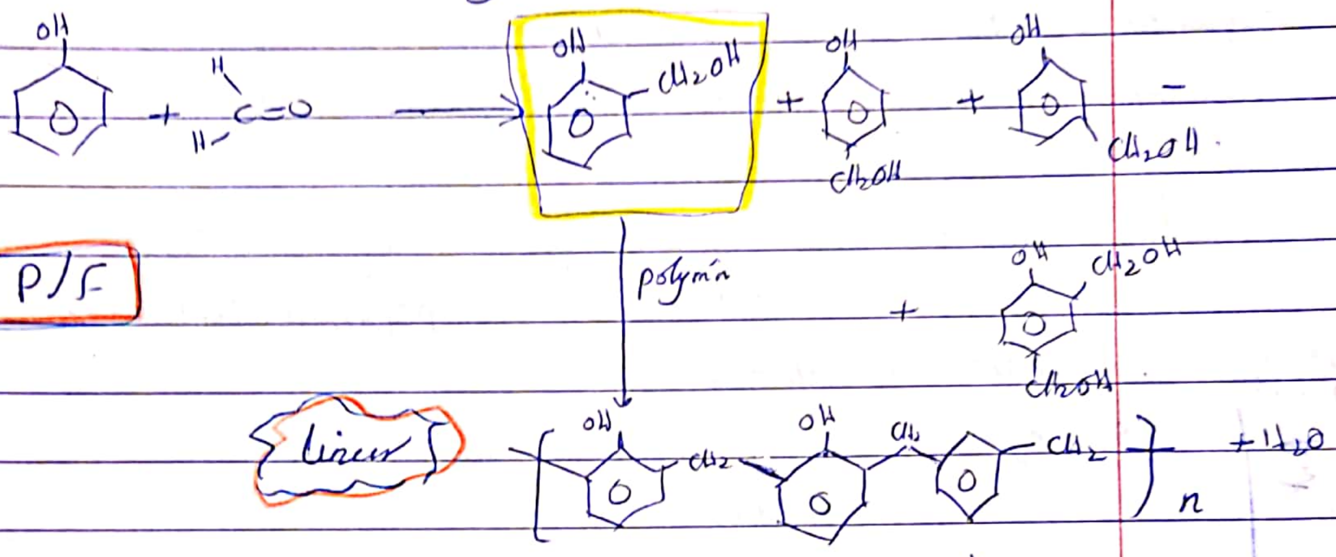
Cross linked

لا يتأثر بالأحماض والقواعد والحرارة والكيماويات

## ⑧ P/F , M/F

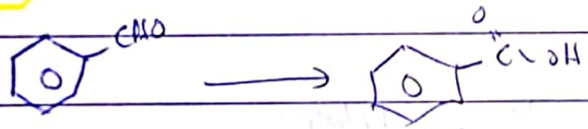
P: phenol , F: Formaldehyde , M: Melamine

**P/F**



P/F (adhesive)

*



solid (more reactive)

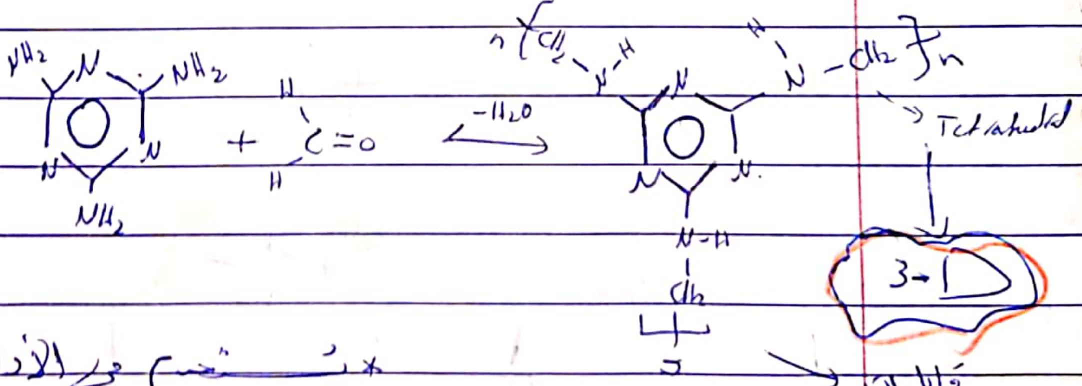
⟹ لذلك الادهان

يتحول الى

تحول الى حمض

**M/F**

Melamine



* يستخدم في الأواني و الصحون

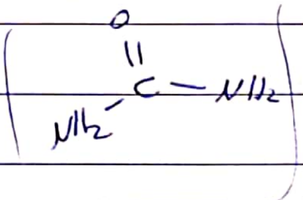
قابل للتلوين بسبب وجود الحلقة

## ⑨ Poly ethers $(\grave{R}-O-R)$

$$\underset{\text{ethylene glycol}}{OH-CH_2-CH_2-OH} \xrightarrow[\text{polym'n}]{\text{self}} \left[CH_2CH_2-O-CH_2CH_2-O\right]_n + H_2O$$

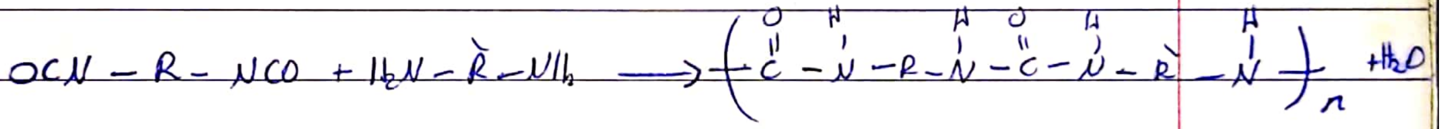
PEG

## ⑩ Poly urea

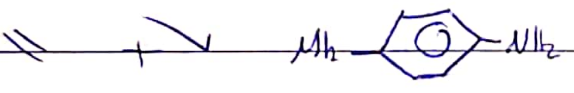


urea

diamine + di isocyanate → $(OCN-R-NCO + H_2N-\grave{R}-NH_2)$



$$OCN-R-NCO + H_2N-\grave{R}-NH_2 \longrightarrow \left(\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-\grave{R}-\overset{H}{\overset{|}{N}}\right)_n + H_2O$$



→ 1) polymer very strong
2) Aromatic + Hydrogen bond.

### Step - Rxn polym'n

⇒ may require hours or days to give reasonable product.

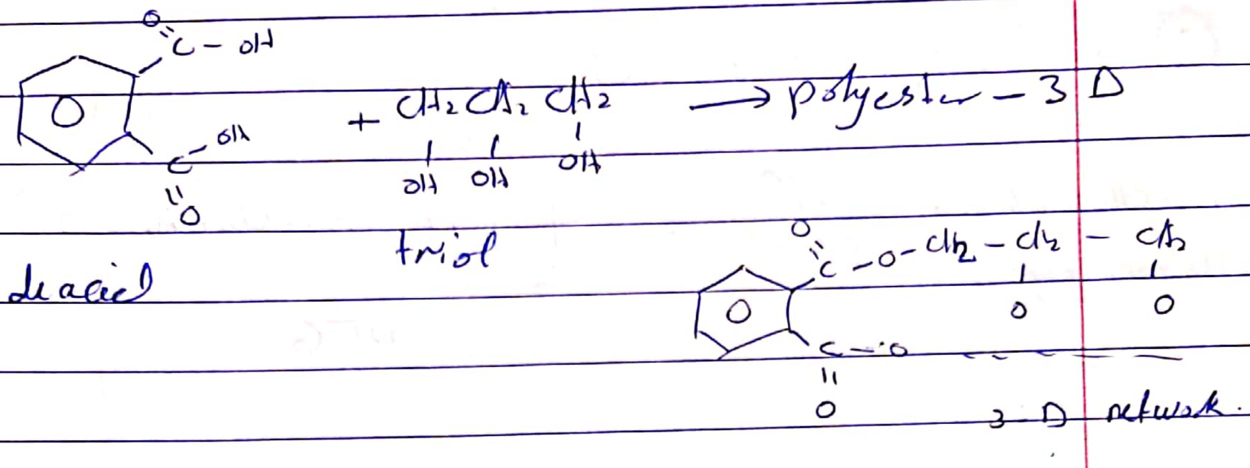
⇒ Conc. of Monomer drops sharply in short time

$\overset{\times}{\boxed{\text{monomer}}}$ → dimer → trimer .....

⇒ most Rxns are endothermic $\overset{R-OH}{H_2O}$

$$\text{diol} + \text{diacid} \xrightleftharpoons{\Delta} \text{polyester} + \boxed{H_2O}\downarrow$$

⇒ polymers mostly are linear, unless we use trifunction monomer → 3-D (Melamine)


C - OH
OH
+ CH2 CH2 CH2
OH OH OH
→ polyester - 3 D
di acid
triol
C -O- CH2 - CH2 - CH2
O O
C - O
3-D network

# ⋇ Chap. 3

Chain - Rxn polymerization (Addition polymers)

⇓

Mechanism [Initiation, propagation, Termination]

monomer must contain double bond. (C=C) ⇒ Successive Addition

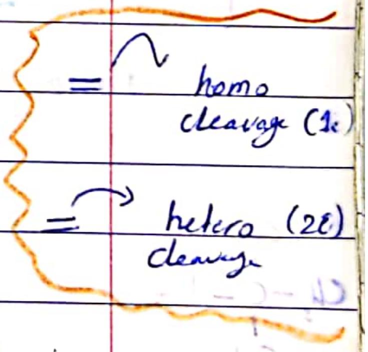
$$C=C \Rightarrow \dot{C}-\dot{C} \quad f=2$$

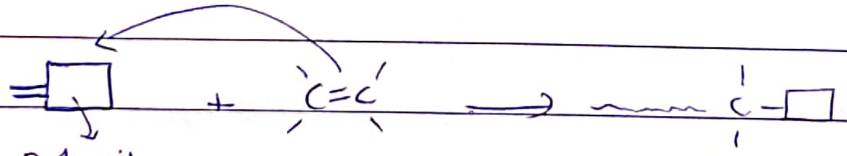
Types of Chain - Rxn according to Initiator (R)

① $R^{\bullet} + C=C \longrightarrow R-C-C^{\bullet}$ free radical polym'n

② $R^{+} + C=C \longrightarrow R-C-C^{\oplus}$ Cationic polym'n

③ $R^{-} + C=C \longrightarrow R-C-C^{\ominus}$ anionic polym'n



④


poly site

(d-orbital)

Coordination polym'n

Zeigler - Natta Catalyst

## ① Free Radical polym'n

* معظم البوليمرات بتم بطريقة ال Free radical

→ Free radical rxn is spontaneous.

Initiation $M \longrightarrow M^{\bullet}$

Propagation $M^{\bullet} + M \longrightarrow MM^{\bullet} \xrightarrow{M} MMM^{\bullet} \longrightarrow$ ~~~~~ $\boxed{\bullet}$

successive addition

active center

Donya
2/8/2022

Termination

a) Combination 

b) Disproportionation عدم تساوي

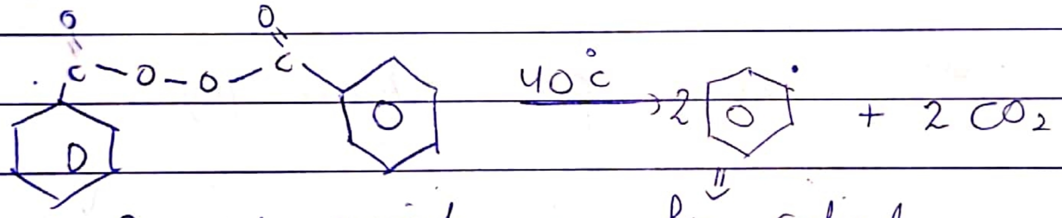
Initiation (Free radical لتشكيل)

1-Thermal 2- UV - radiation 3 - redox rxn

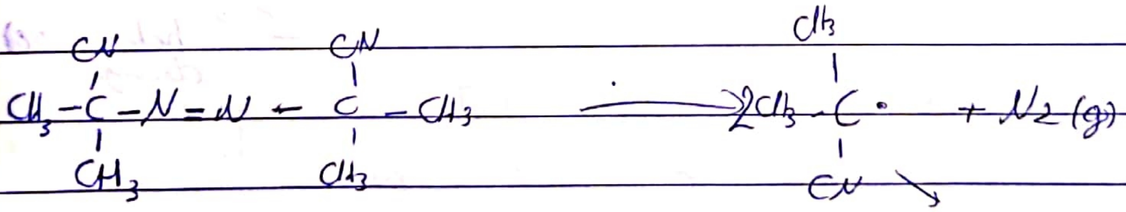
4- Substances that give easy radicals

[peroxides , Hydroperoxide , azo- compund]

R-O-O-R R-O-O-H R-N=N-R



Benzoyl peroxide Free radical



$CH_3-C(CN)(CH_3)-N=N-C(CN)(CH_3)-CH_3 \longrightarrow 2CH_3-\dot{C}(CH_3)(CN) + N_2(g)$

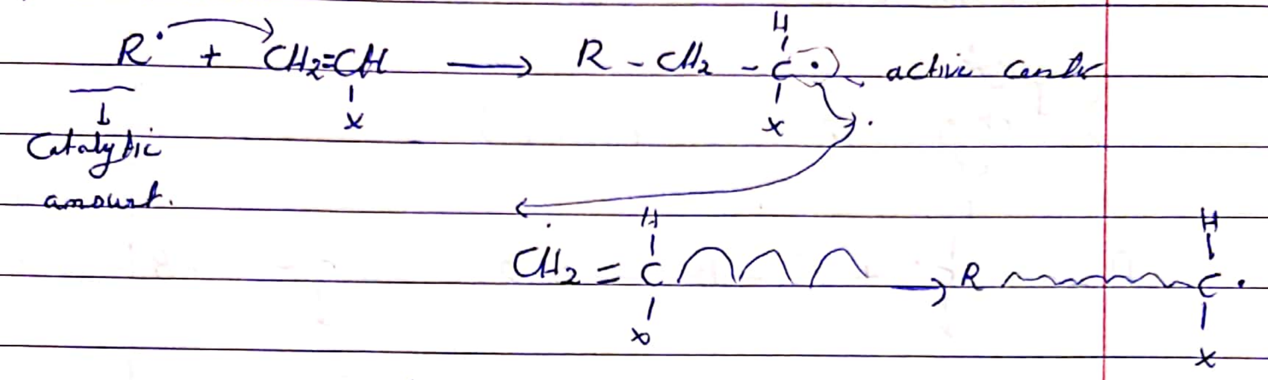
* Azo bis Isobutyl nitrile
(AIBN)

3° → so more stable

32

# Mechanism of free radical

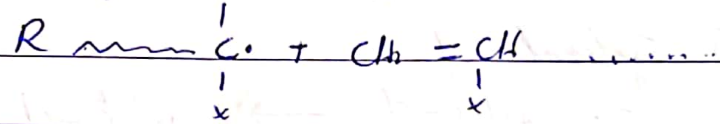
⇒ Initiation



$R^\bullet + CH_2=CH(X) \longrightarrow R-CH_2-\overset{H}{\underset{X}{C}}\bullet$

$CH_2=\overset{H}{\underset{X}{C}} \frown\frown\frown \longrightarrow R\sim\sim\sim\sim\overset{H}{\underset{X}{C}}\bullet$

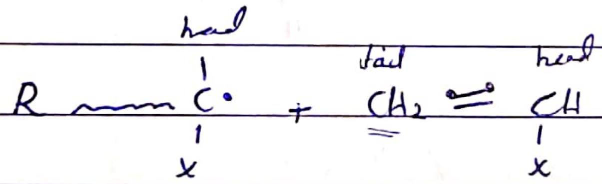
⇒ propagation (successive addition of monomer molecules)



$R\sim\sim\sim\underset{X}{\overset{|}{C}}\bullet + CH_2=\underset{X}{CH}$ ......

Rate Determining step (RDS) ⇓ هذه الخطوة تحدد ...

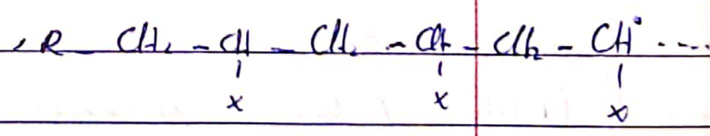
1) M.wt
2) Rate of rxn
3) structure



$R\sim\sim\sim\underset{X}{\overset{head}{C}}\bullet + \overset{tail}{CH_2}=\underset{X}{\overset{head}{CH}}$

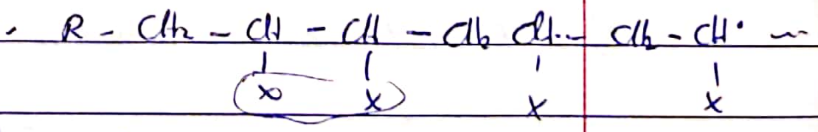
tow possible way of addition

1) head to tail



$R-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}^\bullet$ ....

2) head to head



$R-CH_2-\underset{X}{CH}-\underset{X}{CH}-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}^\bullet$ ~

which is more favored ??

⟹ head to tail because تم شرحه بالسابق؟

a) steric factor

b) Resonance.

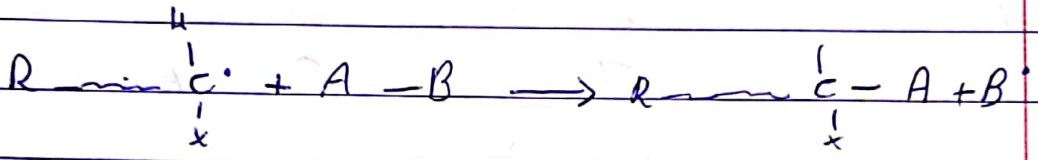
pK 15% head to head
85% head to tail

مُصاحَب بـ

Radical polym'n may accompanied by "chain transfer" ; radical active center goes to another site

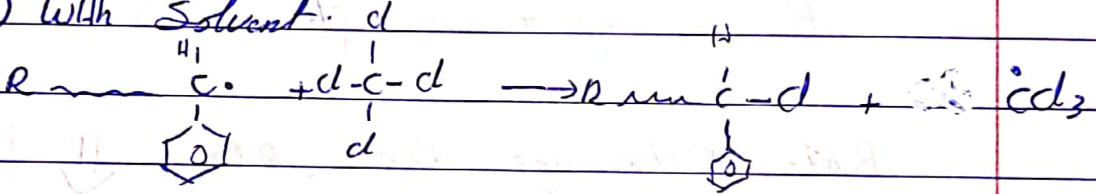
غريبة

1) Foreign material (A – B)



$$R\sim\sim\overset{H}{\underset{X}{C}}{\cdot} + A-B \longrightarrow R\sim\sim\underset{X}{C}-A + B^{\cdot}$$

2) With solvent .

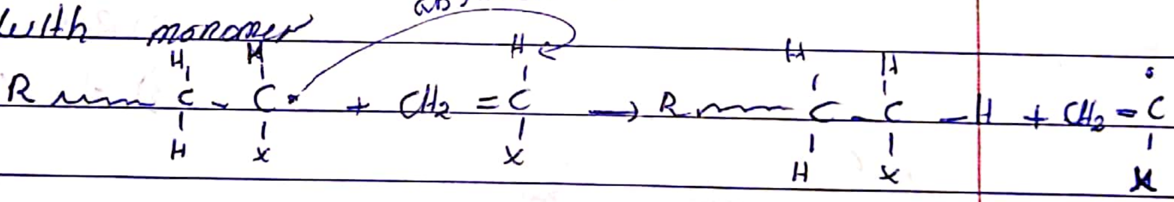


$$R\sim\sim\overset{H}{\underset{C_6H_5}{C}}{\cdot} + Cl-\overset{Cl}{\underset{Cl}{C}}-Cl \longrightarrow R\sim\sim\overset{H}{\underset{C_6H_5}{C}}-Cl + \dot{C}Cl_3$$

3) With monomer

استبدال

abstraction of H

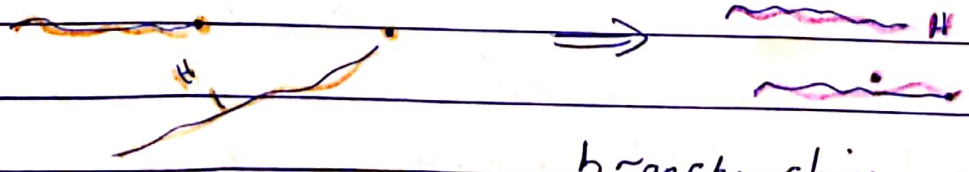


$$R\sim\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}{\cdot} + CH_2=\overset{H}{\underset{X}{C}} \longrightarrow R\sim\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}-H + CH_2=\overset{\cdot}{\underset{X}{C}}$$

1) + 2) + 3) ⟹ decrease of M.wt .

4) With polymer Molecule

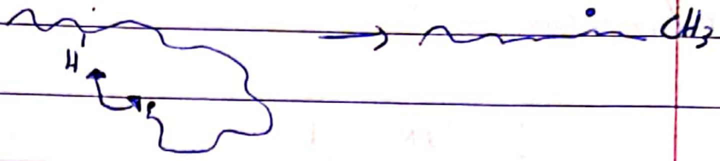
a) Intermolecular : between the molecules .



branching

b) Intramolecular

(Back biting)



PE , Mw 7600,000

↓

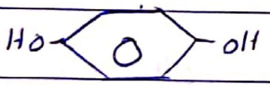
يجب إضافة مواد للحد من M.wt

↓

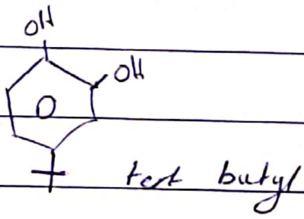
chain transfer : [illegible]

1) Regulators
2) Modifiers

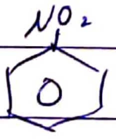
Inhibitors :- added to stop radical polym'n



,



Retardor : Added to decrease rate of polym'n



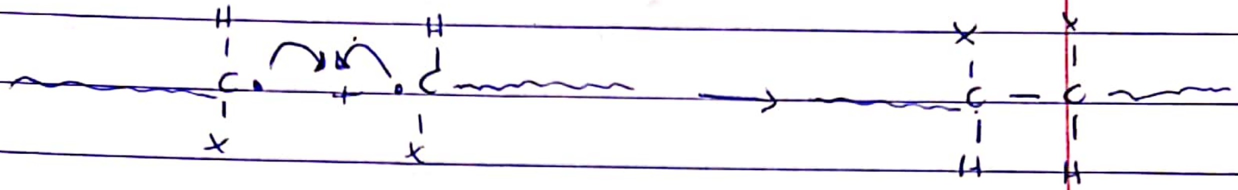
⇒ Retards of styrene polym'n

Rate : 15 min ⟶ 30 min

⇒ Termination

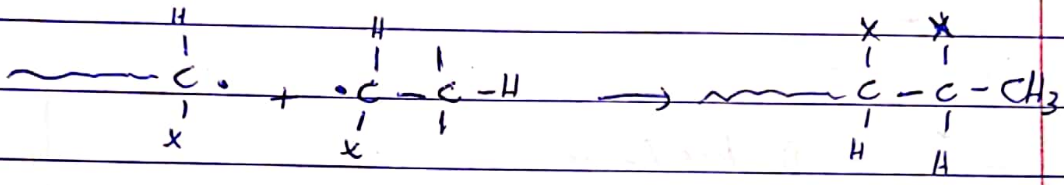
1) Combination

a)



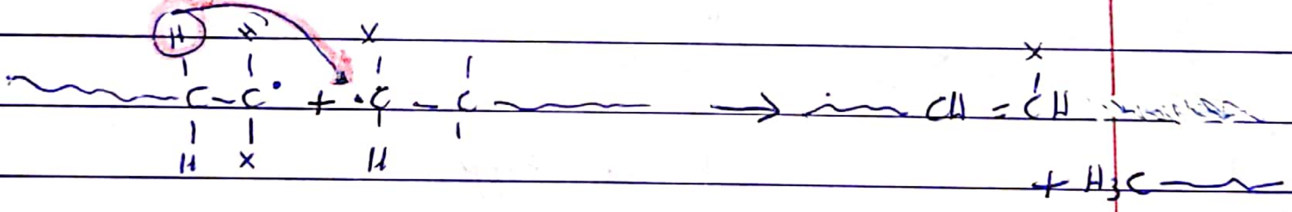
Increace In M.wt

b)



No Increase In Mwt

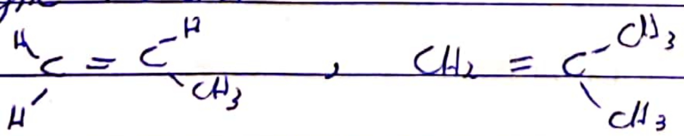
2) Disproportional



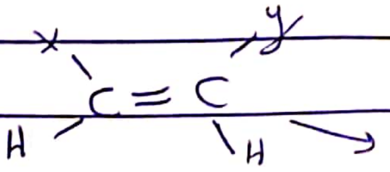
no effect on M.wt

limitation of Free radical polymn.

1) Allylic monomer

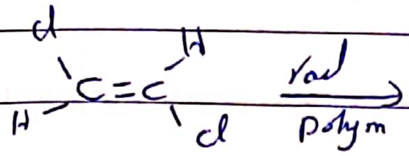


2) 1,2 - disubstituted ethylene

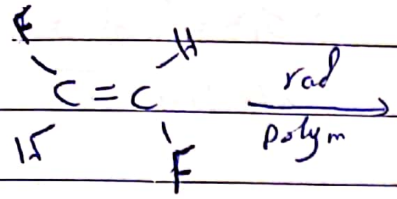


X, Y longer than $CH_3$

no free radical polymn because steric hindrance

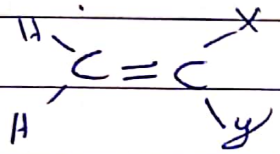


at 200°C & 200 atm



تتفاعل ← لأنه الفلور حجمها صغير جداً

3) 1,1 - substituted ethylene



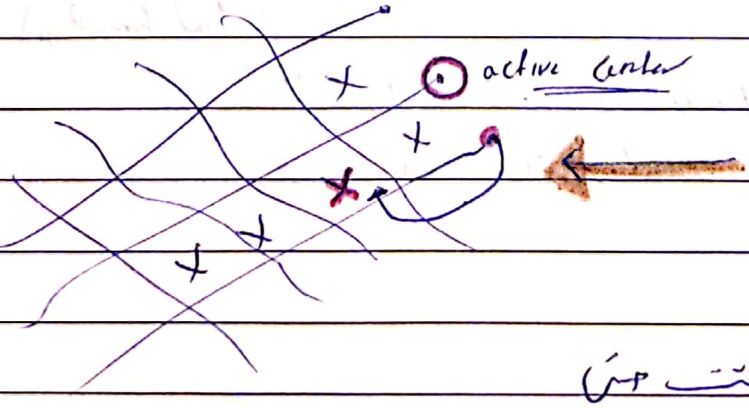
No Rad polym'n

● Some characteristic of Rad polym'n

☐ 1 high Average Mwt is produced Immediately (الثواني الأولى) ⇒ Rxn is left for 24 h to Increase % yield

PS : After 1.24 second $\overline{DP} = 1650$ at 100 C°

$\overline{M_w} = 1650 (104) = 171,600$



x : is the monomer

need time to find monomer

* لذلك التفاعل يأخذ وقت حتى نحصل على تفاعل كل (X) مع

(high % yield)

$\boxed{2}$ This polymn is Exothermic

$$\Delta G = \underset{\overset{\downarrow}{(-)}}{\Delta H} \underbrace{- T\underset{\overset{\downarrow}{(-)}}{\Delta S}}_{(-)(-) \Rightarrow (+)} < 0$$

, spontaneous at low T

$$\text{Monomer} \underset{\text{depolymerization}}{\overset{\text{polymn}}{\rightleftharpoons}} \text{polymer}$$

⇒ Ceiling Temp ($T_c$) : Temperature above which depolymn occur

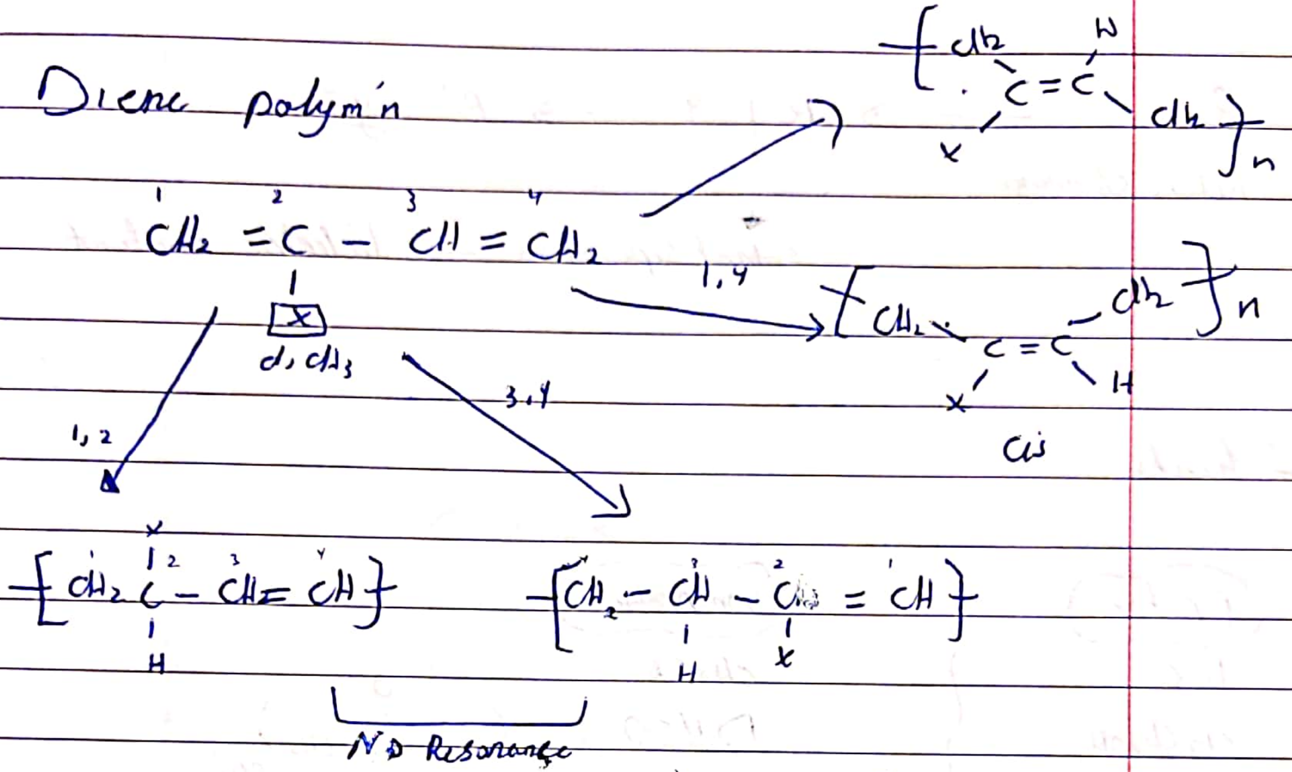
PS , $T_c = 300\ °C$ , $< 300\ °C$

Combination : at Low Temp ①, high Mwt ②, head to head linkage ③
اتحاد (Coupling)

Disproportionation : high Temp , low Mw , Contain double bond
(bond breakage) كسر رابطة

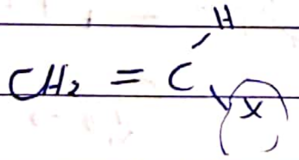
at 60° : poly (acrylonitrile) , 100% combination
poly (vinyl acetate) ; 100% combination.

## Diene polym'n



عندما يأتي نكتب كل الاحتمالات ....

## Ionic polym'n



$CH_2 = C(H)(X)$

X : electron withdrawing ⇒ Anionic polym'n

X : " releasing ⇒ Cationic polym'n

| X | Cationic | anionic |
|---|---|---|
| $CH_3$ | ✓ | – |
| CN | – | ✓ |
| $-\overset{O}{\overset{\|}{C}}-CH_3$ | – | ✓ |

Ion-pair

Cationic → ~~~~ ⊕ ∥ ⊖

anionic → ~~~~ ⊖ ∥ ⊕

$R-Y \longrightarrow R\cdot|\cdot Y \longrightarrow R^{+} + Y^{-}$

hetero cleavage

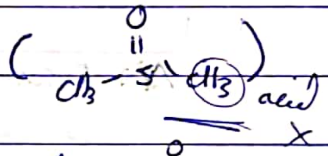
↓

solvent separation $\xrightarrow{\text{ضب}}$ dielectric constant

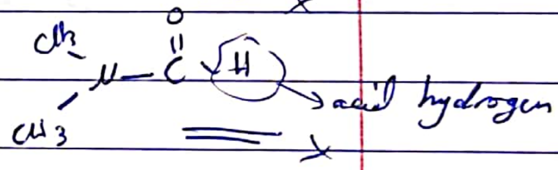
---

Solvents

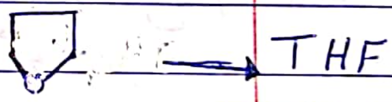
| **protic** | **non protic** |
|---|---|
| $H_2O$ | $CH_3CN$ |
| $CH_3CH_2OH$ | DMSO |
| | DMF |



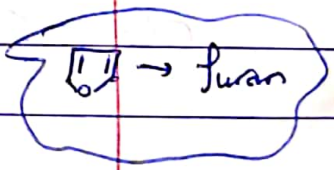
acid



acid hydrogen



THF



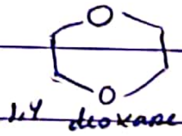
furan

Solvent used in ionic polym n

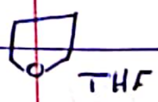
1) Polar solvent ⇒ non polar $-C^{\ominus}$ ⇒ very strong base

لأنه من الممكن أنه يتفاعل مع المونمر

2) Slightly polar $CH_3CH_2-O-CH_2CH_3$



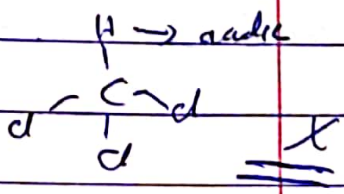
1,4 dioxane



THF

3) Non polar [ organic solvent )

benzene, hexane, Toluene



H → acidic

شروط التفاعل : 1) المادة نقية

2) الادوات نظيفة 3) عدم وجود شوائب

---

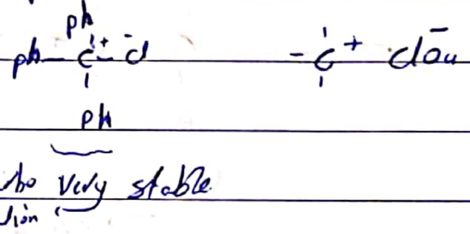
# Cationic Polym'n

1] Initiators Could be

① strong protic acid , $HCl$ , $H_2SO_4$ ---

② Lewis acid $BF_3$ , $AlCl_3$ , $FeCl_3$

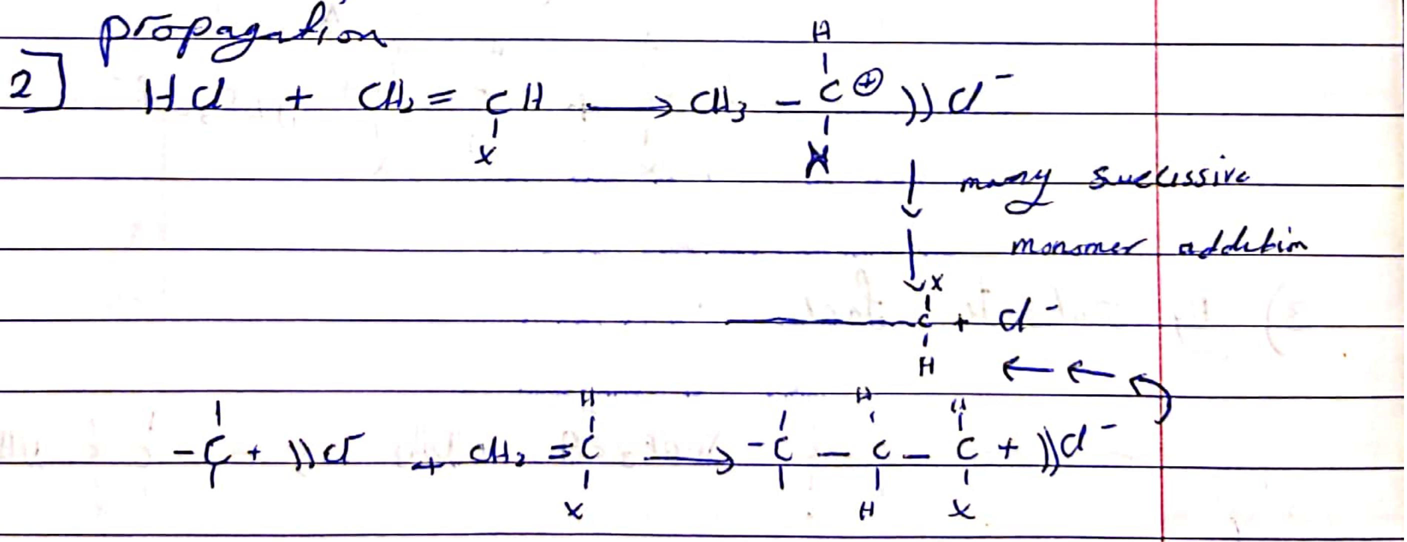
③ Cationic generator , $Ph_3CCl$ , $t\text{-}BuClO_4$ , $I_2$



$$\underset{\underset{\text{Ph}}{|}}{\overset{\overset{\text{Ph}}{|}}{\text{Ph}-\text{C}^{+}-\text{Cl}}} \qquad -\overset{|}{\underset{|}{\text{C}}}{}^{+}\ \text{ClO}_4^{-}$$

3° Carbo Cation , Very stable

## propagation

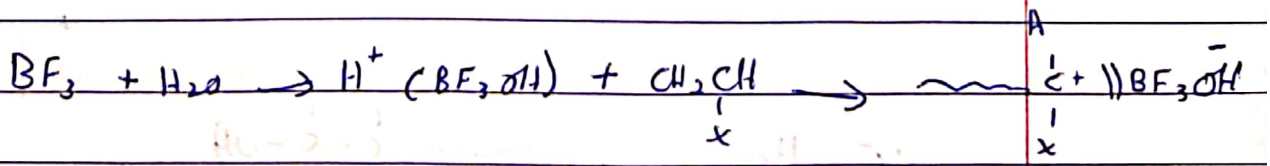
2] 

$$HCl + CH_2=\underset{\underset{X}{|}}{CH} \longrightarrow CH_3-\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{}^{\oplus})) Cl^-$$

$\downarrow$ many successive monomer addition

$$\sim\sim\sim\overset{\overset{X}{|}}{\underset{\underset{H}{|}}{C}}{}^{+}\ Cl^-$$

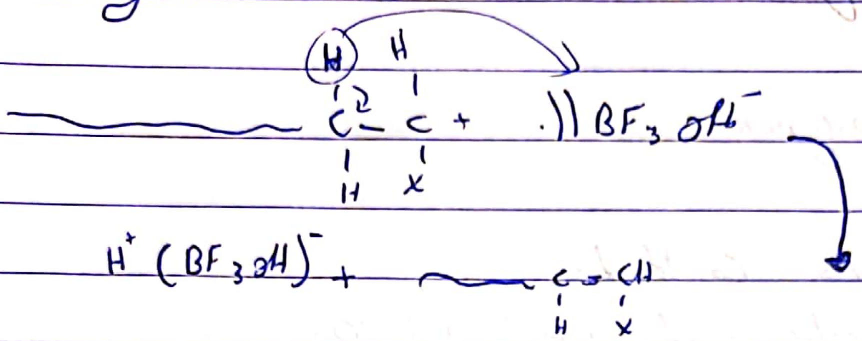
$$-\overset{|}{\underset{|}{C}}{}^{+})) Cl^- + CH_2=\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}} \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{}^{+})) Cl^-$$



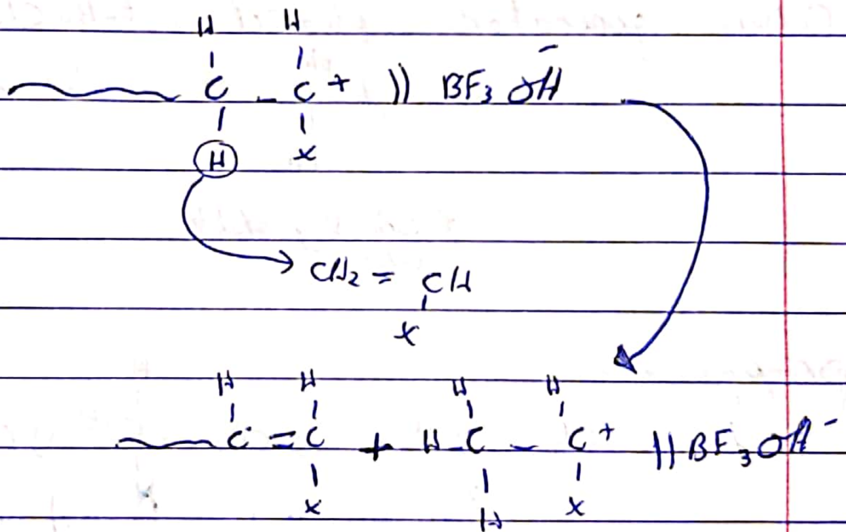
$$BF_3 + H_2O \rightarrow H^+ (BF_3OH) + CH_2\underset{\underset{X}{|}}{CH} \longrightarrow \sim\sim\sim\overset{\overset{A}{|}}{\underset{\underset{X}{|}}{C}}{}^{+})) BF_3\overline{O}H$$

## Termination

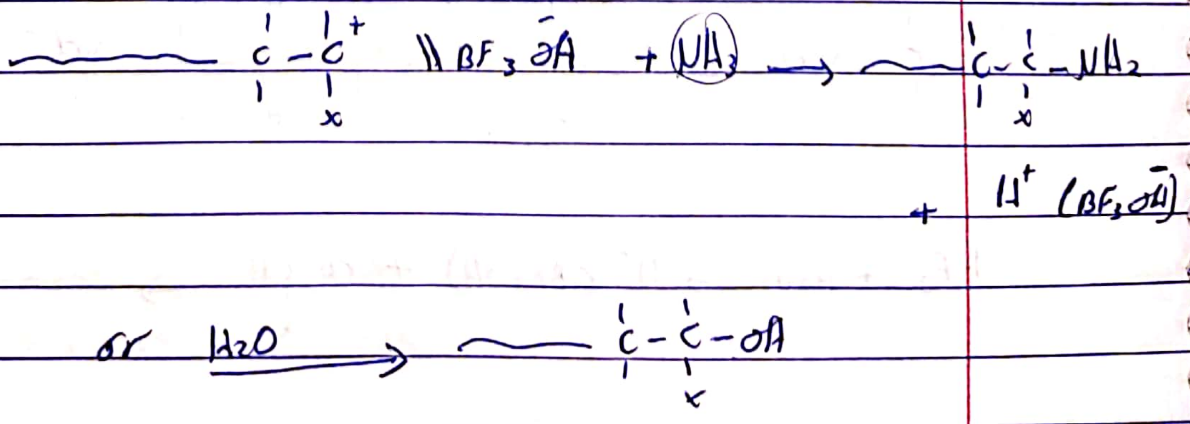
### 1) Rearrangement



### 2) Catalyst



### 3) By outside factor.



ج)

⇒ Some characteristic of Cationic polym'n

① Very fast & give high M.wt.

② As T↓ rate of polym'n ↑

$$T \propto \frac{1}{Rate}$$

Anionic polym'n

Initiators. خامل

① Alkali metals dispersion in inert hydrocarbon solvent,
Na / Naphthalene
Li / hexane

② organometallic Compounds:
R-MgX , n-BuLi ($CH_3CH_2CH_2CH_2^{\ominus}\ Li^{\oplus}$)

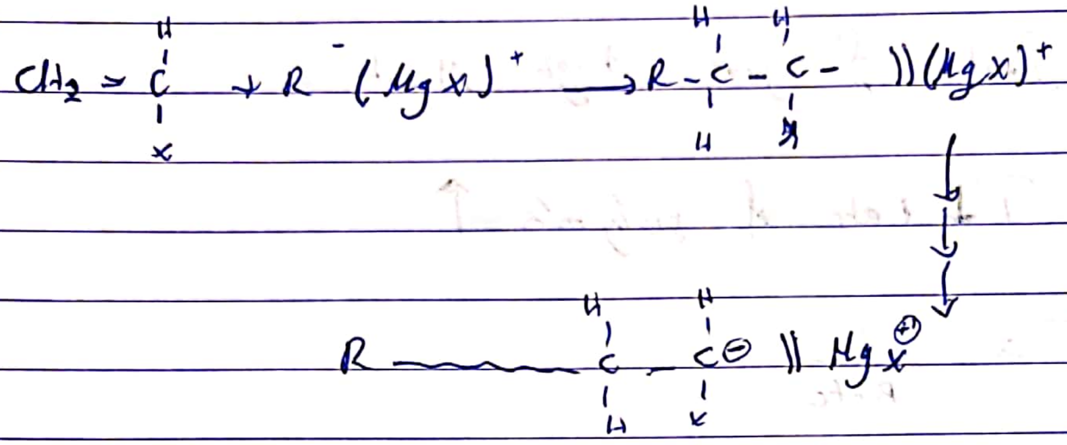
③ Lewis base.
$RO^-M^+ \Rightarrow CH_3CH_2OH + Na \rightarrow CH_3CH_2ONa + H_2(g)$

$K^+NH_2^- \Rightarrow NH_3 + K \longrightarrow K^+NH_2^- + H_2(g)$

⇓

This strong (very strong) bases.

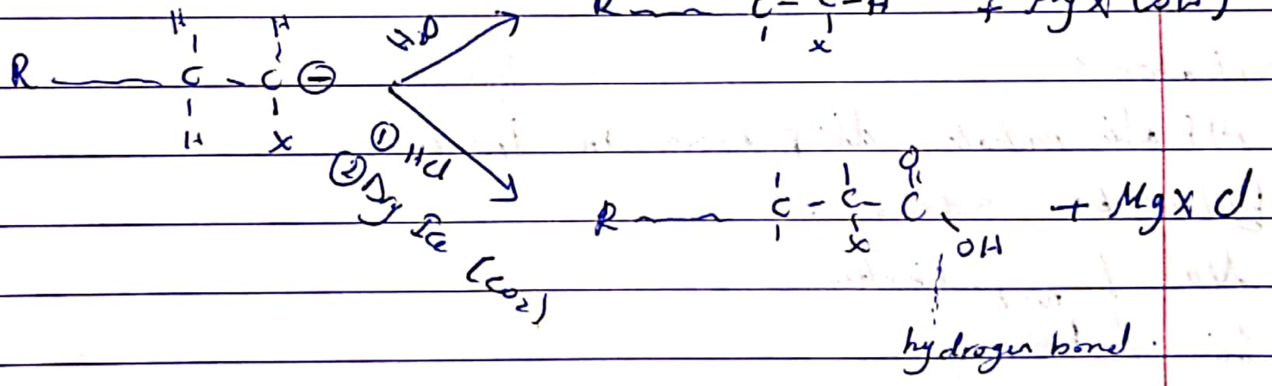
## Propagation.



$$CH_2=\overset{H}{\underset{X}{C}} + R^-(MgX)^+ \longrightarrow R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}- \;))(MgX)^+$$

$$R\sim\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}^{\ominus} \;||\; MgX^{\oplus}$$

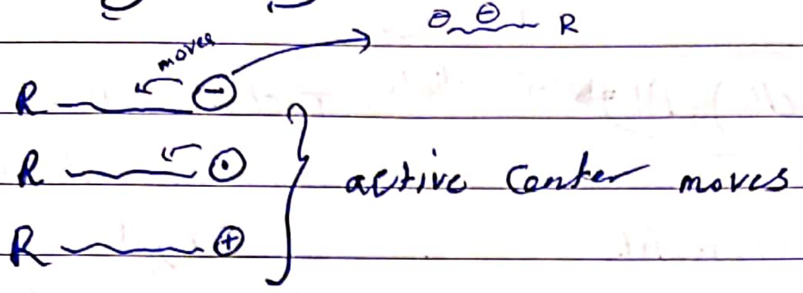
## Termination



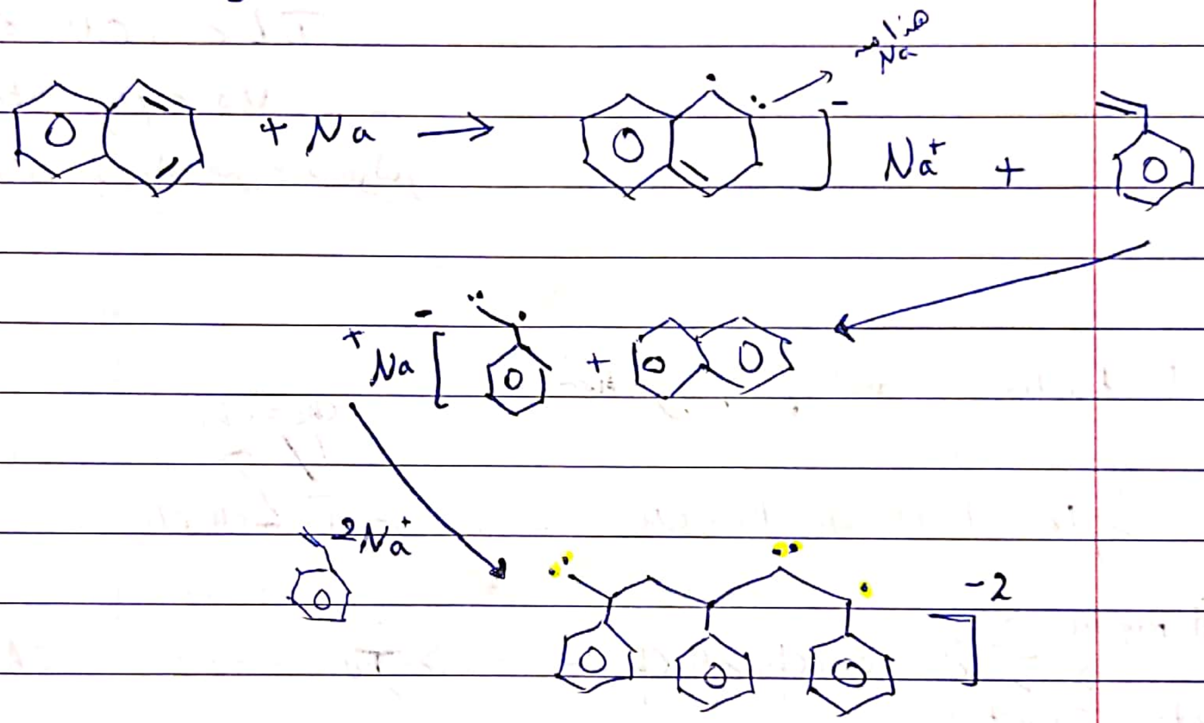
$$R\sim\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}^{\ominus} \xrightarrow{H_2O} R\sim\sim C-\underset{X}{C}-H + MgX(OH)$$

$$R\sim\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}^{\ominus} \xrightarrow[\text{② Dry Ice } (CO_2)]{\text{① HCl}} R\sim\sim C-\underset{X}{C}-\overset{O}{\overset{\|}{C}}-OH + MgXCl$$

# Living Polymer

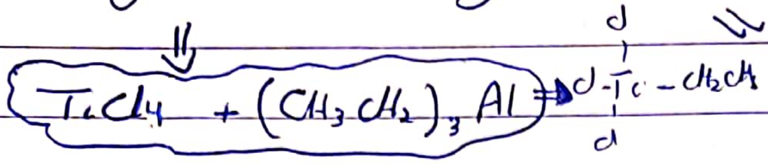


active center moves



# * Chap. 4 Coordination polymer

## 4 Ziegler–Natta Catalyst



$TiCl_4 + (CH_3CH_2)_3Al \Rightarrow Cl-TiCl_2-CH_2CH_3$

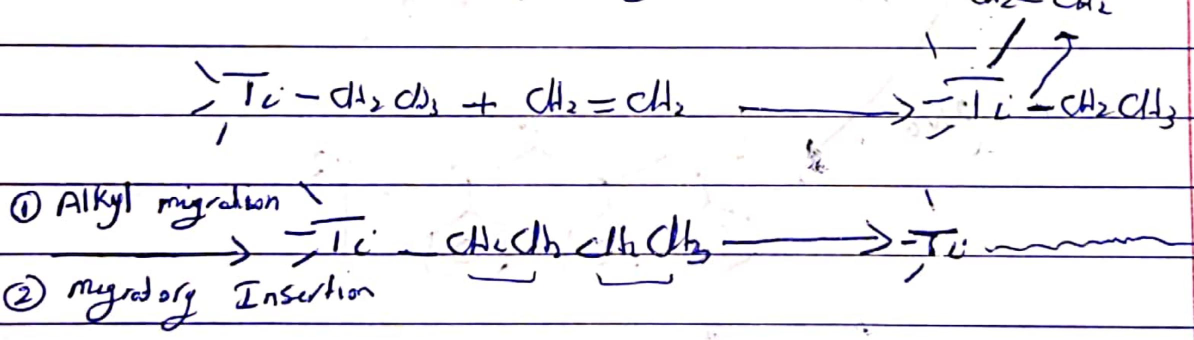
$TiCl_4 \rightarrow CN = 4$
So can used as
Catalyst

شكل آخر للكاتاليست

$TiCl_3 + (CH_3CH_2)_3Al$

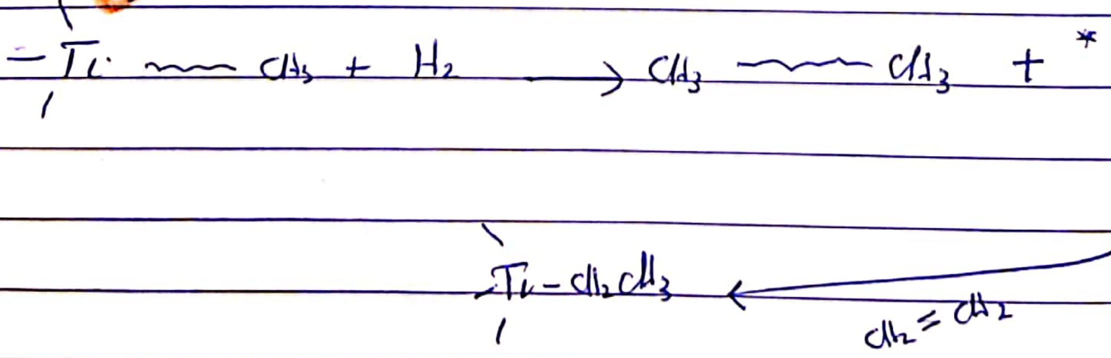
$TiL_6$ , $CN = 6$
No empty site
لا يوجد فراغ حتى يحدث بوليمر

## I) Initiation and propagation



## II) Termination

① Rxn with $H_2$

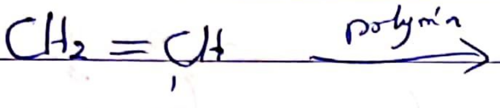


لأنها محفز تستكمل الارتباط مرة أخرى

Donyā
15/8/2022

## ② β – hydrogen elemination

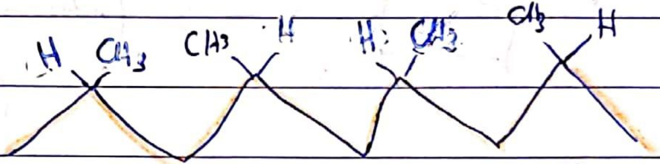
$$-\overset{|}{\underset{|}{Ti}}-\overset{\alpha}{CH_2}\overset{\beta}{\underline{CH_2}}\overset{\gamma}{CH_2}CH_2 \sim\sim poly \longrightarrow -\overset{|}{\underset{|}{Ti}}-H + CH_2=CH \sim\sim poly$$



$$CH_2=\underset{\underset{CH_3}{|}}{CH} \xrightarrow{polymer}$$

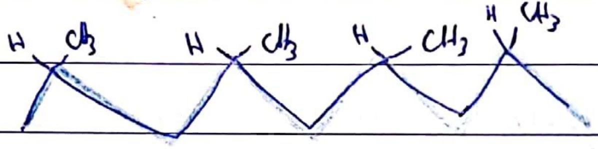
متقابلات

**1** Atactic



منتظم

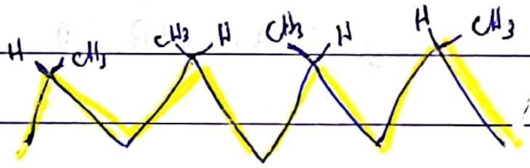
**2** Isotactic



تكوين منتظمة

متوالي

**3** Syndiotactic

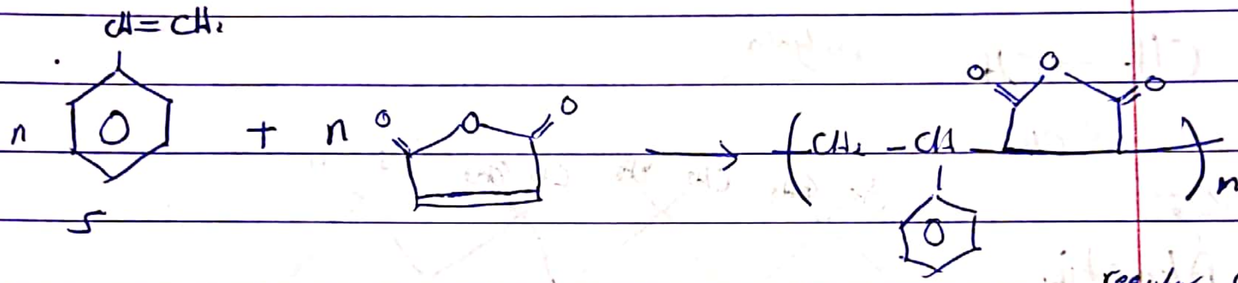


# Copolymerization

Copolymer : two or more different monomers

1- Regular (Alternating) polymers :

$nA + nB \longrightarrow ABABAB$ ——

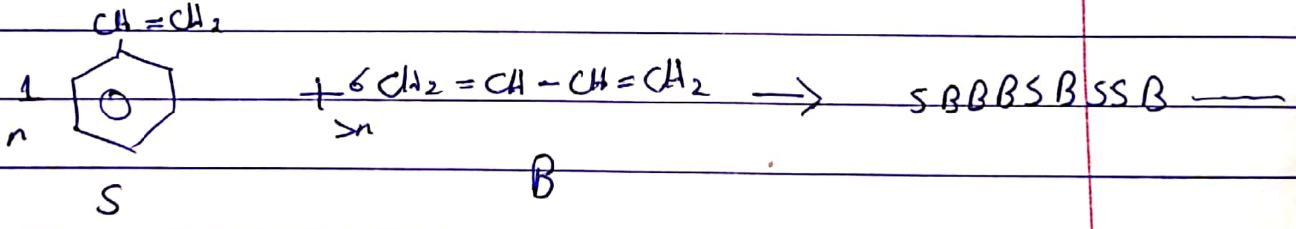


regular chain

2- Random polymer

$A + B \longrightarrow AAA\ BB\ AB$ ----

σ : 1

ⓐ 

$+ 6\,CH_2=CH-CH=CH_2 \longrightarrow SBBBSBSSB$ ——

ⓑ $S + B + A\ (CH_2=\overset{CN}{CH}) \longrightarrow ABS$

Acrylonitrile

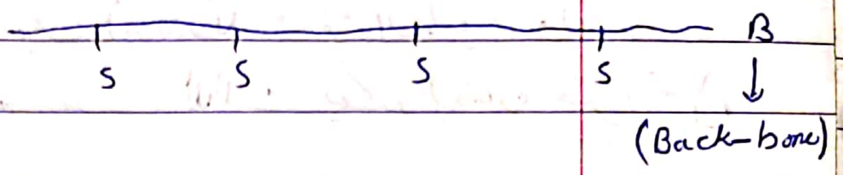
3- Block Copolymer

$S + B \longrightarrow (\underbrace{SSSSS}_{5}\underbrace{BBB}_{3} - \underbrace{SSSSS}_{5}\underbrace{BBB}_{3})$

the most Important

## 4-Graft Copolymer :-

S + B

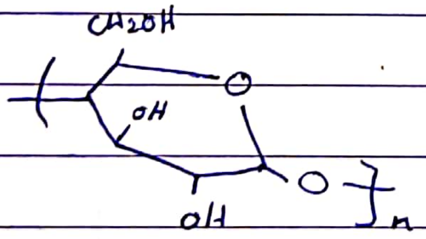


a) prepare butadiene polymer
b) dissolved B polymer in monomer S

## Biodegradable polymer

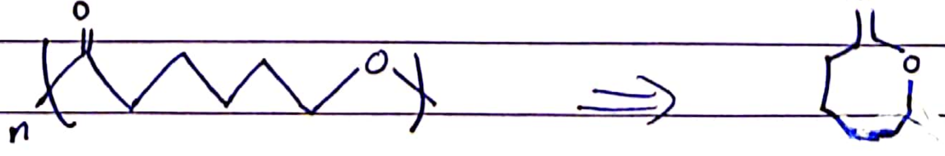
Converted to carbon dioxide under microbial action

$\boxed{1}$ Naturally occuring polymers
ex. ( amylose / amylopectine )



$\boxed{2}$ polymers possessing hydrolysable backbone

Poly Carpolactone (polyester)



monomer ⇒ cyclic

PET ⇒ non biodegradable

البولي إيثيلين تيرفثاليت يمكن أن يتفكك في الطبيعة ولكن بعد آلاف السنين، لذلك يمكن إعتباره غير متحلل

Good Luck

Donya Salman