Zaina Radwan

Polymer:

① Introduction

Definition.

Types of polymers.

M.wt of polymers.

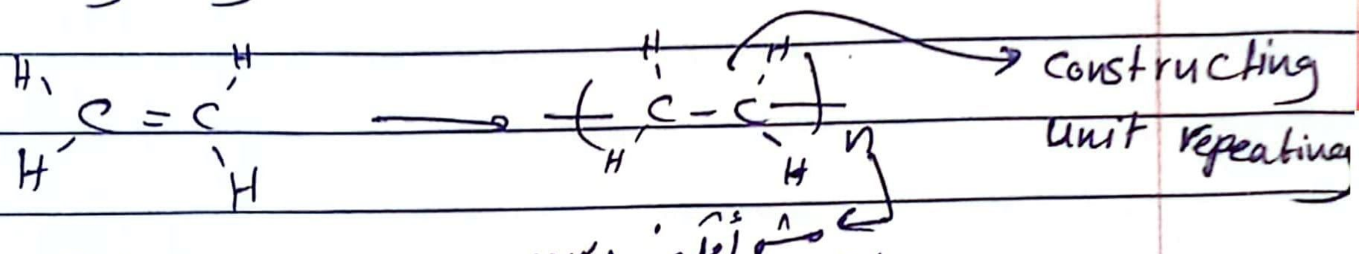
* بوليمر لازم يحتوي على two functional group (عادي لو نفس النوع).
عشان يصير polymerization . (f=2)

② step_ RXn ~~Polym'n~~ polym'n

③ chain-rxn polymerization.

PolyEthylene (PE).

PolyEthyleme Terphthalate PET or PETE



Ethylene

مش أقل من ١٠ آلاف polymer.

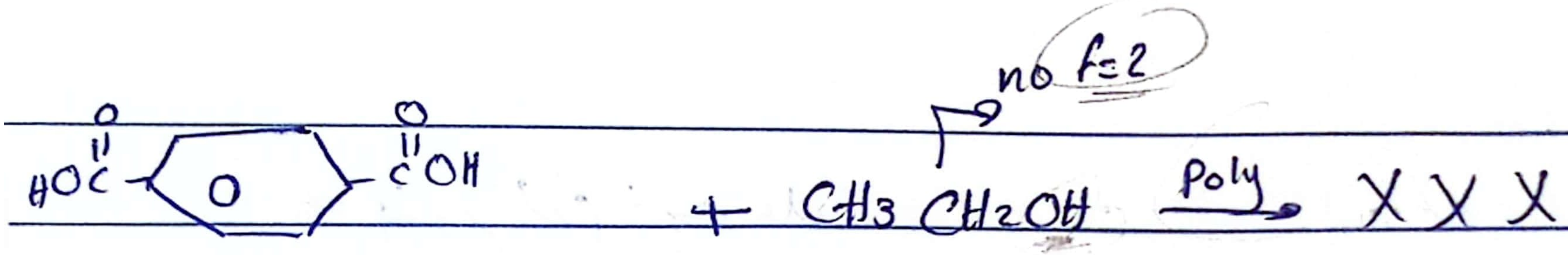
عشان أكونه

$n > \frac{10.000}{28} \rightarrow$ polymer

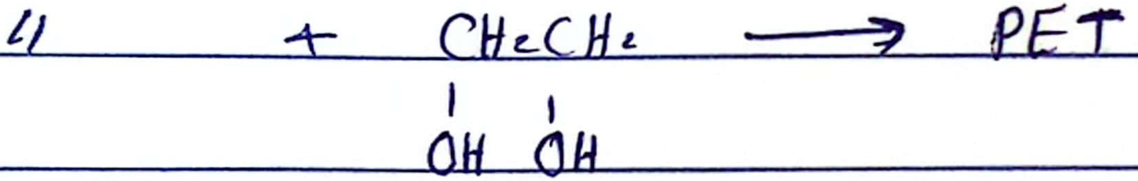
M.wt Ethylene ← 28

monomers

Terphthalic acid



Terphthalic acid



$$〃 + \underset{OH}{CH_2}\underset{OH}{CH_2} \longrightarrow PET$$

4. Co- polymers.

Introduction

Polymer (multi متعدد).

Monomer $\xrightarrow{\text{Polymerization}}$ polymer → $-(A)-_n$

A ,, متعدد AAAA | m.wt ≥ 10,000 (g/mol) dalton

Copolymer [A + B → AAABBB - - -
ABAB - - -

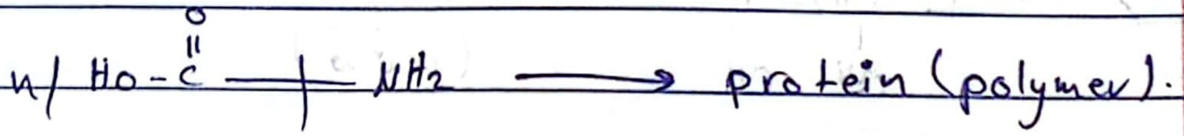
< 10000 oligomer

البوليمرات اللي كتلتها عالية

أقل من ١٠آلاف تسميها oligomer.

Monomer → polymer.

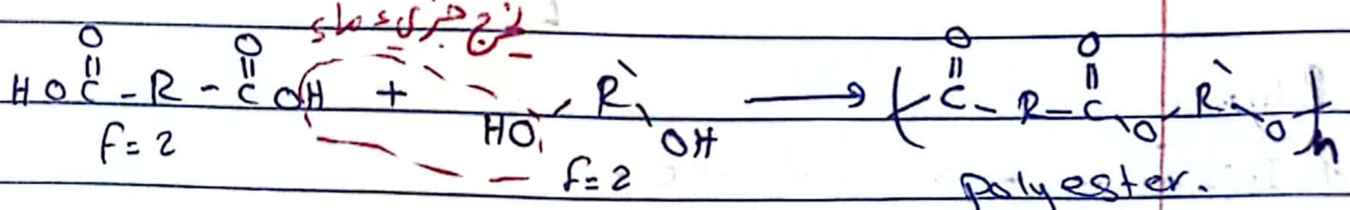
must have 2 functional group.



$n/\ HO-\overset{O}{\overset{\parallel}{C}}-\!\!\!\vdash NH_2 \longrightarrow$ protein (polymer).

ester: acid + alcohol.

Polyester: diacid + diol



$HO\overset{O}{\overset{\parallel}{C}}-R-\overset{O}{\overset{\parallel}{C}}OH + HO-R'-OH \longrightarrow \left[\overset{O}{\overset{\parallel}{C}}-R-\overset{O}{\overset{\parallel}{C}}-O-R'-O\right]_n$

Polyester.

* $CH_3\overset{O}{\overset{\|}{C}}OH + CH_3CH_2OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}OCH_2\cancel{CH_2}CH_3$

$f=1$ $\quad f=1$

ينتج ester فقط لا يستطيع
تكرار نفسه

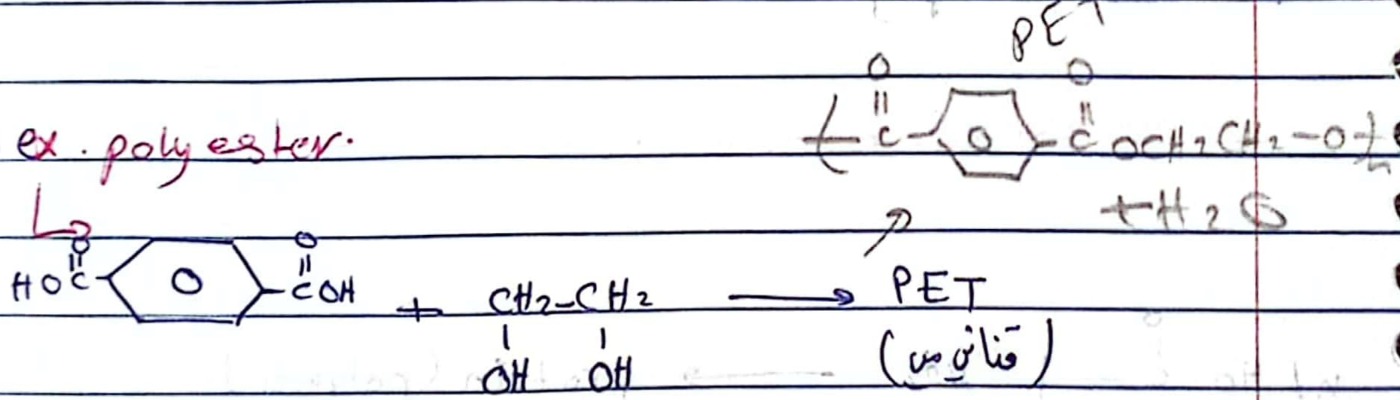
* $HO-\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OH + CH_3CH_2OH \longrightarrow HO-\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}-O-CH_2CH_3$

$f=2$ $\qquad$ CH_3CH_2OH $\quad f=1$

$\longrightarrow CH_3CH_2O\overset{O}{\overset{\|}{C}}CH_2\overset{O}{\overset{\|}{C}}OCH_2CH_3$

$\boxed{f=0}$ لا يمكن التفاعل.

* ex. polyester.



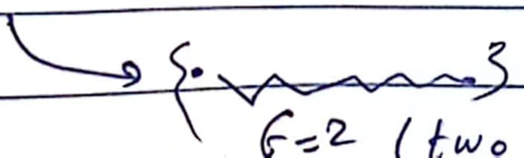
π-bond $(f=1)$ نظرياً

$$n\,(CH_2=CH_2) \longrightarrow \left(\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\right)_n$$

PE

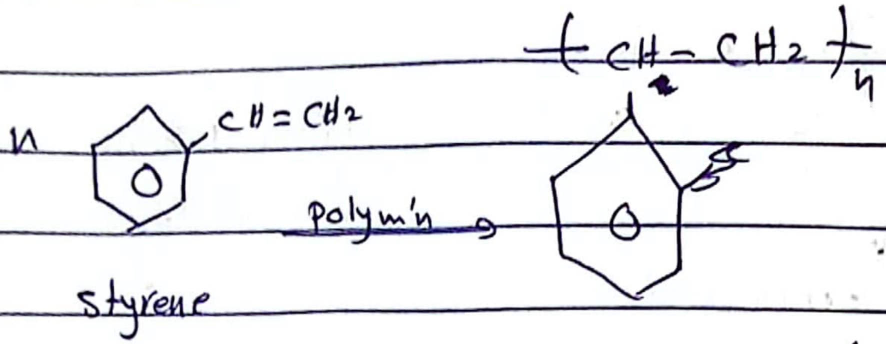
Polym'n

1. Initiation. $\rightarrow \cdot\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot$
2. propagation $\longrightarrow \cdot\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}\cdot$
3. Termination

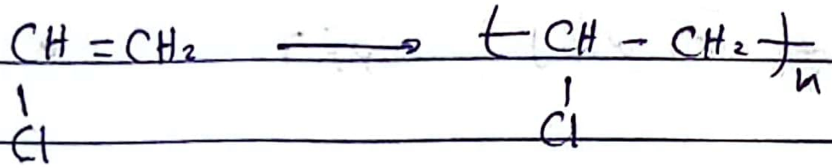


$F=2$ (two radical).

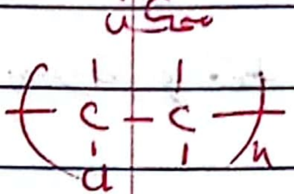
PVC



Polystyrene (PS)



$$CH=CH_2 \text{ (Cl below) } \longrightarrow -(CH-CH_2)_n- \text{ (Cl below)}$$

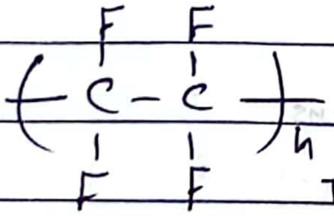


vinyl chloride.

PVC → polyvinyl chloride.

Main polymeric structure:

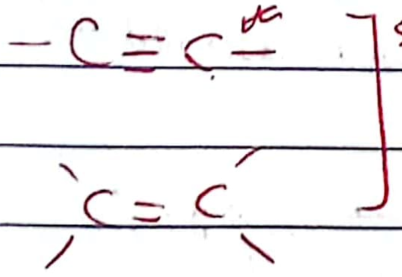
1) Linear structure: ex. PE, PET, PS, PVC



$$-(CF_2-CF_2)_n-$$

Teflon

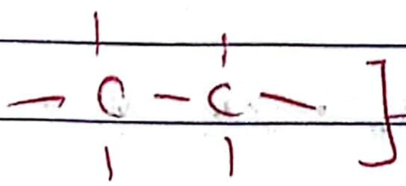
غالباً بيكون مونومرها/ها يحوي (=) double bond.



sp

linear → الكربون + الهيدروجين على نفس الواجهة.

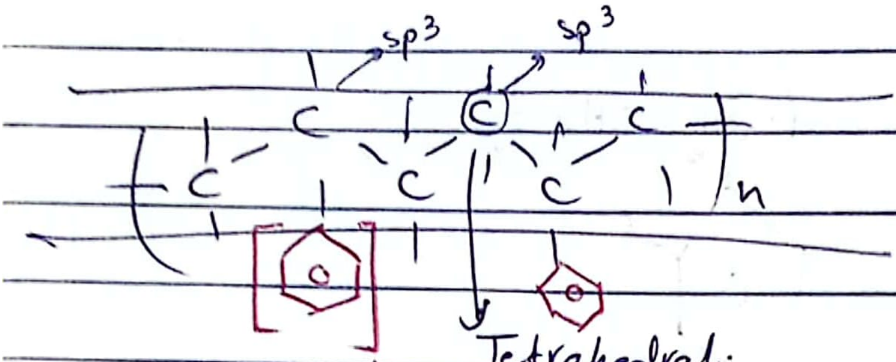
sp^2



→ not linear.

sp^3

→

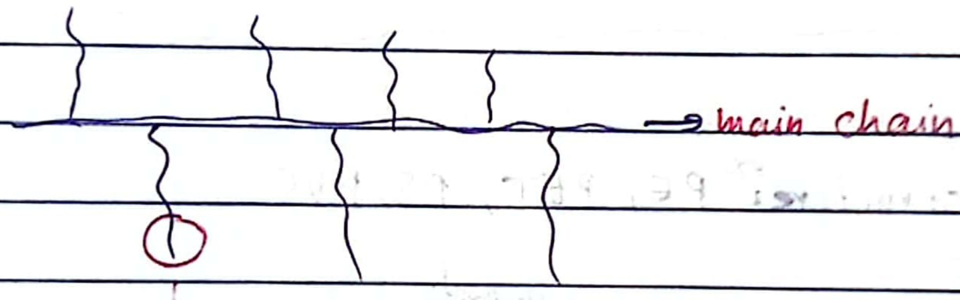


بالمركب كشكل linear
حتى لو كان يحتوي على
C تهجينها sp^3
+ حتى لو احتوت على
حلقات بنزين

لا تعتبر تفرع لأنه
حجم ⌬ صغير جداً
بالنسبة لطول السلسلة

* إذا كان عندي ٦ كربونات بشكل طولي متعلقة بالبوليمر تعتبر تفرع فقط

2 Branched structure:



side chain ≥ 6 carbons

~~Branched~~

plastics
اللدائن

→ Thermoplastics
تنصهر وتتمدد بالحرارة.
قابل للتدوير وإعادة التشكيل

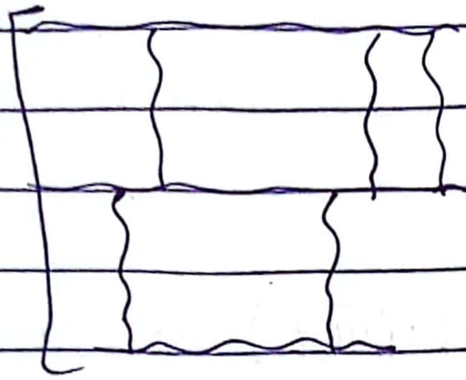
→ Thermosets → غير قابل للتدوير
~~not Branched~~.

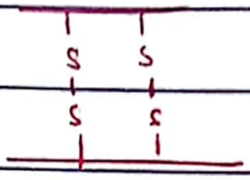
* البلاستيك فش اله درجة غليان وله درجة انصهار ودرجة تزجج

3] 3-Dimensional structure.
(3-D network)

ex:

Parallel cross-linked





Volcanised- rubber.

*Classification of polymers:

double bond
$|| + || + || \longrightarrow \left[\overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} \right]_n$ Addition polymers.

diol + diacid ⟶ polyester + H_2O, Condensation Rxns

تصنيف
1. Carothers polymers
*حسب طريقة التحضير
- → Addition polymers (PE, PS ...)
- → Condensation poly (Polyester, Polyamide, protein cellulose).

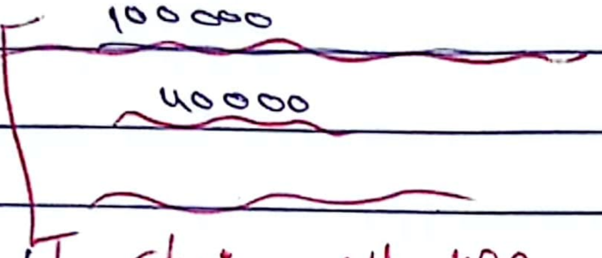
حسب ميكانيكية التفاعل
2. Flory (Mechanism)

*addition $\xrightarrow{\text{سماها}}$ chain rxn polymers (||): (initiation, ...)
* condensation $\xrightarrow{\text{سماها}}$ step-rxn polymers.
" growth
stepwise

Molecular Weight of polymers.

monomer ~~polymiza~~ polymer (macromolecules).

$\longrightarrow$ M.wt > 10000



* عدد من الجزيئات تختلف
في كتلها وفوق ال ١٠ آلاف

→ Chains with different M.wt

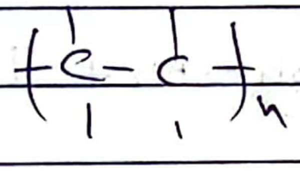
→ Average molecular weight ($\overline{Mwt}$) نعبر عنها بـ

$\overline{Mwt}$ = DP x molar mass of CRU.

DP: Degree of Polyerization, n

CRU: Constructing repeating unit.

$n\,CH_2=CH_2 \longrightarrow$



$-(C-C)-_n$

M.wt: 30000

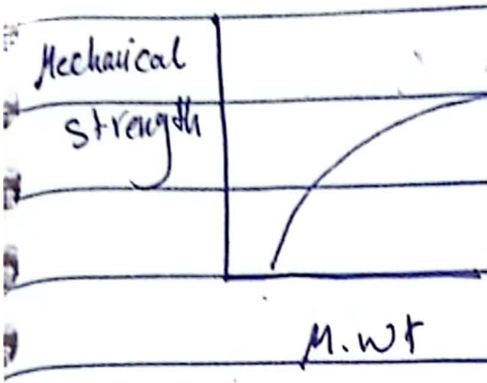
$\overset{30000}{\overline{Mwt}} = \overset{(n).}{\underline{DP}} \times 28$ → الكتلة المولية للإيثيلين

$DP = \frac{30000}{28} = 1071,4$

---

* Many properties of polymer depends on molecular weight

لما M.wt أكبر ← درجة انصهار أكبر



Molecular weight Calculation

I Number Average of molecular weight ($\overline{M}_N$)

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

M: M.wt of each no. of series

N: no of series. — * ممكن نعوضها مولات أو جزيئات .

ex:

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

$$\overline{M}_n = \frac{(5 \times \overset{1200000}{40000}) + (15 \times \overset{٤٥٠٠٠٠}{30000})}{(15+5)} = 325{,}000 \text{ g/mol}$$

Colligative properties:

1. Freezing point depression → $\boxed{\Delta T_f = m \cdot K_f}$ تجمدية
2. Boiling " elevation. → $\boxed{\Delta T_b = m \cdot K_b}$
3. Vapour pressure. → $\boxed{\Delta P = P^o X_A}$
4. osmotic pressure.
   → $\pi = i m R T$

ركز

2. Weight Average of molecular weight ($\overline{M_w}$)

$$\overline{M_w} = \frac{\sum_{i=1}^{N} N_i (M_i)^2}{\sum_{i=1}^{N} N_i M_i}$$

نفس الـ
ex : $\overline{M_w} = \frac{5(40{,}000)^2 + 15(30{,}000)^2}{5(40{,}000) + 15(30{,}000)} = 330{,}769$ g/mol

★ M.Wt عالي بالمساهمة في الوزن الجزيئي أكبر

★ notes

$\overline{M_N} < \overline{M_w}$ ★ .1

التشتت

2. Poly dispersity $= \frac{\overline{M_w}}{\overline{M_n}}$ → مستحيل تكون أقل من 1

≈ 1 متساوي يعني (homogenous).

أكبر من 1 بكون مقدار ⇒ التشتت أكبر.

different in chain lengths ↲

2017

3. Z - Average Molecular weight ($\overline{M_z}$)

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

السابق
ex :

$M_n = 32500$ g/mol

$M_w = 330\,769$ g/mol

$M_z = 337{,}209$ g/mol

اللزوجة.

4. Viscosity Average MW ($\overline{M_v}$)

* M_v depends on concentration and length of molecule. (الـ Mwt)

$\propto$ وتناسب طردي

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

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

*

M_z, M_v → not common

$\overline{M_{wt}}$, $\overline{M_N}$ → common. ⇒ polymer ⇒ polydispersity

نعرف منهم

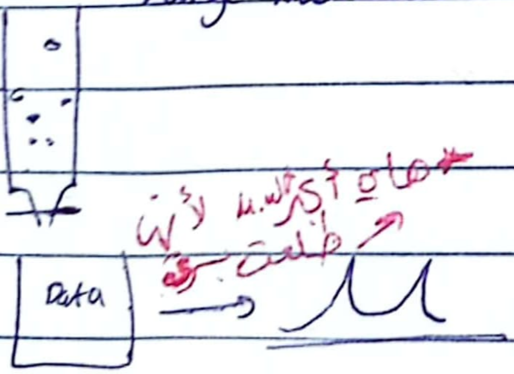
* Molecular weight analysis of polymers.

① Gel Permeation Chromatography (G-PC)

↳ depends on size of molecule.] M.wt

Large molecule → small molecules.

الأثقل ع بيمشي أسرع.

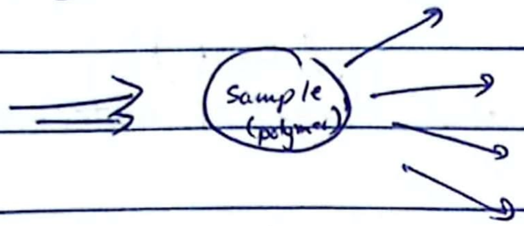


*أول ما الأكبر M.wt لأني
يطلع

→ Retention time.

تشتت

② Light scattering



Intensity of scattered light depend on:

1- concentration.
2. size of particle.

} ⇒ M.wt + shape

3. polarizability. الإستقطاب

③ X-Ray Scattering ⇒ sample (semi crystal).

↳ نقدر نعرف منها طول البوليمر وشكله و زواياه.

* wavelength (0,001 nm to 0,2 nm).

* two types of X-Ray

1. wide angle X-Ray scattering (WAXS) ⇒ orientation of crystals
2. Small " " " (SAXS)
↳ electron density

Cl, C

كثافة الالكترونية في Cl أكبر

e

④ Osometer

a. vapor - pressure osometry
b. membrane osometry

$$\left.\right\}\ \pi = \mu R T$$

$$\mu = \frac{n}{V} = \frac{\frac{m}{m.wt}}{V}$$

$\underline{\wedge}$ M.wt 10,000 - 40,000

← طالتول

Ex. A polymer sample has 5 macromolecules of M.wt = 10,000 da g/mol
20 " of " = 30,000 da
25 " of " = 40,000 da
10 " of " = 20,000 da

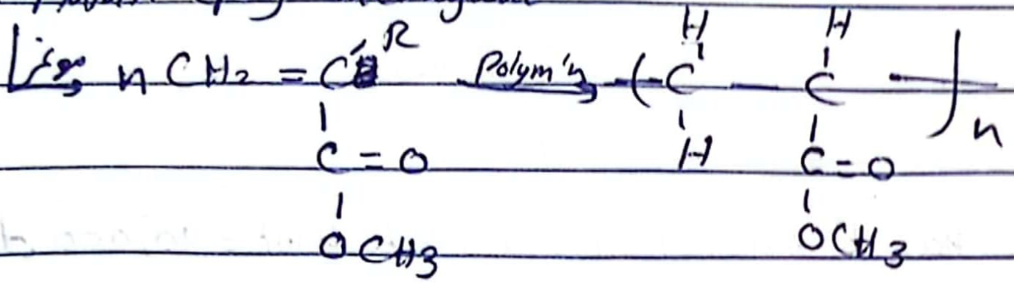
Find $\overline{M}_n$ + $\overline{M}_{wt}$ + polydispersity ??

Example of polymers.

⇒ Addition polymers.

1. PE. 2. PP (↳ polypropen.) 3. PS. 4. PVC 5. Teflon

6. PMMA (poly methylene

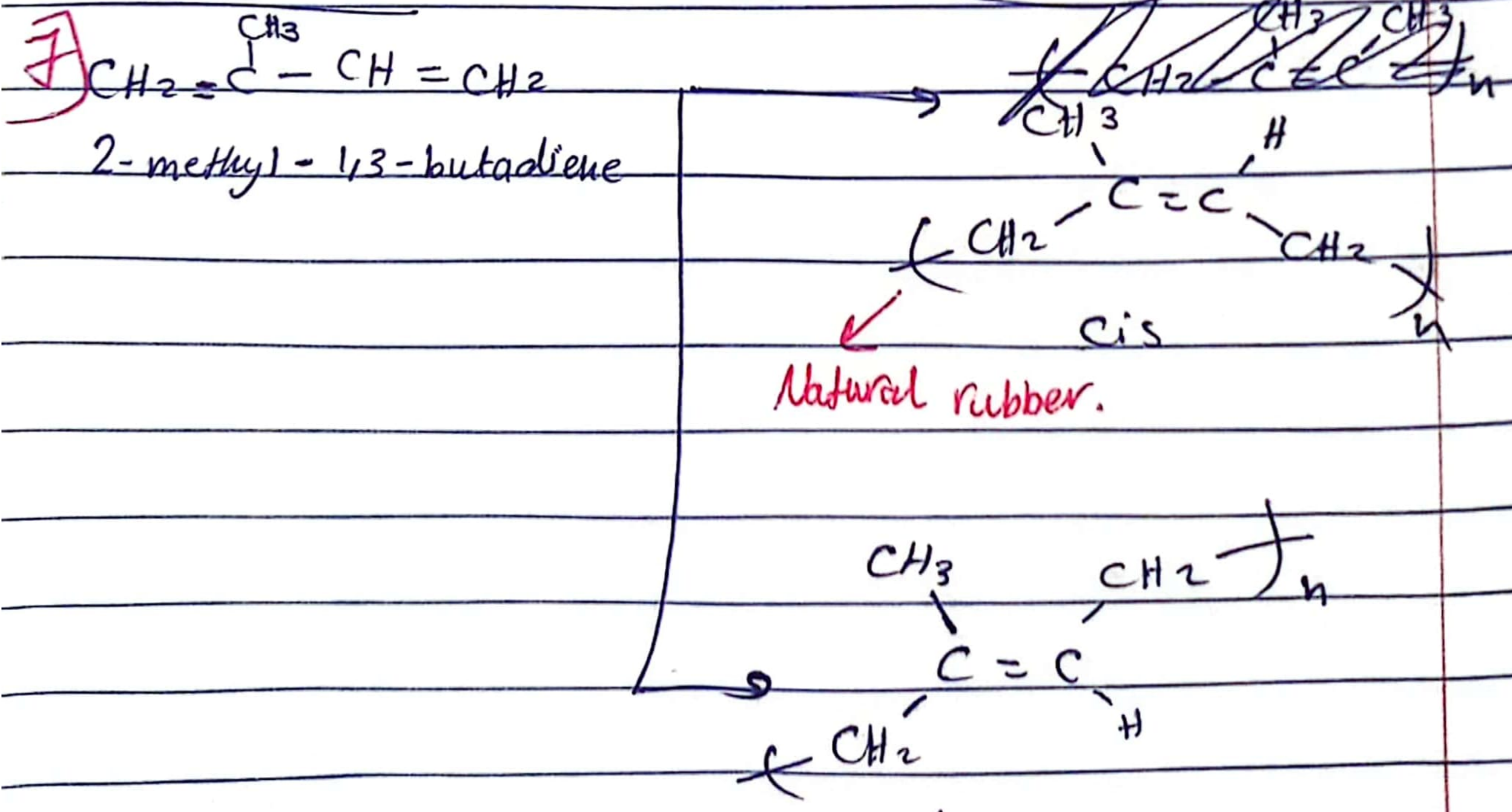


methyl methacrylate

R = H PMMA (poly ~~meth~~ methy acrylate)

R = CH_3 PMMA (~~n H meth 4~~) poly methyl meth acrylate

7)



$CH_2=C(CH_3)-CH=CH_2$

2-methyl-1,3-butadiene

cis

Natural rubber.

trans.

8] $H-C\equiv C-H \xrightarrow{polym} \left(\overset{H}{\overset{|}{C}} = \overset{H}{\overset{|}{C}} \right)_n$

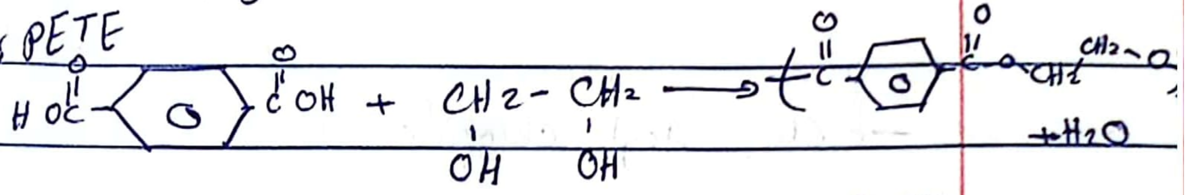
Acetylen — Poly Acetylen (PA).

$\cdot \overset{|}{C} = \overset{|}{C} \cdot$

f = 2.

⇒ condensation polymers:

1. PET or PETE

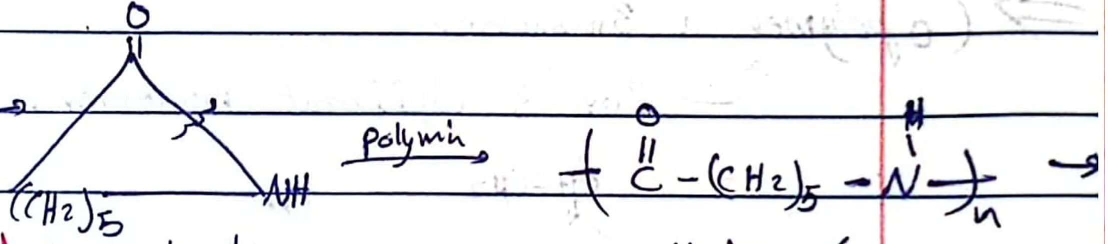


$HO\overset{O}{\overset{\|}{C}}-⌬-\overset{O}{\overset{\|}{C}}OH + \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}} \longrightarrow$ + H_2O

PET

2. Polyamide

* Nylone 6 → diamine + diacid



Capro lactam — Nylon-6

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

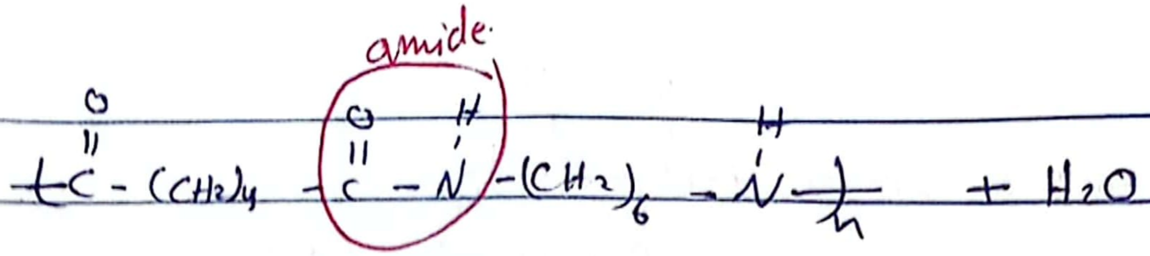
$\left(\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_5-\overset{H}{\overset{|}{N}} \right)_n$ -----

الرقم 6 ⇐ عدد الكربونات.

* Nylone 6,6

C in acids ← 6 , 6 → C in amine.

$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + H_2N-(CH_2)_6-NH_2 \longrightarrow$ الشكلها ورا

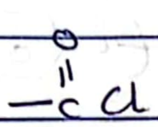


$-\!\!\left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}\right]\!\!-_n + H_2O$

Nylon-6,6

* Acid derivative:

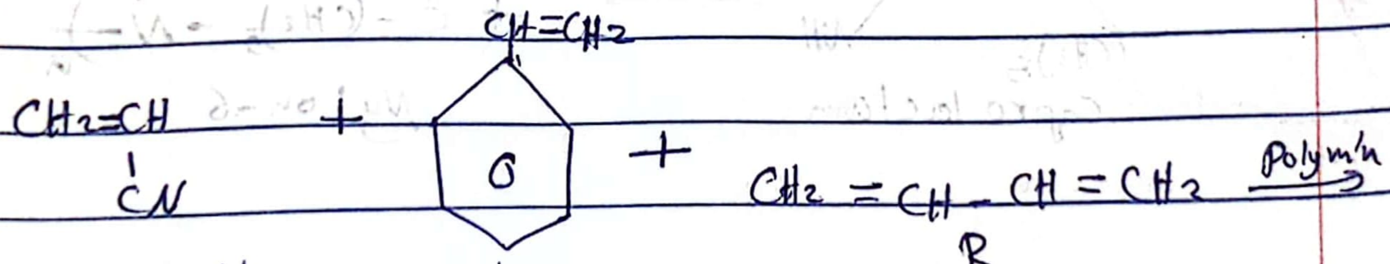
$-\overset{O}{\overset{\|}{C}}OH \Rightarrow -\overset{O}{\overset{\|}{C}}OR$ ester.



$-\overset{O}{\overset{\|}{C}}Cl$ Acyl chloride.

more reactive than the acid itself

⇒ Copolymer : 3monomer
2or 3 different monomer.



$\underset{CN}{\underset{|}{CH_2=CH}}$ + styrene ($C_6H_5CH=CH_2$) + $CH_2=CH-CH=CH_2 \xrightarrow{Polym'n}$

Acrylonitrile
(A

styrene

B

ABS

Some characteristic polymeric structure.

1) Configuration: related structure which are not converted into each other unless bond are broken or reformed.

(cis or trans)

Butadiene → cis and trans

2). Conformation: boat ⇆ chair
clipsed ⇄ staggered. } → heat

بتشغيل الحركة
بنخفض الحرارة أو
بنزيد الحركة.

→ No bond broken or reformed

a) Zig Zag 

b) folded chain 

c) helix 

} ordered.

d) random coil  عشوائي

ممكن الـ ordered يتحول لعشوائي بدون تكسير روابط
بس العكس X .

Conformation:

Polymer →(heating) semi crystals

Tm (درجة الانصهار)

↓ cooling

Semi crystals (rare crystal نادراً.)

↓ cooling

نسميه ✱ Tg (glassy point).

Natural rubber:

Tm = 17°C

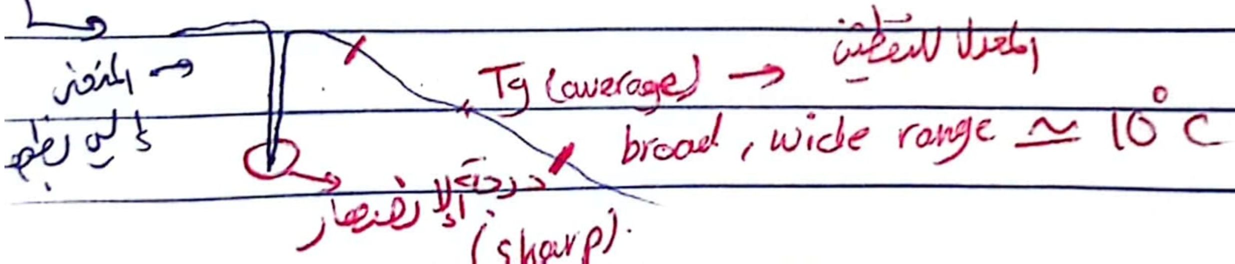
Tg = −73°C } →

glassy	زي الزجاج
hard	قاسي:
fragile	قابل للكسر
brittle	قابل للتفتت

$N_{2(l)}$ = −180°C

✱ Tm and Tg are measured by:

1. Hot stage microscope.
2. differential thermal analysis (DTA) ← الأكثر استخداماً
3. differential scanning calorimetry (DSC)



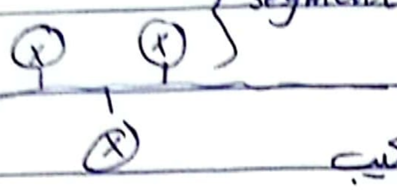
Conformation.

↓

AT Tg the stop

حركة القطعة أو حركة داخلية .

segment motion is never stop حتى لو قللنا الحرارة من هنا لا تتغير

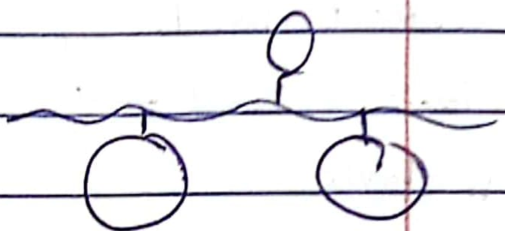


البولمر الأرطأ أفضل من أجل إجراء تغيير في التركيب

* Restrict the segment motion

تقليل ديناميكيات *

1] Bulky Pendant group

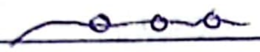


تشنج

2] stiffening groups in main chain:

↓

بتكون داخل السلسلة



Ex: aromatic, double bond ← stiffening groups.

2-methyl-1,3 butadiene → PET + Acetylene مثل الـ ←

* PET is 3 times stronger than cellulose

3] strong Intermolecular forces:

* H-bond, dipole-dipole, London forces

ترتيب من حيث القوة. →

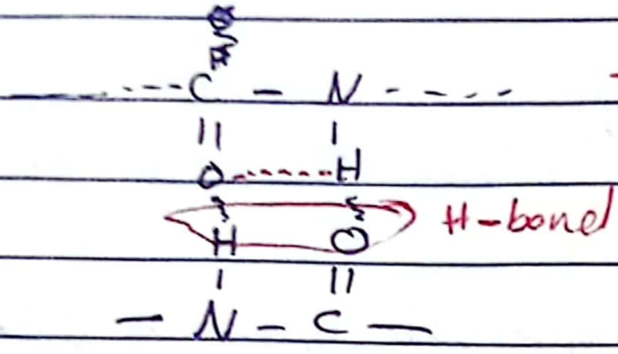
$\left(CH_2\,CH_2\,CH_2\,CH_2 \,---\right)$

Poly ethylene → London forces $\left(CH_2\,CH_2\,CH_2\,CH_2 \,--\right)$

4] Cross-Linking ⇒ ✗

PVC → dipole - dipole.

Nylon-6,6



very strong

Tm = 265°C

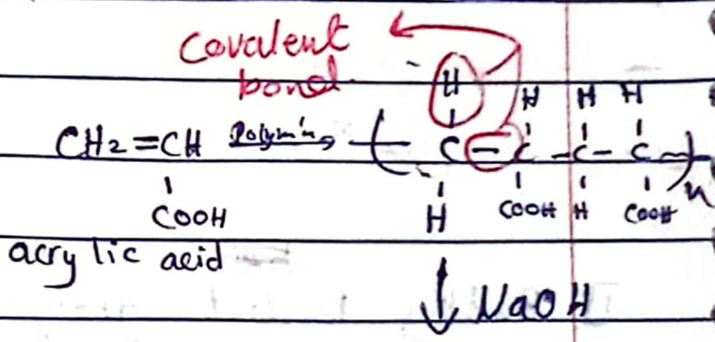
لاتتأثر بالمحاليل

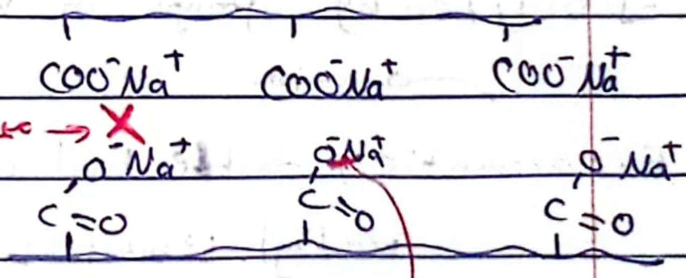
Bonding in polymers:

1] primary Bonding.

- * covalent bond ✓
- * ionic bond → Ex.
- * metallic "

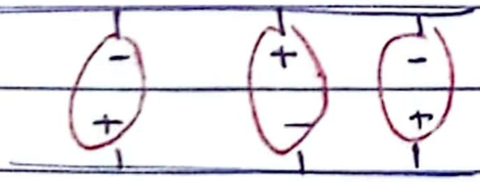
ترتيبهن حسب تواجدهن في البولمرة





ممكن يصير تجاذب → ✗

نعتبرها رابطة أيونية داخلية.



← ionic bond

2] Secondary bonding:

H-bond, dipole-dipole, London forces.

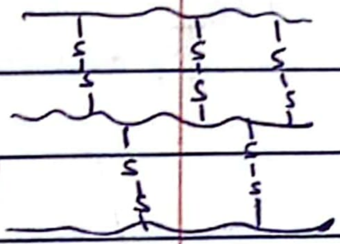
6-10 Kcal 2-6 kcal 2 k cal

segment motion

*

4. Cross Linking

 → cis trans → Natural rubber 1,0 mol $\xrightarrow{S_8,\ heating}$ 0,02 mol



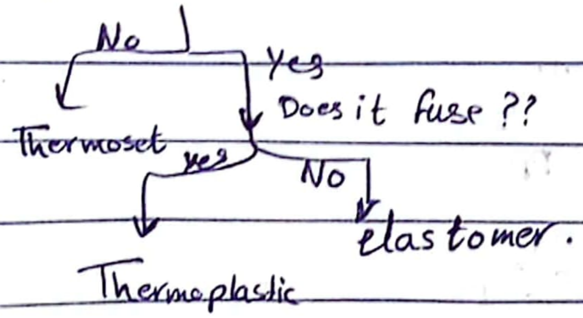
(تقسية المطاط بالكبريت) Vulcanization ←

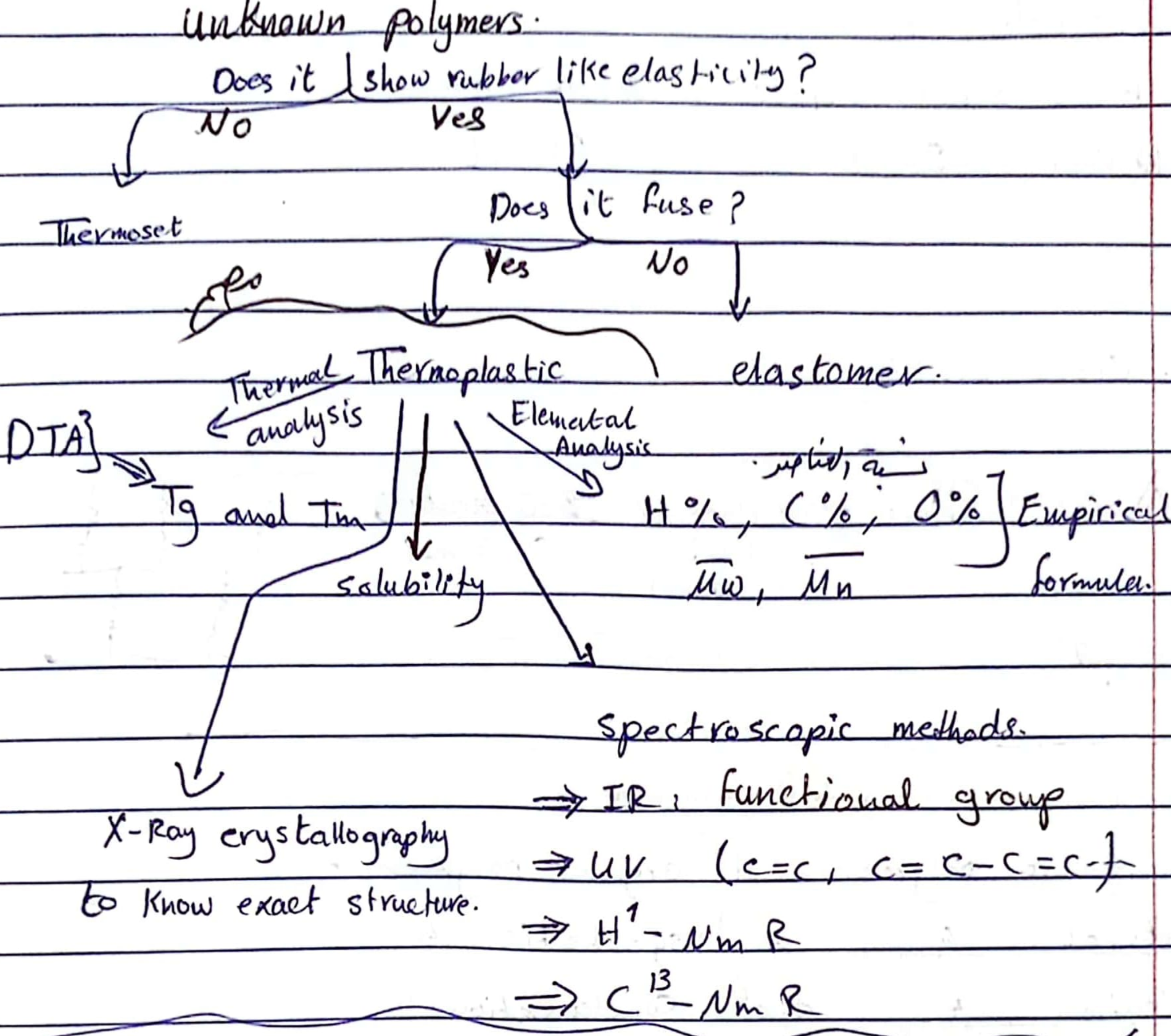
* Classification of polymer.

1. Inorganic polymer and organic polymer.
2. Natural " and synthetic "
3. Addition " and condensation "
4. homo and hetero polymer.] نفس الفكرة
5. homo " and Copolymer polymer] بس الاسم تغير

* Unknown polymers. (Identification of polymers)

↳ Does it show rubber like elasticity? مرونة





unknown polymers.

Does it show rubber like elasticity?

No → Thermoset

Yes → Does it fuse?

Yes → Thermoplastic

No → elastomer.

Thermoplastic:

Thermal analysis — DTA → Tg and Tm

solubility

X-Ray crystallography to know exact structure.

Elemental Analysis → نسبة العناصر H %, C %, O % Empirical formula. $\overline{M_w}$, $\overline{M_n}$

Spectroscopic methods.

⇒ IR : functional group

⇒ UV (c=c, c=c−c=c−)

⇒ H^1 − NmR

⇒ C^{13} − NmR

* Recycled polymers

≈ only Thermoplastic polymers.

1 PETE	4 LDPE Low density PE ↳ branch, cheap.
2 HDPE High density PE ↳ Linear	5 PP
	6 PS
3 PVC	7 Others

Chap 2

Step - Reaction polym'n (condensation).

Method of synthesis of polymer by reaction of bi- or polyfunctional compound. in step-step mechanism.

monomer ⟶ dimer ⟶ trimer ⟶ tetramer ---- --- polymer.

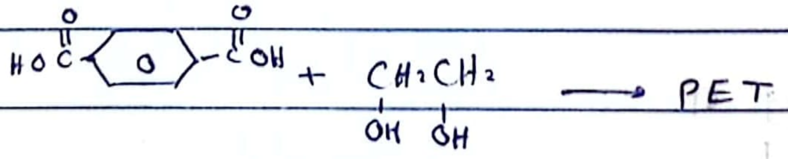
* rxn accompanied by elimination of small molecules | H_2O
HCL
ROH

except in Nylon-6 because It start from ~~[illegible]~~ cyclic monomer.

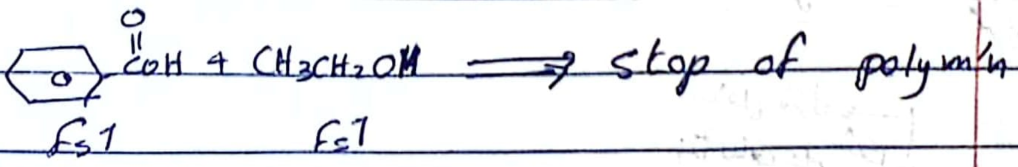
For successful condensation polym'n

1. stochiometry: balance between Reacting molecules
   diacid + diamine ⟶ polyamide.
   1 : 1.

2. Reactant must be very pure (ultra pure) and equipment must be very clean.



Possible impurity
شوائب



3. Reaction must be selected to give high percentage yield and high Mwt

* choose more reactive derivative.

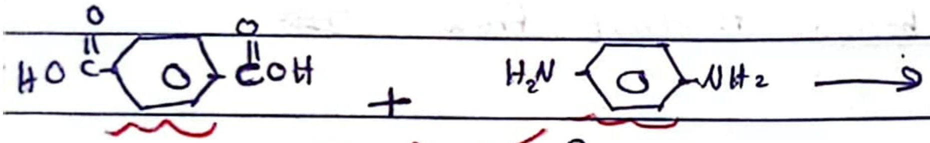
Instead of $R\overset{O}{\overset{\|}{C}}OH$ use $R\overset{O}{\overset{\|}{C}}Cl$ ← * نفس تفاعل نقطة 2 بـ

Examples of step- rxn polymers.

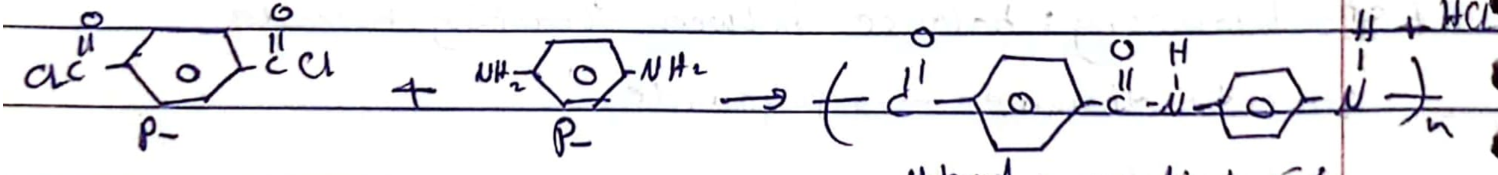
① polyamide

Nylon 6, Nylon-6,6 [Aliphatic]

Aromatic polyamides :



الأروماتك تعيق ال segment motion. ← Para amino aniline



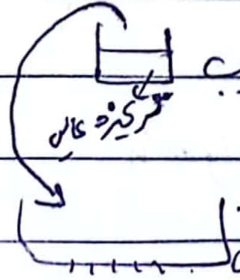
Kevlar. يستخدم في صناعة الألياف (fiber)

* طريقة عمل الفايبرة ١. Melt spining → صهر → لسيحا → منخل فيه ثقوب

→ Fiber

٢. Wet spining

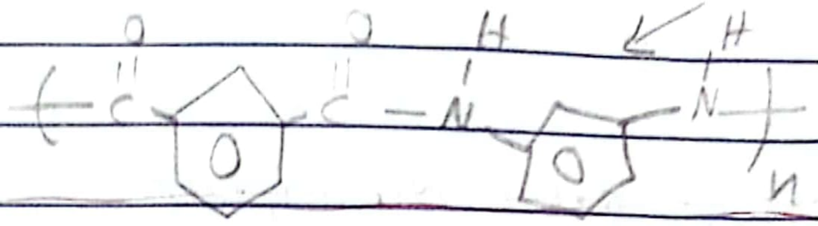
يذاب في مذيب



* يستخدم في صناعة المطاط المقوى.

نفس المعادلة اللي قبل بس meta

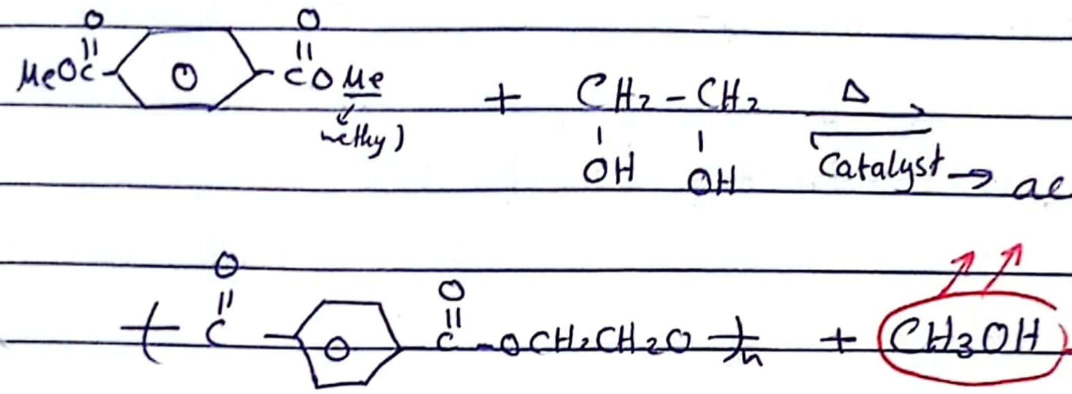
m − + m − ⟶ Nomex



Aromatic + H-bond
⇓
stiffning

very strong
very hard.

2. Polyester:



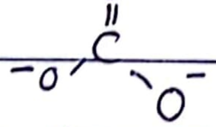
low boiling point

* يمكن التخلص منه بالحرارة

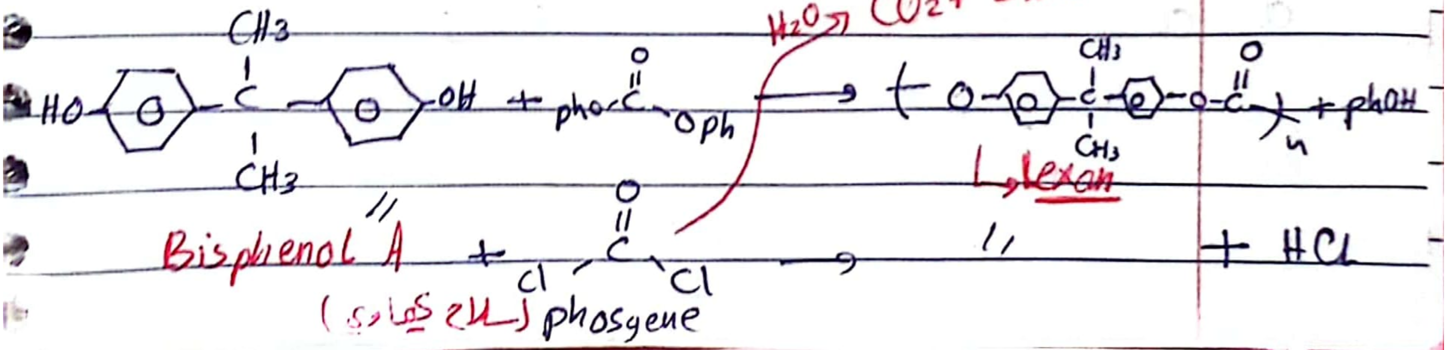
PET
1. fiber → صناعة نسيجية.
2. plastic

→ *Aromatic أقوى من السليلوز لأنه يوجد فيه
* Resistance of hydrolysis.

3. Poly Carbonate:



*بعرف العلماء تحت الكربونات إنها تشكل polyester.

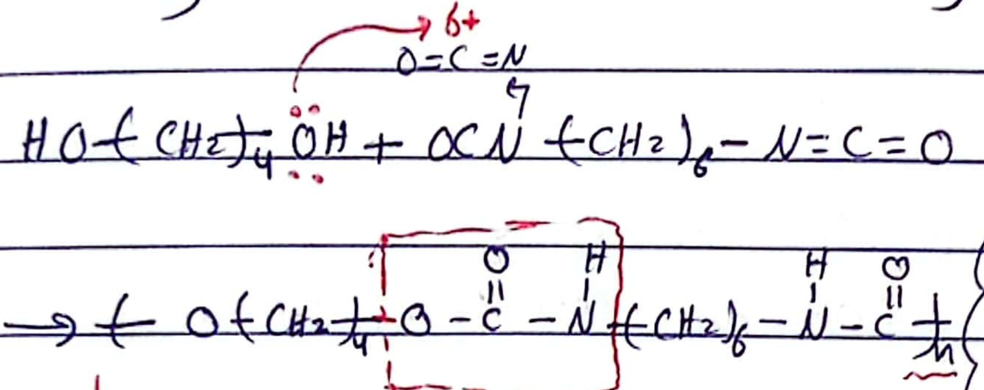


(سلاح كيماوي) phosgene

خواصه.

Lexan → Transparence شفافية as glass.
↳ strong as steel.

4. Polyurithane ⇐ diol + diisocyante



$$HO\!-\!\!(CH_2)_4\!-\!\ddot{O}H + OCN\!-\!\!(CH_2)_6\!-\!N\!=\!C\!=\!O \quad \overset{\delta+}{O\!=\!C\!=\!N}$$

$$\rightarrow \left(O(CH_2)_4\!-\!\boxed{O\!-\!\overset{O}{\overset{\|}{C}}\!-\!\overset{H}{\overset{|}{N}}}\!-\!(CH_2)_6\!-\!\overset{H}{\overset{|}{N}}\!-\!\overset{O}{\overset{\|}{C}} \right)_n$$

↓

urithane (ester + amide)

CN⁻ cyanide
CNO⁻ cyanate
CNS⁻ thiocyanate.
OCN⁻ isocyanate
SCN⁻ isothiocyanate

↳ polymer : Perlon-U (في الصناعات الإسفنجية)
اسمه

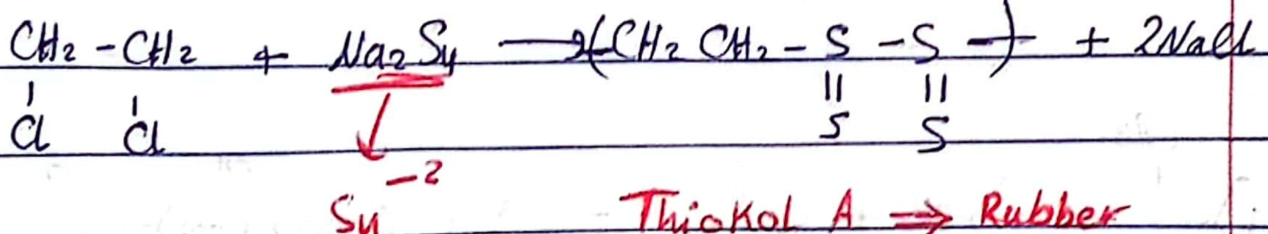
الرطوبة

* In the absence of moisture (H_2O)
⇒ dry condition.

?

$R-NCO + H_2O \longrightarrow RNH_2 + CO_2$] decomposition

5. Polysulfide:



$$\underset{\underset{Cl}{|}}{CH_2}-\underset{\underset{Cl}{|}}{CH_2} + \underset{\underset{S_4^{-2}}{\downarrow}}{Na_2S_4} \longrightarrow 2\left(CH_2\,CH_2-\underset{\underset{S}{\|}}{S}-\underset{\underset{S}{\|}}{S}-\right) + 2NaCl$$

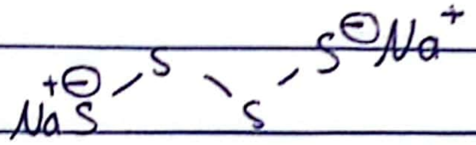
Thiokol A ⇒ Rubber

S_8

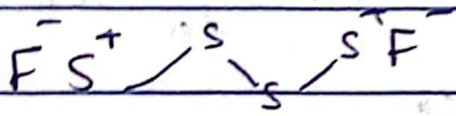
→ Crown تاجي

S_n^{-2}
S_n^{+2}] cyclic + open chain

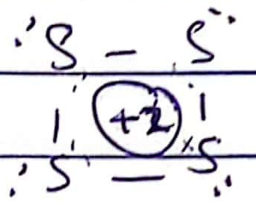
S_4^{-2} ,



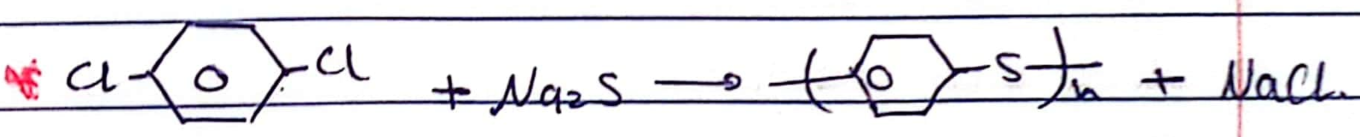
F_2S_4



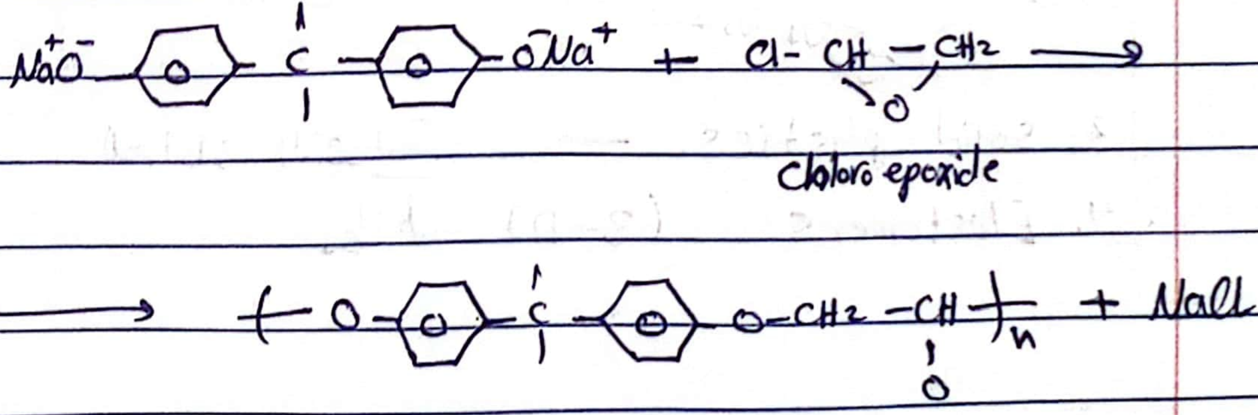
S_4^{+2} →



Aromatic

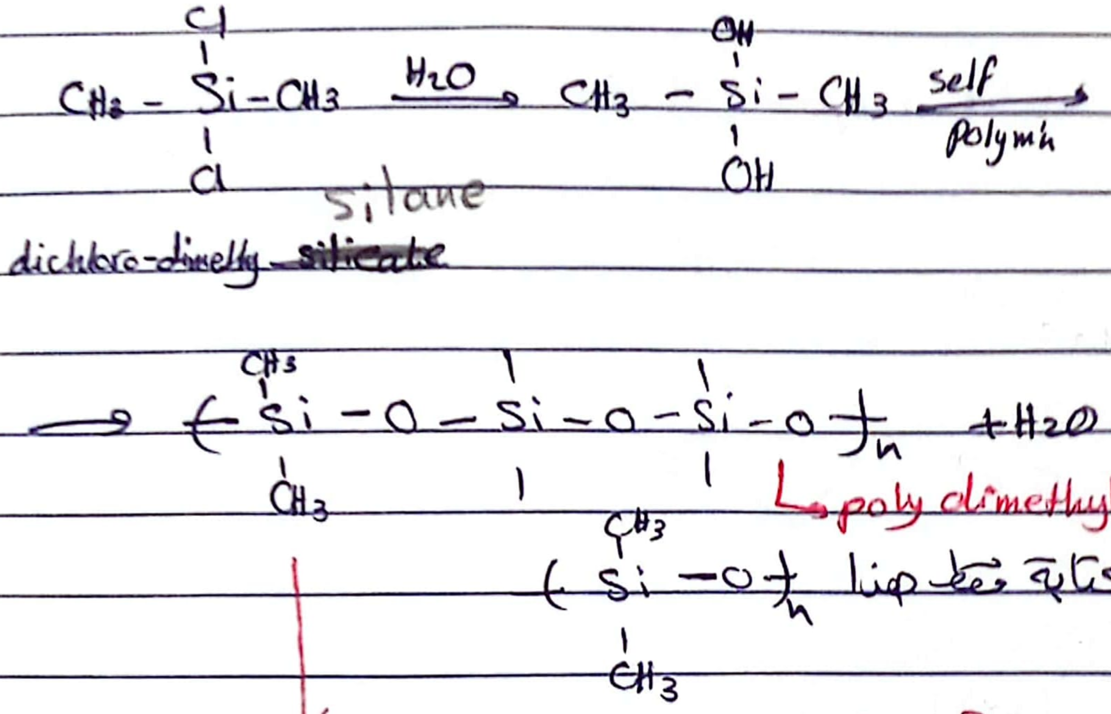


6) Epoxy Resined Adhesive) اللاصقة



low Mwt ⇒ liquid.

7. Polymer of silicons (poly siliosane)



$$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{Si}}-CH_3 \xrightarrow{H_2O} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{Si}}-CH_3 \xrightarrow[\text{Polymn}]{\text{self}}$$

silane

dichloro-dimethy ~~silicate~~

$$\rightarrow \left(\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O\right)_n + H_2O$$

↳ poly dimethyl siloxane

$$\left(\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O\right)_n$$ يمكن كتابة فقط هيك

more active

$Si-Cl >> C-Cl$

$\downarrow H_2O$ $\downarrow H_2O$

$Si-OH$ ✗✗

* حالتين بعتمد على Mwt

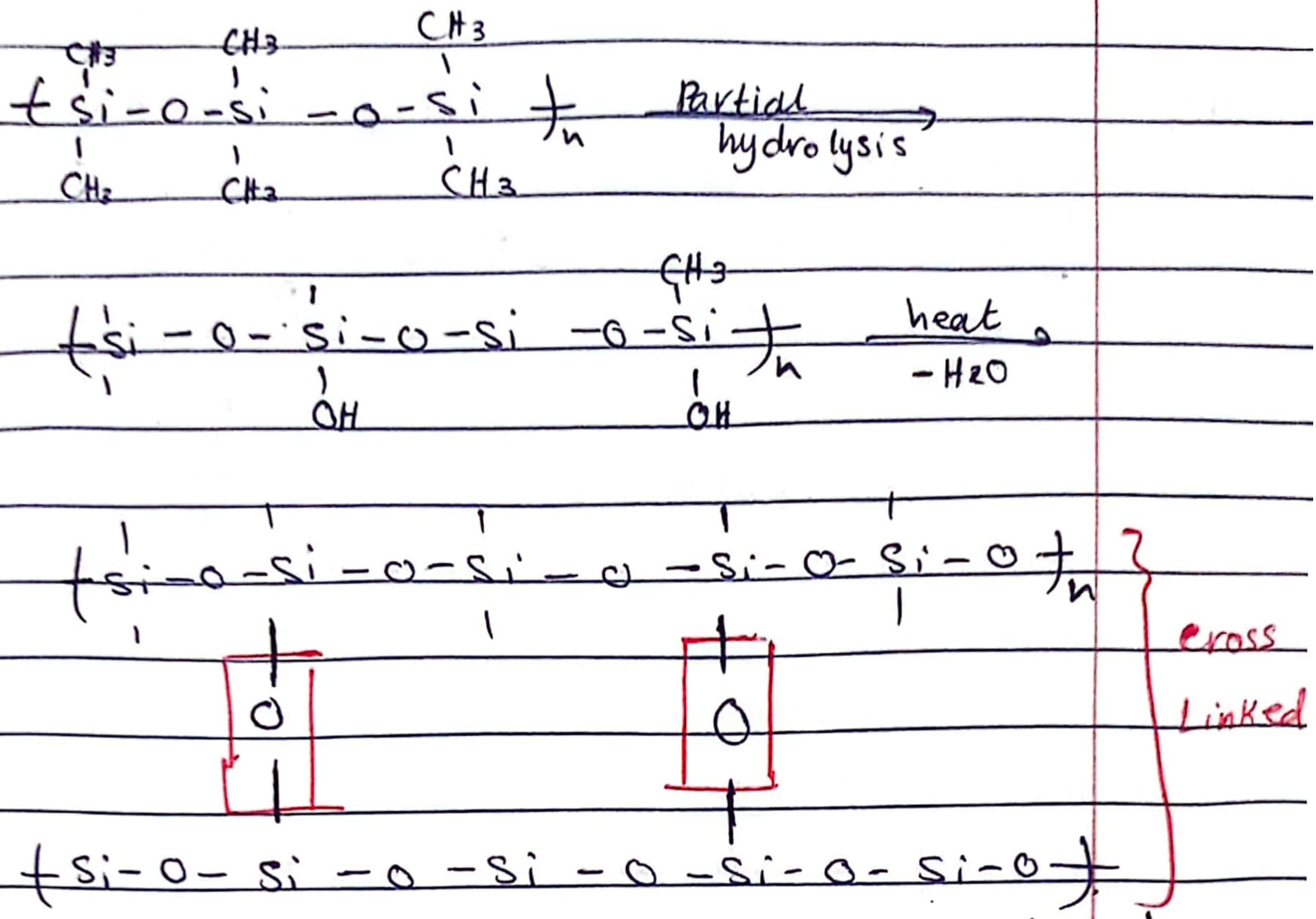
low M.wt → liquid

high M.wt → Solid

*استخدامات:

M.wt

1. Oil (Silicone oil)
2. grease → تدهن فيه أدوات المختبر من أجل سهولة التركيب.
3. solid plastics. → الجراحات التجميلية.
4. Elastomers (3-D) مطاط

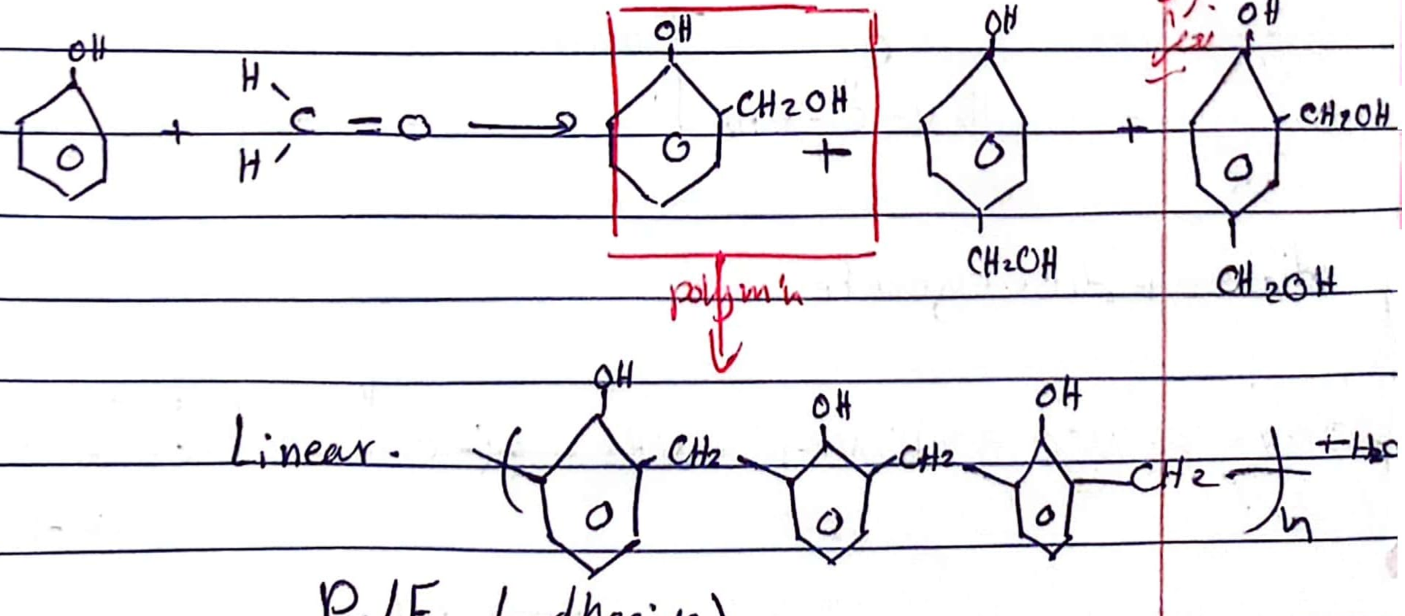


لا يتأثر بالأحماض والقواعد والحرارة والكيماويات.

8. P/F, M/F

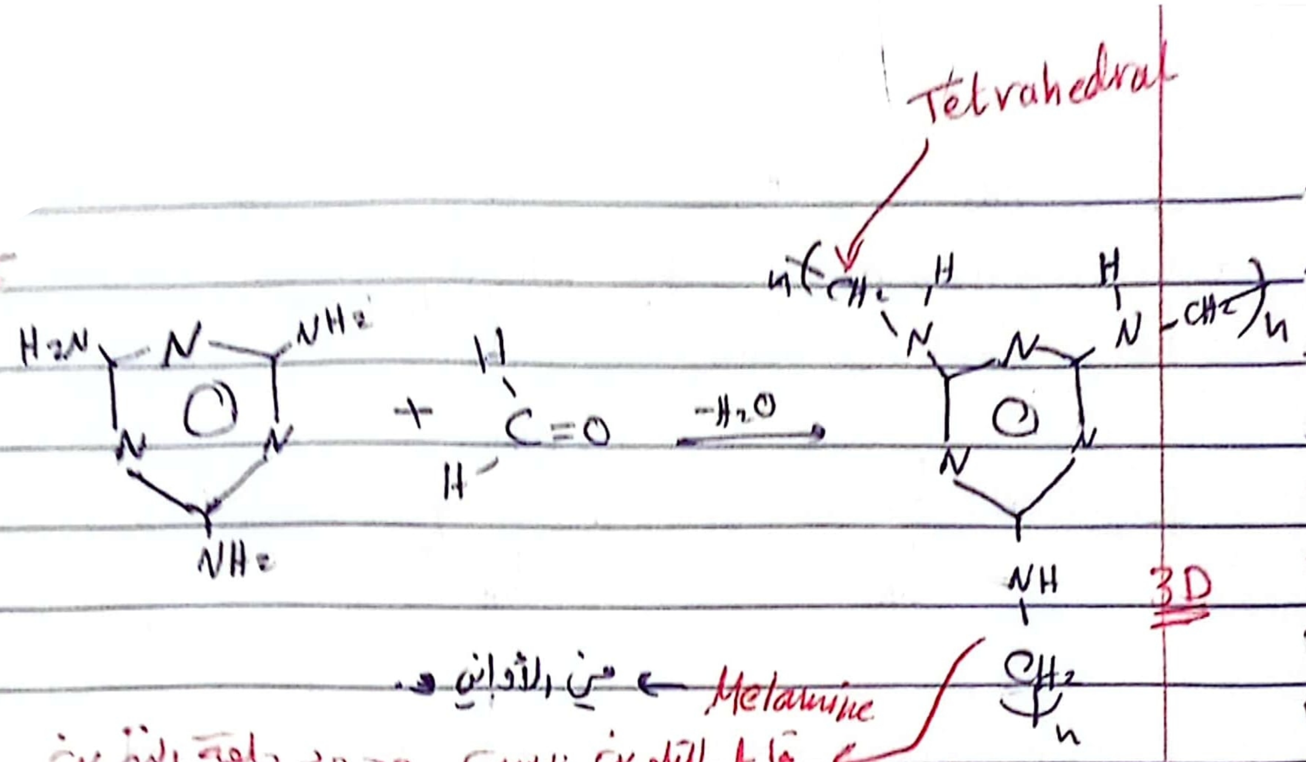
P: phenol , F: Formaldehyde , M: Melamine.

إذا أعطاله بلمرة بصير 3D



P/F (adhesive)

M/F



Melamine ← من الأواني .

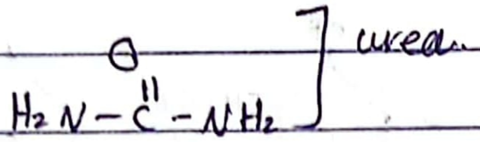
قابل للتلوين بسبب وجود حلقة البنزين

9. Polyethers (R`-O-R)

$$\underset{\text{ethyleneglycol}}{H-O-CH_2-CH_2-OH} \xrightarrow[\text{Polym'n}]{\text{self}} \underset{\text{PEG}}{\left(CH_2CH_2-O-CH_2CH_2-O\right)_n} + H_2O$$

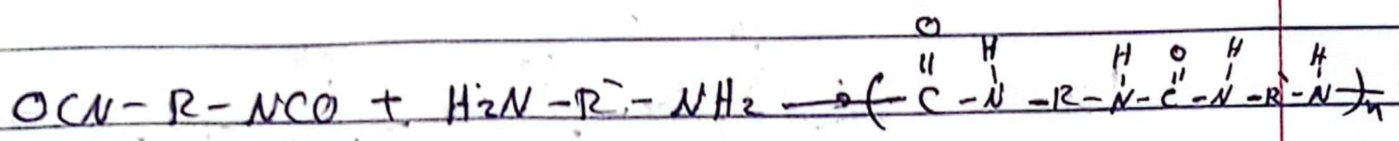
polyethyleneglycol

10. polyurea



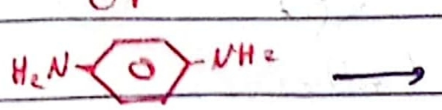
$$\left.H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2\right] \text{urea}$$

diamin + diisocyanate



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

or



→ polymer very strong

Step-RXn polym'n

⇒ may require hours or days to give reasonable product

⇒ Concentration of monomer drops sharply in short time.

monomer → dimer → trimer

ع مباشرة بحضر أول ما يلاقي التقا على ~~monomer~~

dimer + trimer → tetramer

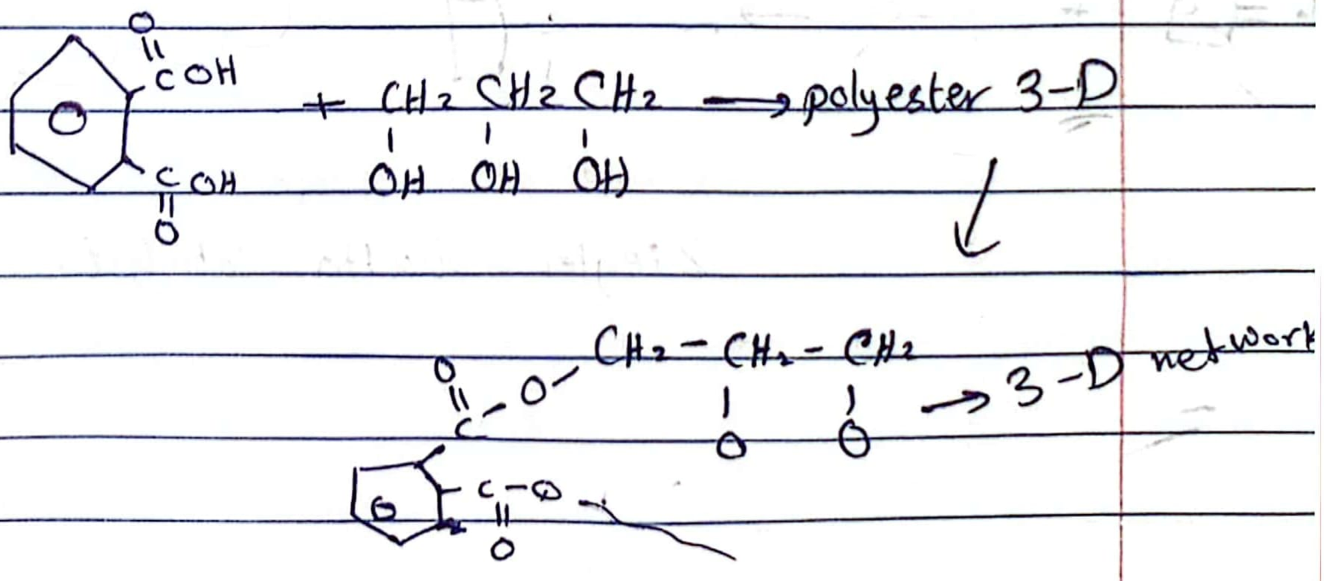
dimer + tetramer → X   مش بالترتيب

⇒ Most rxns are endothermic

$$(\text{diol} + \text{diacid} \overset{\Delta}{\rightleftharpoons} \text{polyester} + \overset{\text{ROH}}{\underset{\downarrow}{\overset{\text{HCl}}{H_2O}}}$$

تخفيف التركيز ←

⇒ polymers mostly are Linear, unless we use trifunction monomer → 3-D [Melamine]



Ch 3. Chain-Rxn polymerization (Addition polymers)

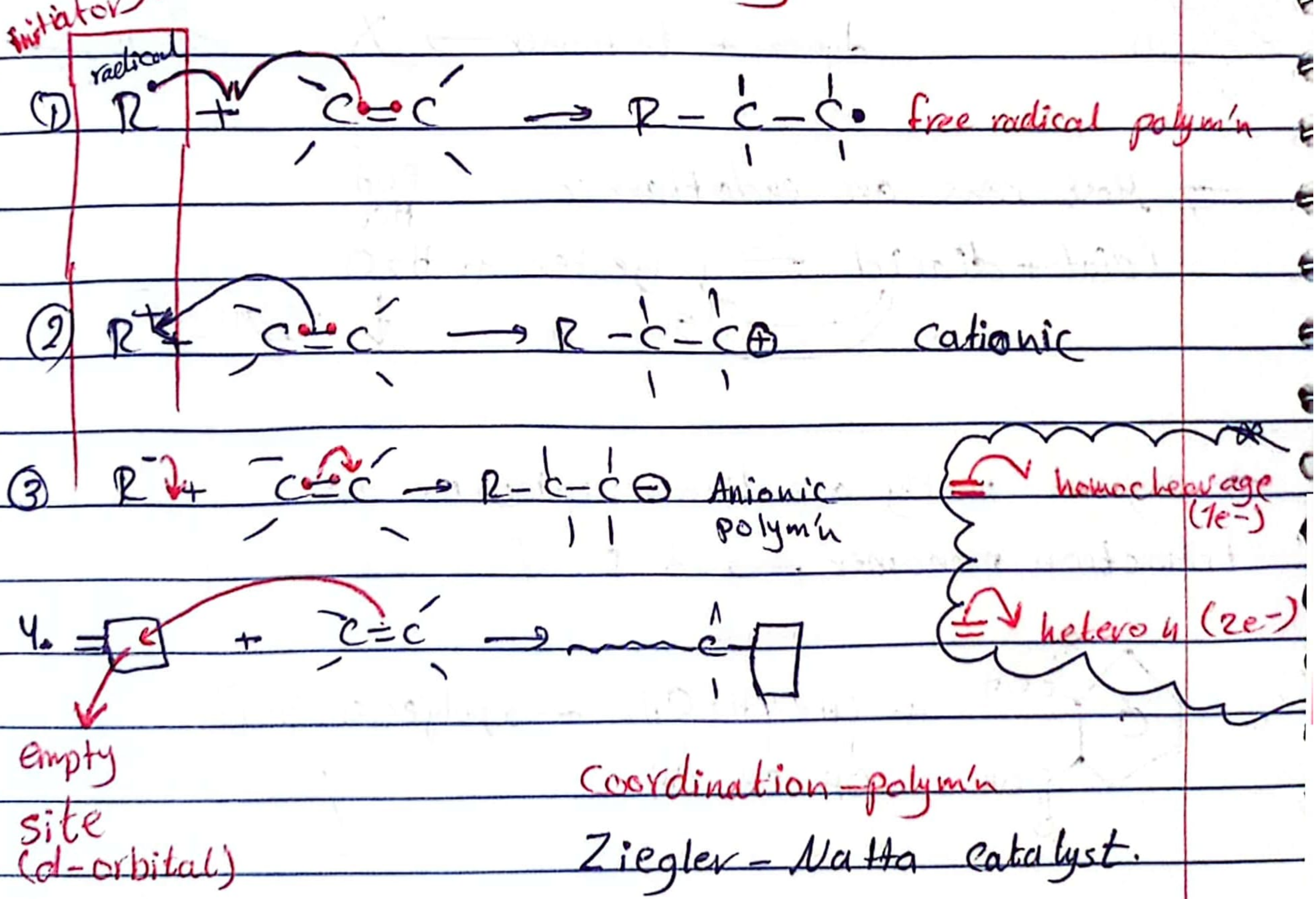
⇓

Mechanism [initiation, propagation, Termination]

* monomers must contain double bond (c=c) ⇒ Successive addition

$C=C \rightarrow \dot{C}-\dot{C}$ (f=2)

* Types of chain-rxn according to initiator



Free radical ~~RXNS~~ Polym'n

* معظم البوليمرات بتم بطريقة ال free radical

* free radical is spontanuous.

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

propagation $\underbrace{M^{\bullet} + \underset{\text{monomer}}{M} \longrightarrow MM^{\bullet} \xrightarrow{M} MMM^{\bullet} \rightarrow \sim\sim\sim\boxed{\bullet}}$ active center

↳ Successive addition.

termination: a) Combination $\sim\sim\boxed{\bullet \quad \bullet}\sim\sim \rightarrow \underset{\text{Polymer.}}{\sim\sim\sim\sim}$

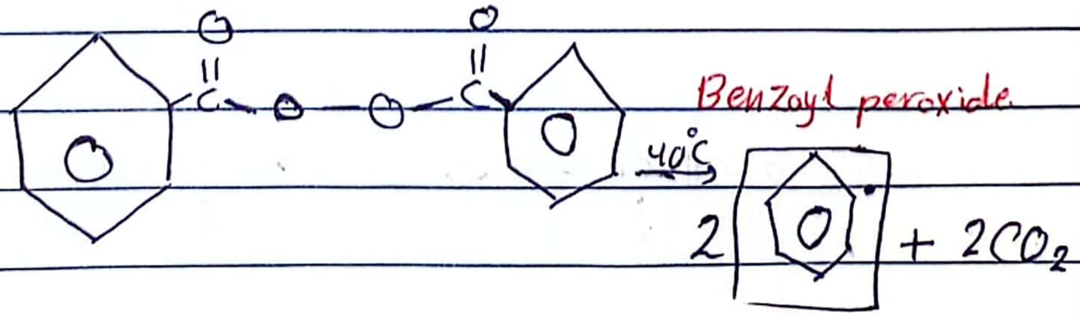
عدم تساوي b) disproportionation

Initiation:

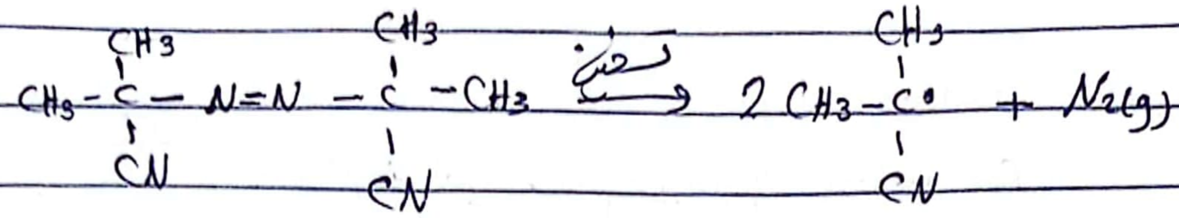
1. Thermal.
2. UV-radiation.
3. Redox rxns.
4. Substances that give easy radicals.

Peroxides, Hydroperoxides, azo-compound.

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



Benzoyl peroxide.

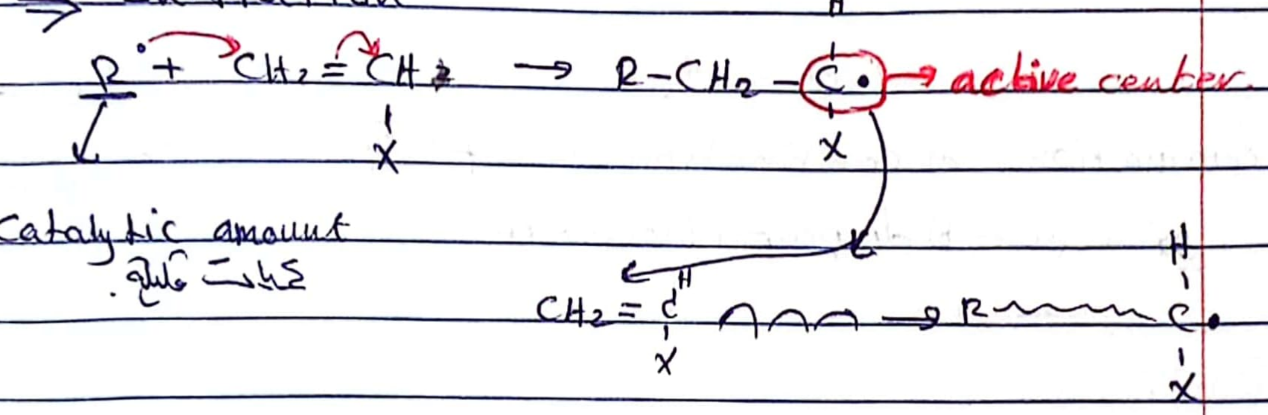


$$CH_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-CH_3 \xrightarrow{\text{تسخين}} 2\,CH_3-\underset{CN}{\overset{CH_3}{C}}\cdot + N_{2(g)}$$

Azo isobutylnitrile
bis (AIBN)

Mechanism of free radical

⇒ Initiation



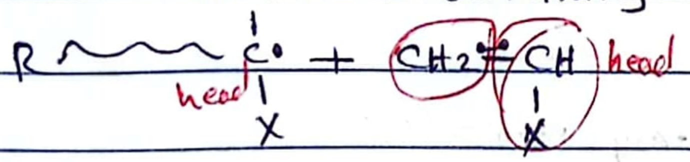
$$R^\cdot + CH_2=\underset{X}{CH} \rightarrow R-CH_2-\boxed{\underset{X}{\overset{H}{C}}\cdot} \rightarrow \text{active center.}$$

$$CH_2=\underset{X}{\overset{H}{C}} \frown\frown\frown \rightarrow R\sim\sim\sim\underset{X}{\overset{H}{C}}\cdot$$

Catalytic amount
كمية قليلة.

⇒ propagation (successive addition of monomer molecules)

↳ Rate Determining step (RDS) ⇒ 1) M.wt
2) Rate of rxn
3) structure.



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

* two possible way of addition:

1) head to tail addition, $R-CH_2-\underset{X}{CH}-CH_2-\underset{X}{CH}^\cdot---$

2) head to head $R-CH_2\underset{X}{CH}-\underset{X}{CH}-CH_2-\underset{X}{CH}\,CH_2-\underset{X}{CH}\cdot$

* which is more favored ??

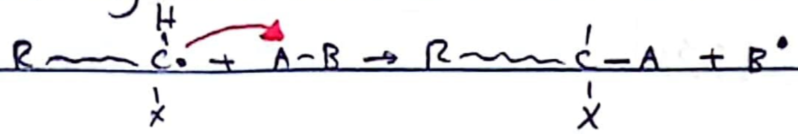
⇒ head to tail because a) steric factor.
b) resonance, $CH_2-\underset{X}{CH}^\cdot$

PVC: 15 % head to head.
85 % head to tail.

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

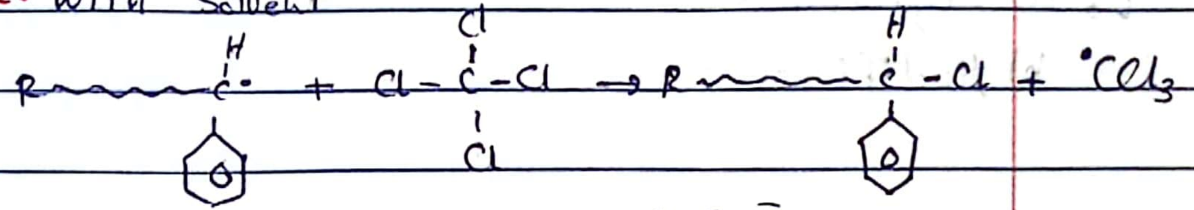
شي غريب

1. foreign material (A-B).



$R\sim\sim\overset{H}{\underset{X}{\dot{C}}}\cdot + A{-}B \rightarrow R\sim\sim\underset{X}{\overset{|}{C}}{-}A + B^{\bullet}$

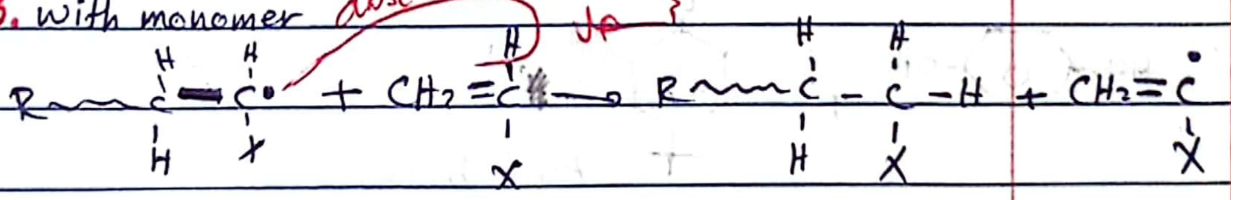
2. with Solvent



اذا موجودة بـ X

3. with monomer abstraction of H

عل



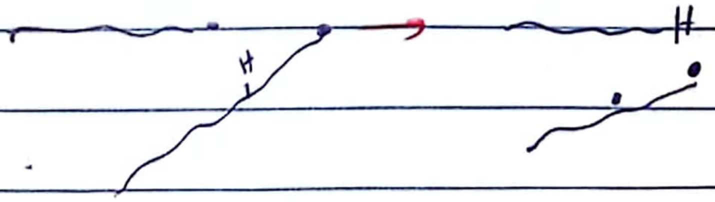
$R\sim\sim\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{X}{C}}\cdot + CH_2{=}\overset{H}{\underset{X}{C}} \rightarrow R\sim\sim\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{X}{C}}{-}H + CH_2{=}\overset{\bullet}{\underset{X}{C}}$

اول تنتين اكثر اشي.

* 1) + 2 + 3 ⇒ decrease of M.wt

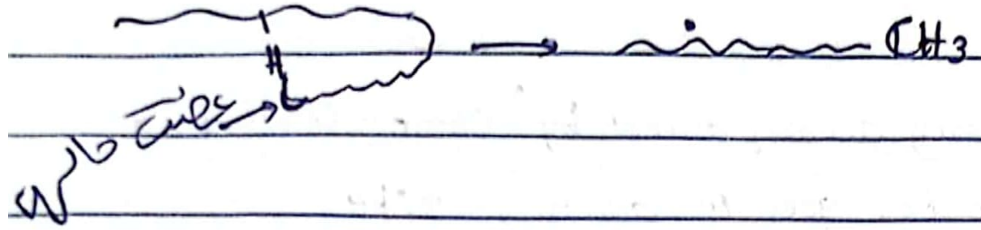
4. with polymer molecule

a) Intermolecular: between the molecules



⇒ branching

2) intramolecular (back biting)



PE , MW > 600,000 → عملية تكوينه شبه مستحيلة

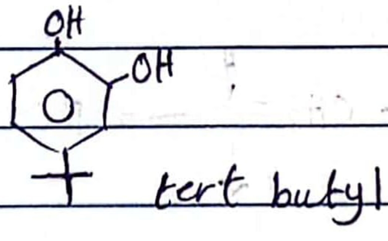
لهيك يجب إضافة مواد للحد من Mwt

تسبب chain transfer

- a) Regulators.
- b) Modifiers.

Inhibitors: added to stop radical polym'n

,



Retardor: added to decrease rate of polym'n.

Retards of styrene polym'n

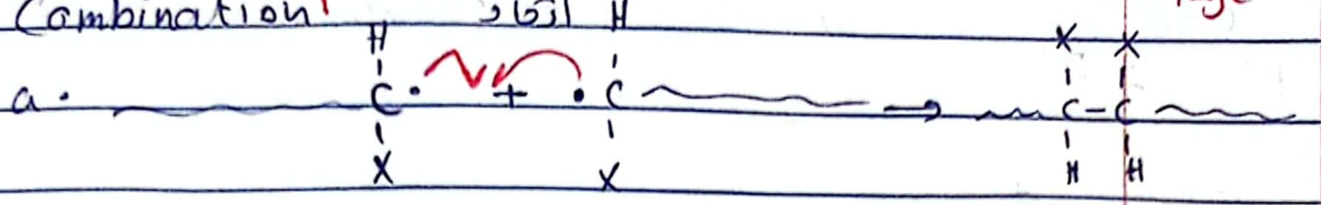
Rate: 15 min → 30 min

2 بحالة ملاحظتنا درا

① ② coupling يحدث ③

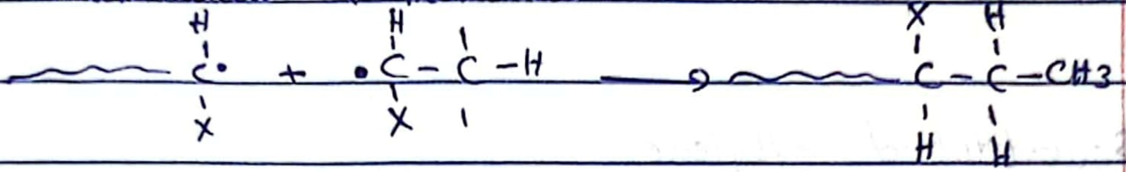
Termination. → * at low Temp. , high M.wt, head to head LinKage -

1. Combination



(increase in M.wt). M.wt يحدث زيادة في *

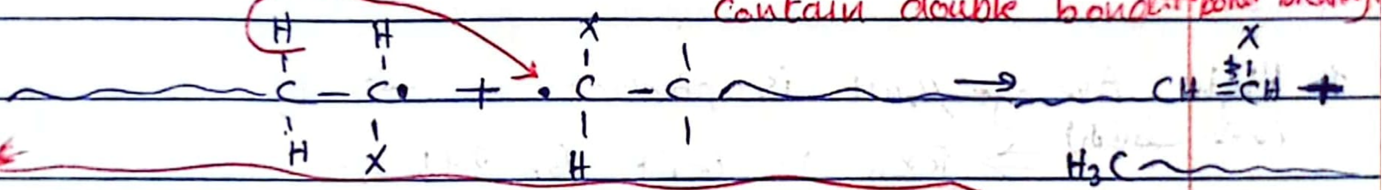
b. macromolecule + monomer.



No increase in M.wt

2. Disproportionation. → * at high Temp, low ~~[illegible]~~ M.wt

contain double bond + bond breakage



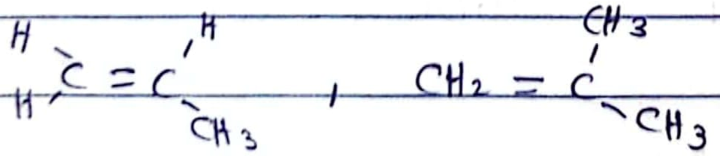
at 60°C poly(acrylonitrile) , 100% combination

poly (vinylacetate) , 100% disproportionation

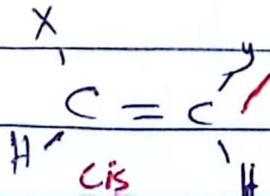
No effect on M.wt

Limitation of free radical polym'n

1) Allylic monomer

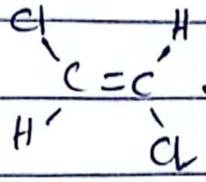


2. 1,2- disubstituted ethylene.

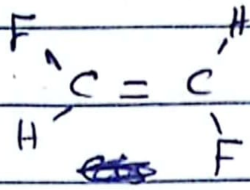


→ No free radical polym'n because steric hindrance.

X, y = larger than CH3 →



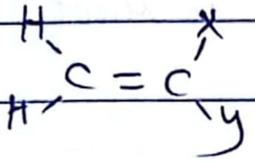
radical polym'n at 200°C and 200 atm



radical polym'n → بطيء التفاعل لأنه الفلور حجمه صغير جداً.

~~1~~ trans or cis → بطيء التفاعل

3. 1,1-substituted ethylene.



No radical polym'n

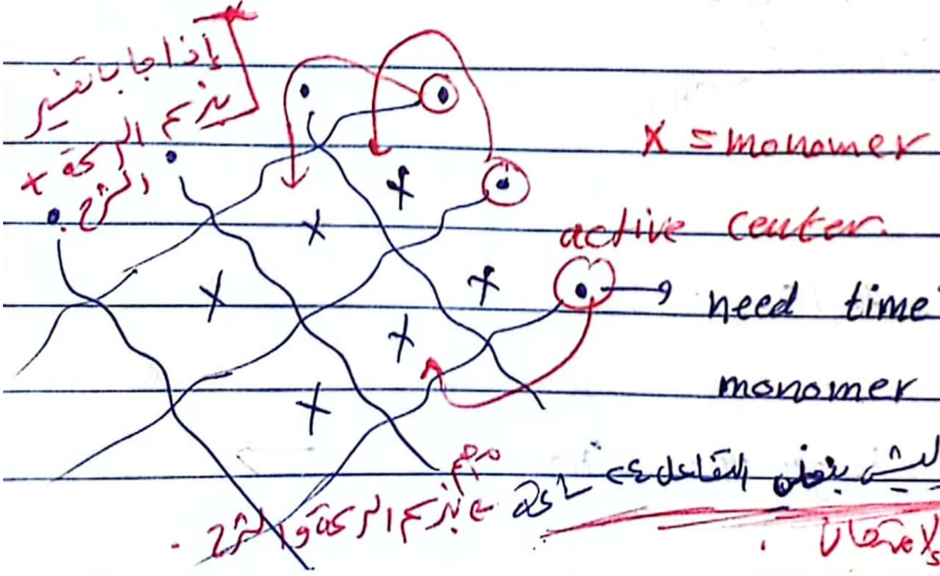
*Some characteristic of radical polym'n

1. High Average M.wt is produced immediatly

(الدقائق الأولى) ⇒ Rxn is left for 24h → to increase % yield.

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

M.wt = 1650 × 104 (m.wt for monomer) = 171,600



إذا جاب تفسير برفع الحركة + الرج

X = monomer

active center → need time to find monomer

* تفسير ليش بطول التفاعل 24h ← عشان برفع الحركة والرج. مهم بالامتحان.

2] This polym'n is Exothermic.

$$\Delta G = \underset{(-)}{\Delta H} - T\underline{\Delta S} \rightarrow \text{بقلل الترتيب} \overset{(-)}{<0}\text{, spontanious at low T}$$

exothermic → (−)

ΔS ↓ (−) →

low temp.

\+

* التفاعل بيصير تلقائي لما يكون ΔG سالبة،

$$\text{monomer} \underset{\text{depolymerization}}{\overset{\text{polym'n}}{\rightleftarrows}} \text{polymer}$$

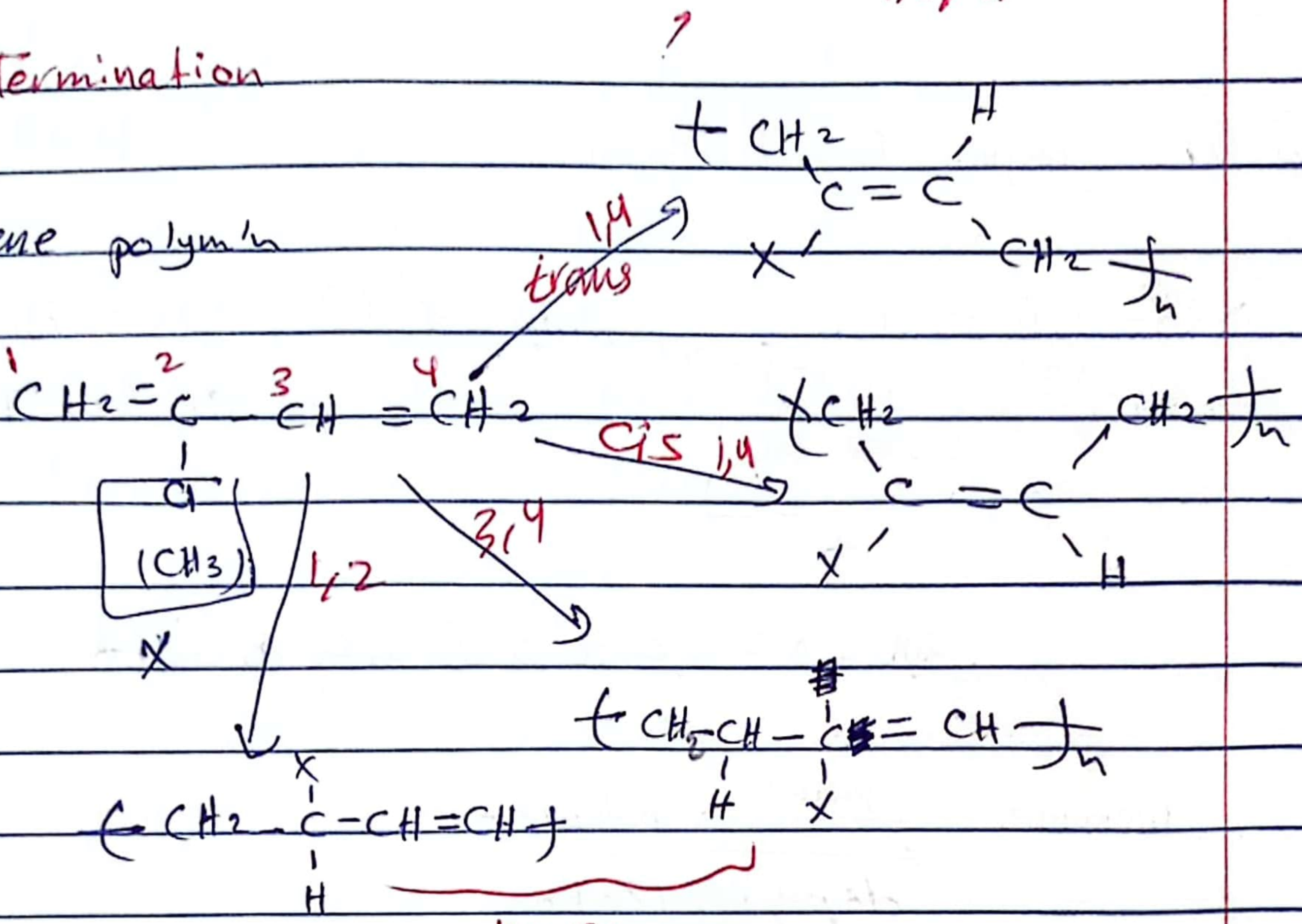
~~[illegible]~~ Ceiling Temp (Tc): Temperature above ~~wich~~ which depolym'n occurs.

PS, Tc = 300°C, < 300°C

cis, trans more stable than 1,2 / 3,4.

* Termination

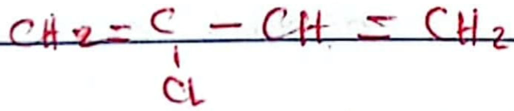
Diene polym'n



no resonance.

Question.

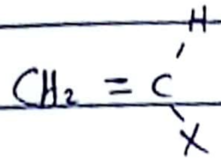
اكتبي نواتج عملية البلمرة للمركب الآتي



$CH_2=C(Cl)-CH=CH_2$

* بحسب الـ٤ مركبات.

*Ionic polym'n


$CH_2=\overset{H}{\underset{X}{C}}$

مجموعة ساحبة

X: electron withdrawing ⇒ Anionic polym'n ~~~ ⊖ || ⊕ ion-pair

X: " releasing ⇒ Cationic " ~~~ ⊕ || ⊖

X = ~~CH3 releasing~~		Cationic	anionic
CH_3		✓	—
CN		—	✓
$-\overset{O}{\overset{\|}{C}}-CH_3$		—	✓

$R-Y \longrightarrow R\{Y \longrightarrow R^+ + Y^-$

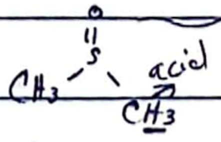
Heterocleavage   solvent separation

dielectric constant حسب

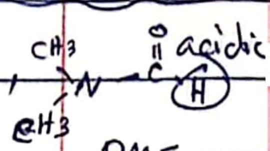
هيدروجينية مرتبطة مع O او N ،

solvents

protic	nonprotic
H_2O	CH_3CN
CH_3CH_2OH	DMSO
	DMF
	ethers



DMSO



DMF

THF →


Solvents used in ionic polym'n:

تفاعل سريع

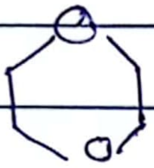
1. polar solvents ⇒ nonprotic ← مش فيه H بنقدرش نستخدمها

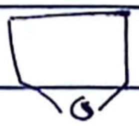
$\sim\sim C^{\ominus}$ very very strong base

لازم تتفاعل مع solvent ← 2 عشان هيك ، بنستخدم THF

لا بزبطش نستخدمه

2. slightly polar $CH_3CH_2-O-CH_2CH_3$

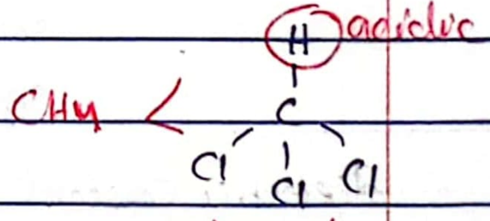

1,4-dioxane



ما كان بنقدرش نستخدمها لأنه فيها نسبة تفكك

3. nonpolar (organic solvent).
benzene, hexane, Toluene

لازم مادة نقية + والأدوات نظيفة وجافة

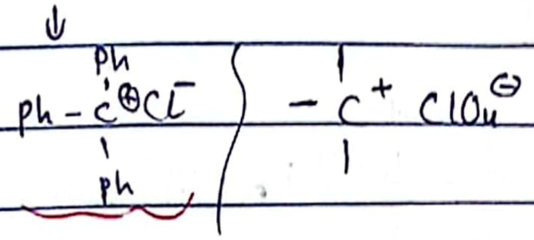


لا بزبطش نستخدمه لأنه acidic

Cationic polym'n:

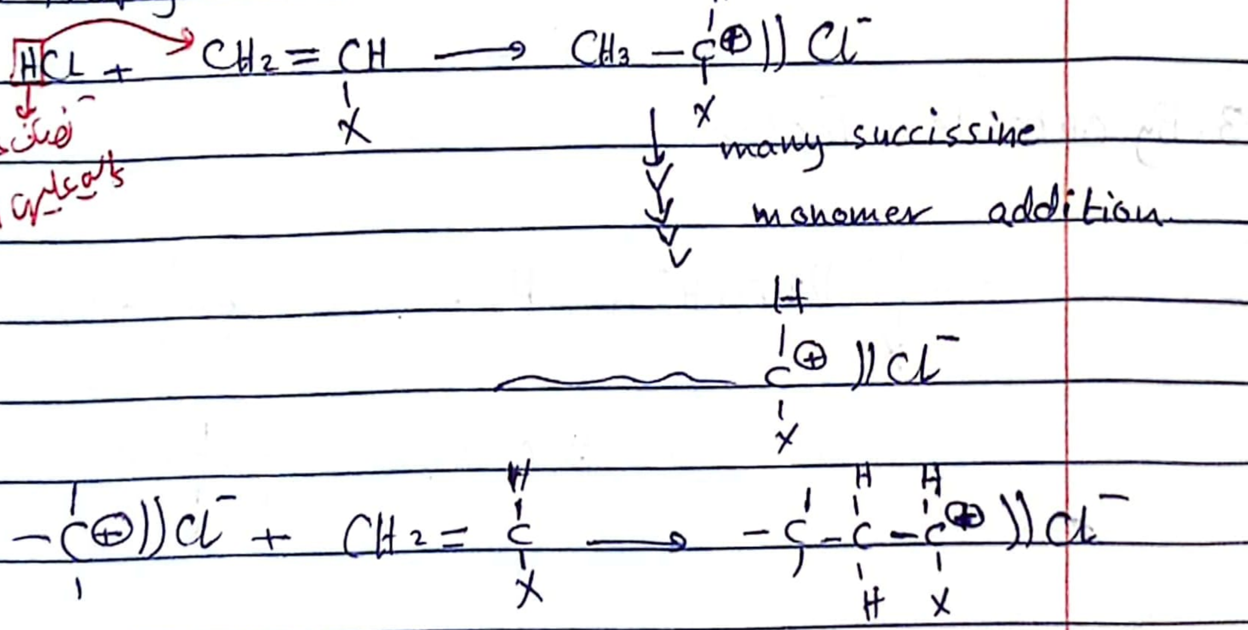
1) Initiators Could be

- Strong protic acid, HCl, H_2SO_4
- Lewis acid BF_3, $AlCl_3$, $FeCl_3$
- Cationic generator, Ph_3CCl, $t\text{-}\overset{very}{Bu}ClO_4$, I_2

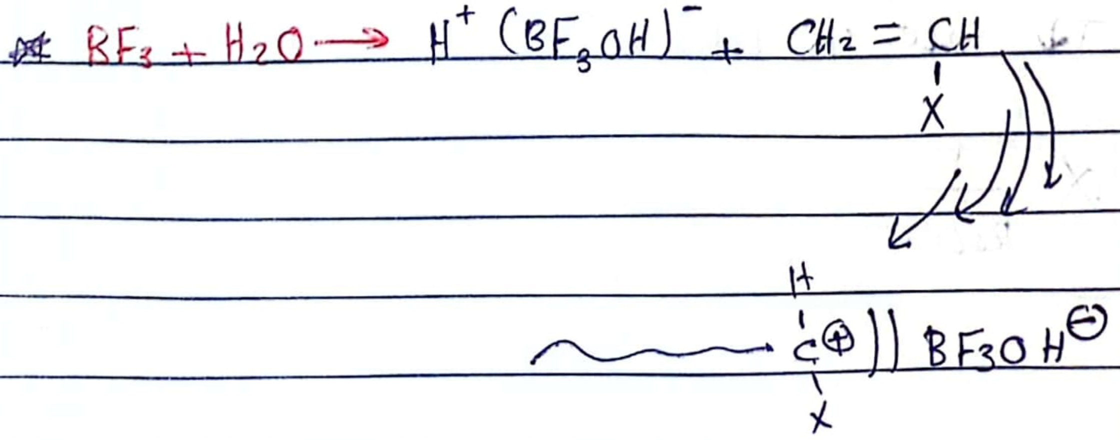


3° Carbocation very stable.

2) Propagation



ضيف على الكربونة اللي عليها H's أكثر

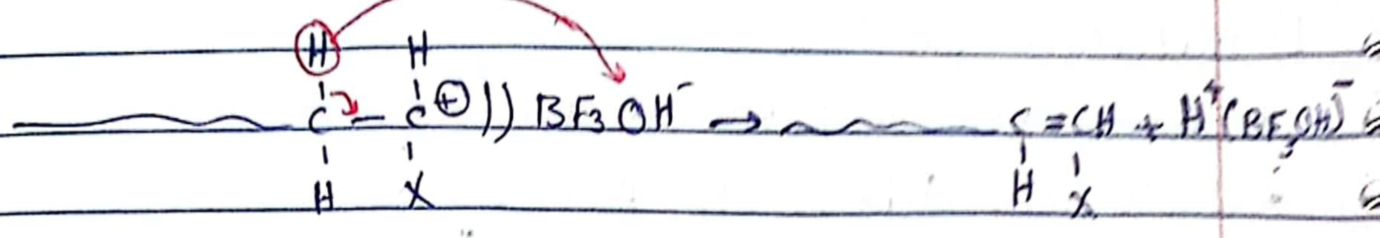


$BF_3 + H_2O \rightarrow H^+(BF_3OH)^- + CH_2{=}CH\text{–}X$

$\sim\sim\sim C(H)(X)^{\oplus}\,))\,BF_3OH^{\ominus}$

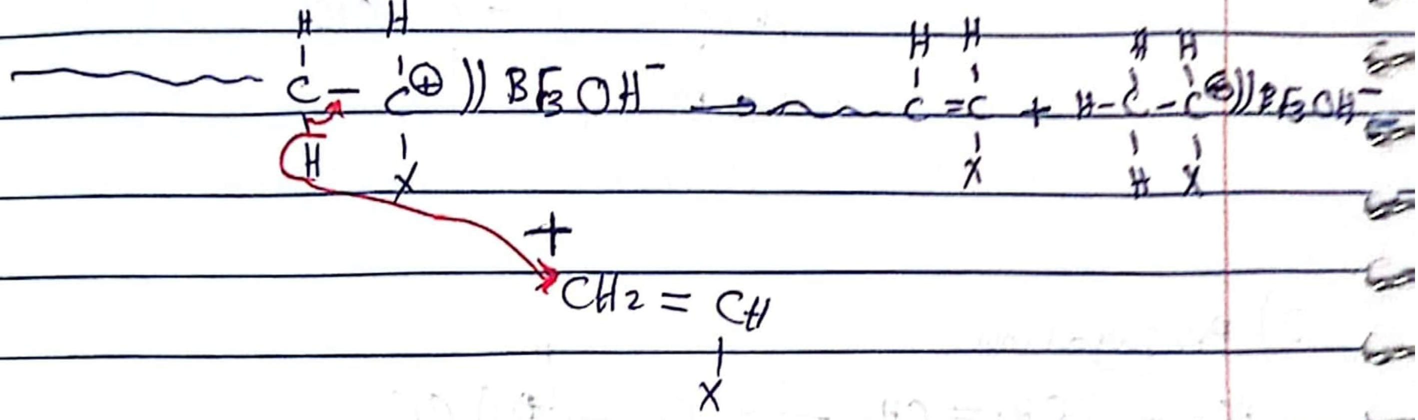
Termination:-

1) Rearrangement:



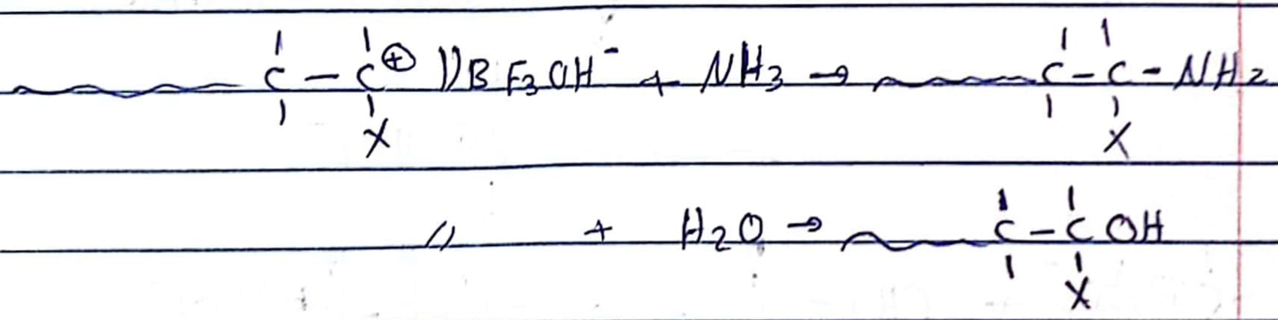
$$\sim\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}{}^{\oplus}\,))\,BF_3OH^- \rightarrow \sim\sim\underset{H}{C}=\underset{X}{CH} + H^+(BF_3OH)^-$$

2. Catalyst



$$\sim\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}{}^{\oplus}\,))\,BF_3OH^- + CH_2=\underset{X}{CH} \rightarrow \sim\sim\overset{H}{C}=\overset{H}{\underset{X}{C}} + H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}{}^{\oplus}\,))\,BF_3OH^-$$

3. By outside Factor.



$$\sim\sim\overset{|}{\underset{|}{C}}-\overset{|}{\underset{X}{C}}{}^{\oplus}\,))\,BF_3OH^- + NH_3 \rightarrow \sim\sim\overset{|}{\underset{|}{C}}-\overset{|}{\underset{X}{C}}-NH_2$$

$$\text{''} + H_2O \rightarrow \sim\sim\overset{|}{\underset{|}{C}}-\overset{|}{\underset{X}{C}}OH$$

⇒ Some characteristic of cationic polym'n

① very fast and give high M.wt.

② As T↓ rate of polym'n ↑

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

*Anionic Polym'n

Initiators

1. Alkali metals dispersion in inert hydrocarbon solvent.

Na(Naphthalene)
Li(hexane)

2. Organometallic compounds.

RMgX, n-BuLi
↳ n-Butyl Li : $CH_3CH_2CH_2CH_2^{\ominus}\,Li^{\oplus}$

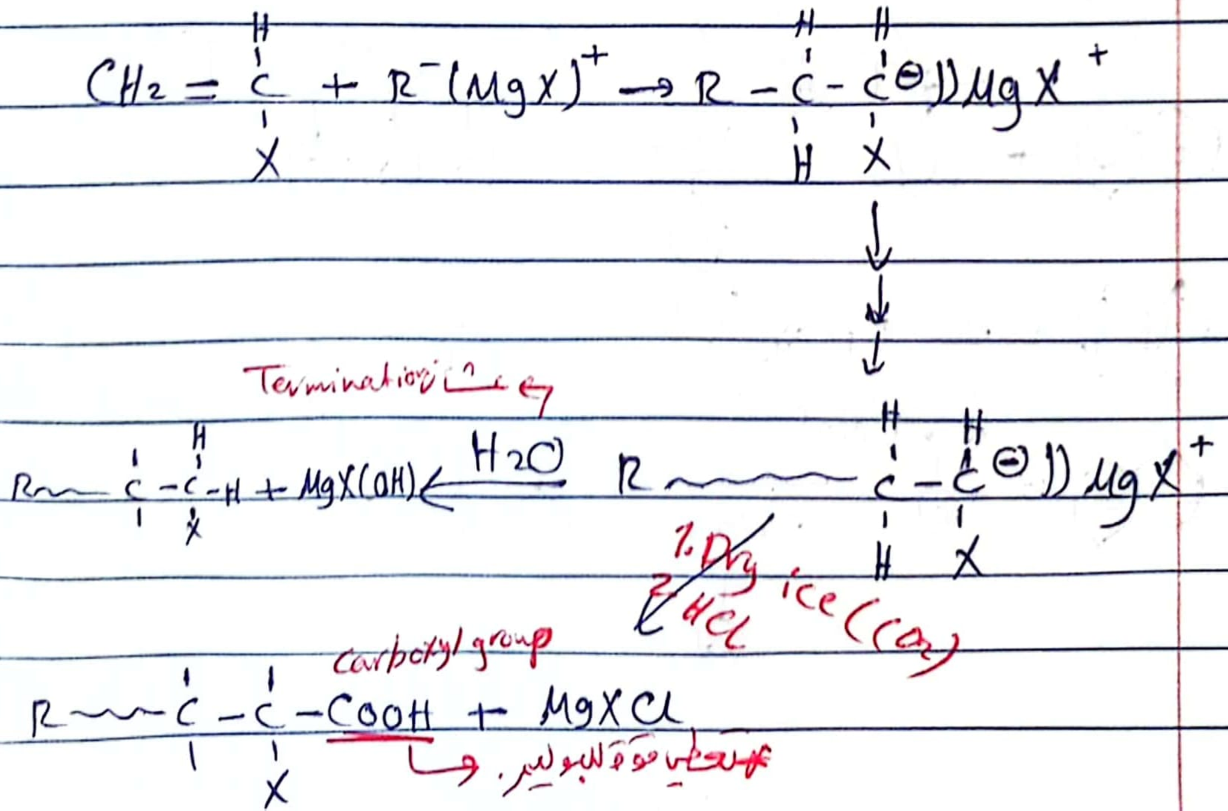
3. Lewis base

alkoxide
$RO^-M^+ \Rightarrow CH_3CH_2OH + Na \rightarrow CH_3CH_2O^-Na^+ + H_2(g)$

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

← أقوى من NaOH بكثير

* Propagation.



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

$$\downarrow$$

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

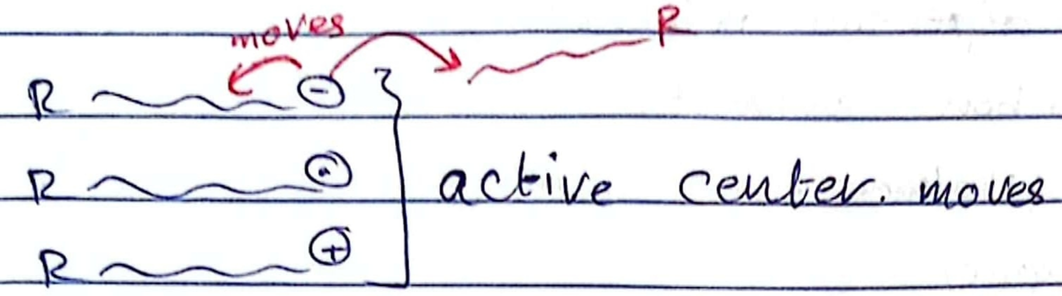
Termination تسمى

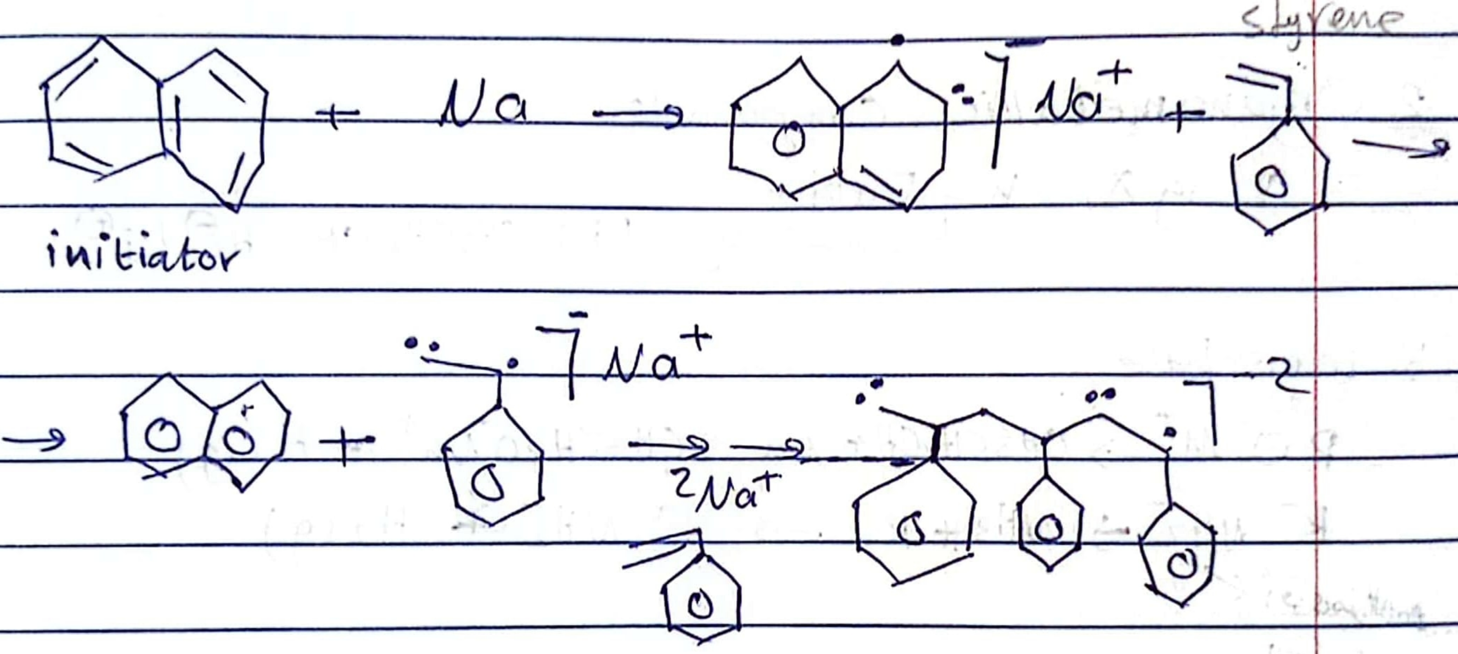
$$R\sim\sim\sim\overset{H}{\underset{H}{C}}-\overset{H}{\underset{X}{C}}^{\ominus}))MgX^+ \xrightarrow[\text{2. HCl}]{\text{1. Dry ice }(CO_2)} R\sim\sim\underset{|}{\overset{|}{C}}-\underset{X}{\overset{|}{C}}-COOH + MgXCl$$

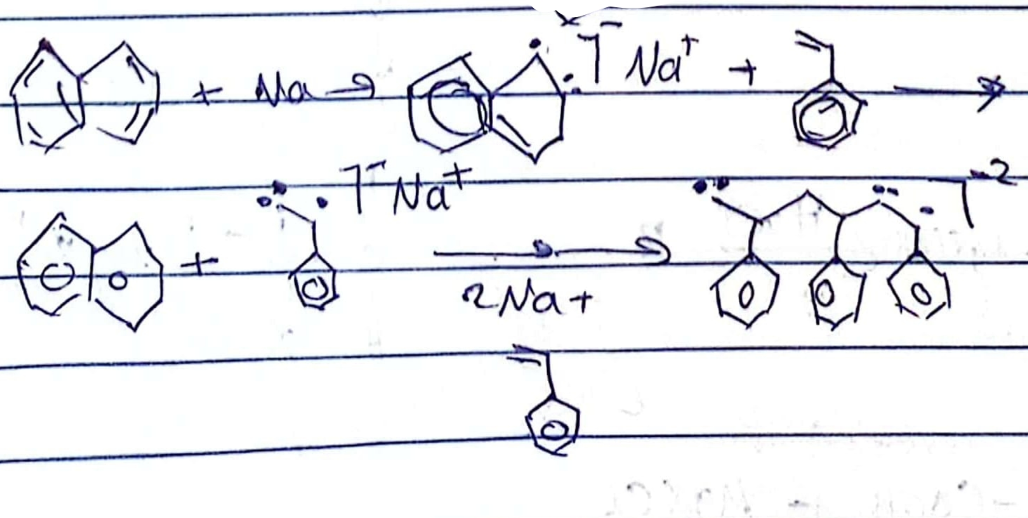
carboxyl group

يعطي قوة للبوليمر.

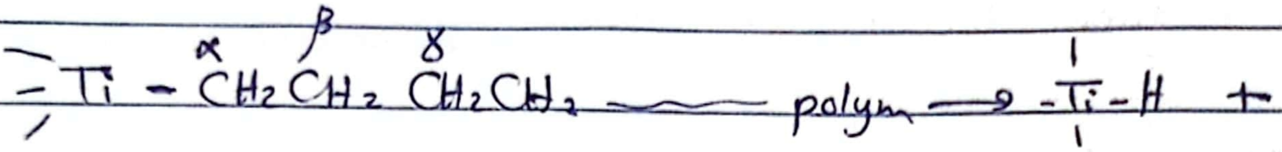
* Living polymer.







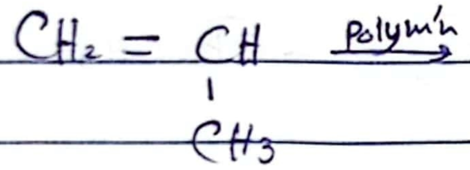
2] β – hydrogen elimination



$\equiv Ti - \overset{\alpha}{C}H_2 \overset{\beta}{C}H_2 \overset{\gamma}{C}H_2CH_2$ ~~~~ polym $\rightarrow$ $-\underset{|}{\overset{|}{Ti}}-H$ +

$CH_2 = CH$ ~~~~ poly

* ethylene + substituent



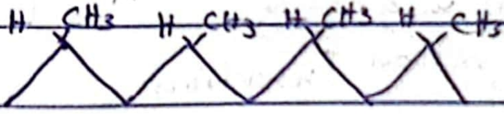
$\underset{\underset{CH_3}{|}}{CH_2 = CH} \xrightarrow{Polym'n}$

alternation

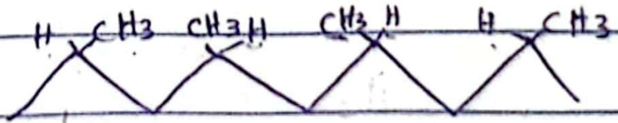
1) Atactic

the same side

2) ~~[illegible]~~ Isotactic



3) Syndiotactic



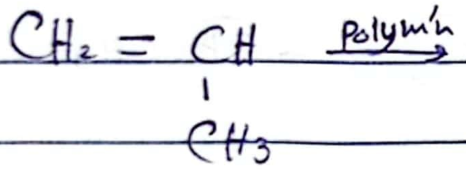
random

2] β – hydrogen elimination

$$\equiv Ti - \overset{\alpha}{C}H_2 \overset{\beta}{C}H_2 \overset{\gamma}{C}H_2 CH_2 \sim\sim \text{polym} \rightarrow -\overset{|}{\underset{|}{Ti}}-H \; +$$

$$CH_2 = CH \sim\sim \text{poly}$$

* ethylene + substituent.



$$CH_2 = \underset{\underset{CH_3}{|}}{CH} \xrightarrow{\text{Polym'n}}$$

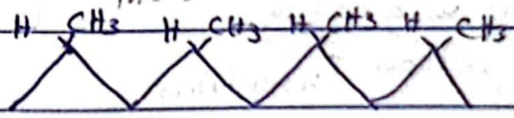
1) Atactic

alternative

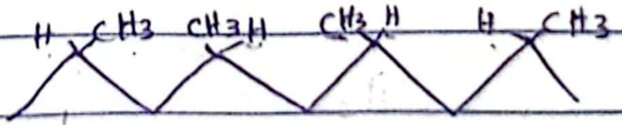
~~randomly along the~~ chain

2) ~~[illegible]~~ Isotactic

the same side



3) Syndiotactic



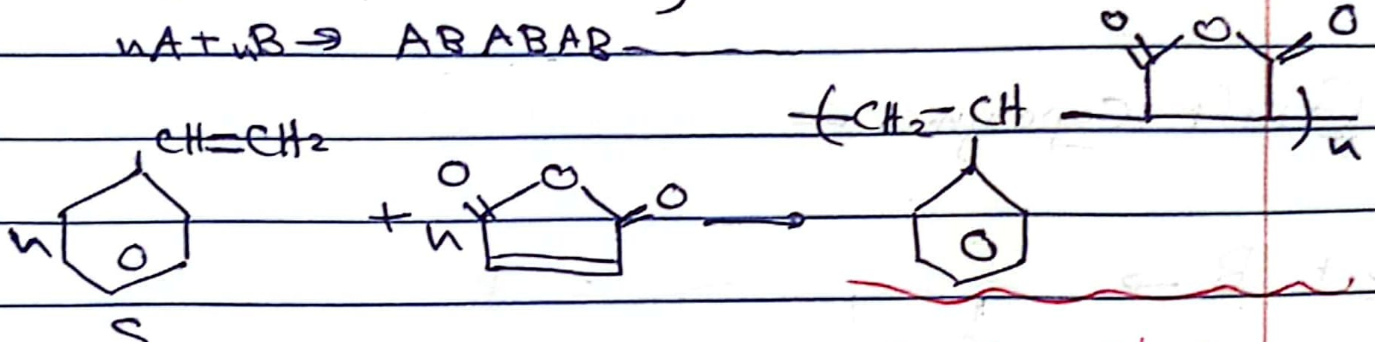
~~alternative~~. random

Copolymerization:

Copolymer: two or more different monomers.

1- Regular (Alternating) Copolymers:

$nA + nB \rightarrow ABABAB$ ——

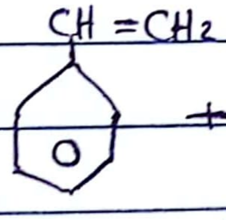


Regular chain.

2. Random Copolymer:

$A + B \rightarrow AAABBAB$ ——

6 : 1 ← . النسبة بتكون مختلفة

* 

\+ ~~Butadiene~~

$6\ CH_2=CH-CH=CH_2 \rightarrow$

$(> n)$

n) 1 mol

$(S) + B \rightarrow SBBBSBSSB.$

* $S + B + \underset{CN}{CH_2=CH} \rightarrow ABS.$

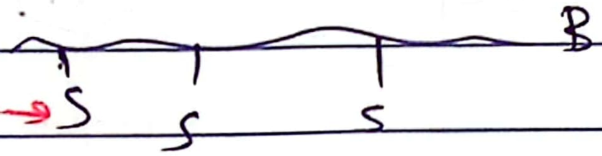
Acrylonitrile (A)

3\. Block Copolymer:

$$S + B \longrightarrow \left(\overset{5}{SSSSS}\,\overset{3}{BBB}\,\overset{5}{SSSSS}\,\overset{3}{BBB} \right)$$

4\] Graft Copolymer: أهم واحد.

$S + B \rightarrow$



(Back bone).

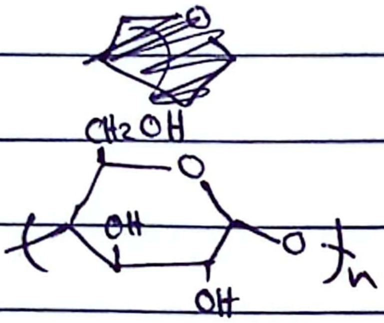
بتعلق.

a. prepare B polymer.
b. dissolved B polymer in monomeric S

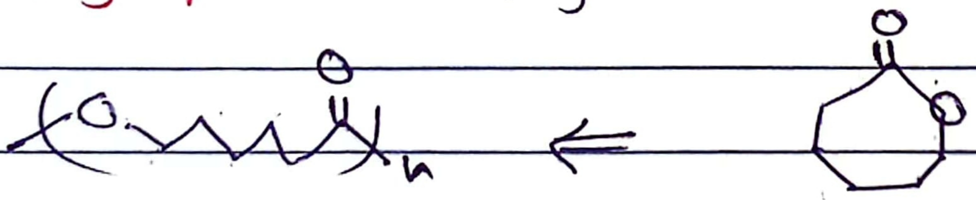
* Biodegradable Polymer: $\xrightarrow[\text{organism}]{\text{micro}}$ CO_2
Converted to carbon dioxide under microbial action

a) Naturally occuring polymers.

Ex: Amylose, amylopectine



b) Polymers possessing hydrolysable backbone:
* poly Caprolactone (polyester).



monomer → cyclic → بكون نشيط

PET → non biodegradable.