σ_{yield} ↑ & elongation % ↑

σ_{yield} ↑ E ↑

This is also a strengthening mechanism.

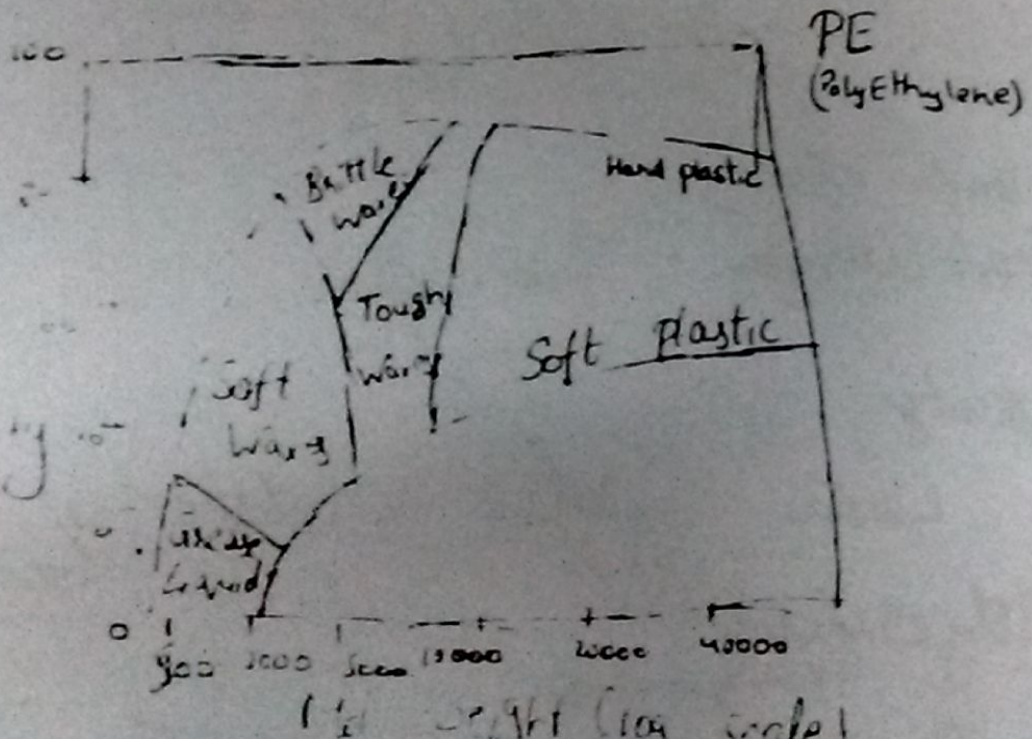
Heat Treatment

semicrystalline material

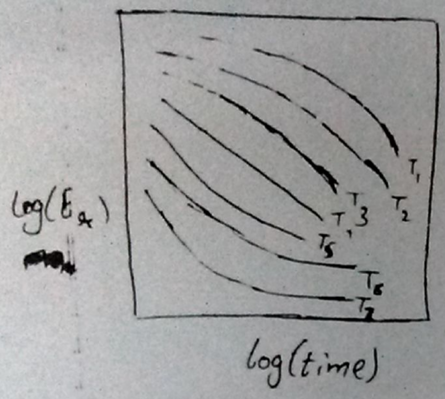
crystalline is thermodynamically stable than amorphous.

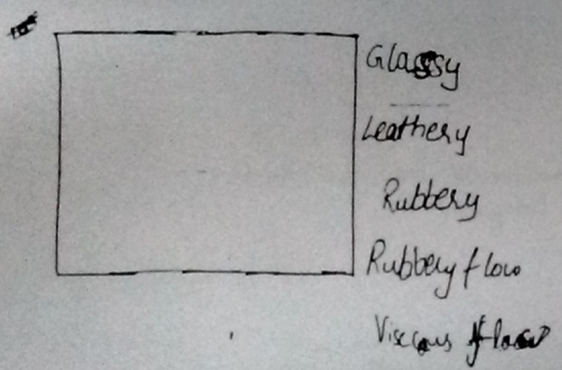
% crystaline ↑

T ↑ σ_{ys} ↑ % ε ↓



Molecular weight (log scale)



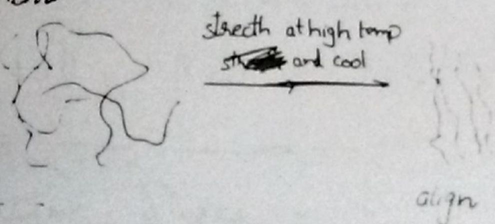


Restraint in Polymer ~~bonds~~ movement

1. Increasing Mol. weight
   chain length ↑ ⇒ entanglement ↑ ⇒ movement ↓
2. Introducing Polar groups to increase bonding

Modulus increasing

1. Increasing Mol. weight (chain length)
2. crystallinity
3. Secondary bond strength (Vander walls forces)
4. Chain alignment



Chain length effect
Tensile Strength $= TS_\infty - \frac{A}{M_n}$

Crystallinity
Elastic modulus ∝ degree of crystallinity

Polyethylene

Modulus ... crystallinity ...

unetic effect (... heating)
ystalline size effect (...)

size ↓ ⟹ ΔG_v ↑
⟹ T_m ↓

Flory Higgins

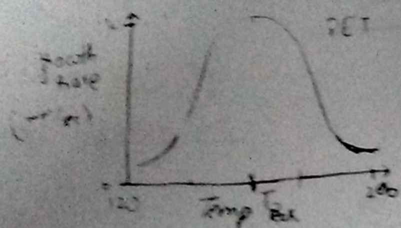
$$\frac{1}{T_m} - \frac{1}{T_m^{\circ}} = \frac{R}{\Delta H_v} \left(\frac{V_u}{V_1} \right) \left(\phi_1 - \chi_{12}\phi_1^2 \right)$$

V_u → Molar volume of Repeating unit

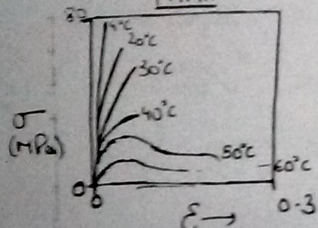
χ_{12} → Interaction parameter between diluent & Polymer

ϕ_1 → Vol. fraction of diluent

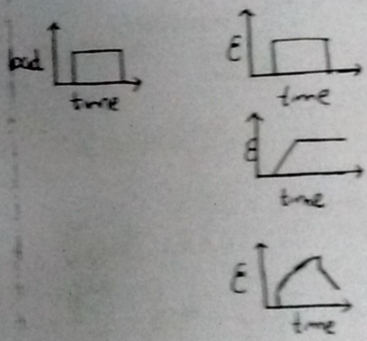
V_1 → Diluted Molar Volume



PMMA



At Neck during Necking elongation occurs due to chain mobility and orientation of C–C bond occurs.

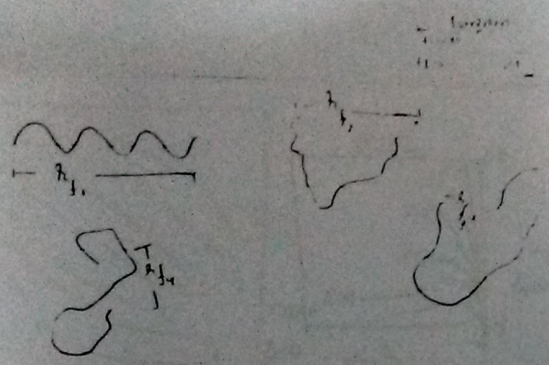


Elastic

Viscous

Relaxation modulus $E_{r(t)} = \frac{\sigma_t}{\varepsilon_0}$

Scanned by CamScanner



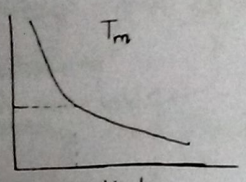
Contour unit Structures

n_f = total freedom
n_o = with restriction → unperturbed

avg length for molecule

Mol weight before which entanglement does not occur

Polystyrene	31000
Polycarbonate	5000



Reptation

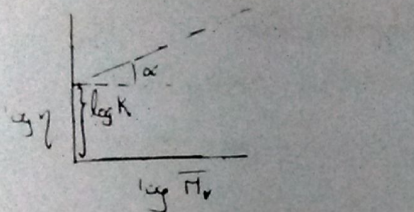
Iso viscous state
Iso thermal
Iso entropic state

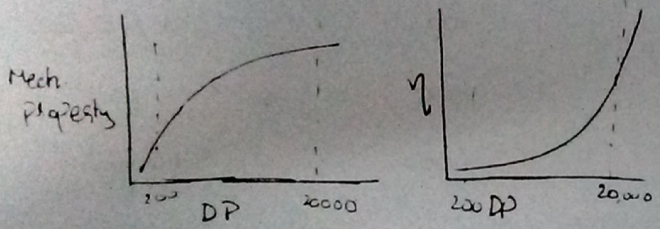
	ΔH_v° (cal/mol)	ΔS_v (cal/mol°K)	T_m° (°C)	T_m Actual
Poly ethylene	960	2.3	146	98-135
Poly propylene	1386	2.9	200	171
Poly carbonate	6343	10.4	335	227

$$\Delta G_v = \Delta H_v - T_m \Delta S_v$$

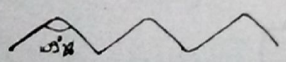
at melting point $\Delta G_v = 0$

$$T_m^\circ = \frac{\Delta H_v}{\Delta S_v}$$





1) Contour Length 2) Random Walk model



$\cos\theta \approx -\frac{1}{3}$

$n = 500$ 629 A°
~ 49 A°

$\langle r_f \rangle = \frac{n_1 r_{f_1} + n_2 r_{f_2} + \cdots}{n_1 + n_2 + \cdots}$ ← no of polymers of a type

$\langle r_f^2 \rangle^{1/2} = \sqrt{\left(\frac{\sum n_i r_{f_i}}{\sum n_i}\right)}$

$\langle r_0^2 \rangle = l^2 n \frac{1-\cos\theta}{1+\cos\theta}$
≈ 2

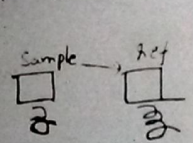
$\langle r_f^2 \rangle^{1/2} = l n^{1/2}$
↓ no of segments

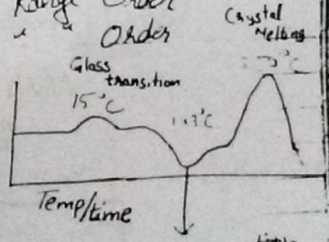
Polyethylene $\frac{1-\cos\theta}{1+\cos\theta} \approx 2-6$

$\langle r_0^2 \rangle = N \langle r_f^2 \rangle^{1/2}$

solid LRO
Liquid SRO
gas

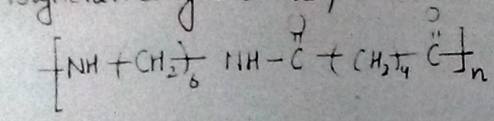
Long Range Order
Short Order





Random Walk Model Restriction →
⟹ but not possible as it is in 2-D
allowed in random walk

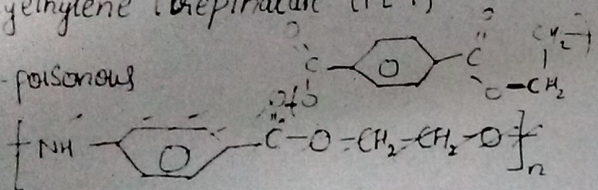
Polyhexamethylene adipamide



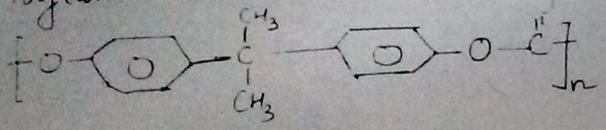
Nylon 6,6

Polyethylene terephthalate (PET)

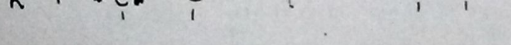
non-poisonous



Polycarbonate



Addition polymerisation

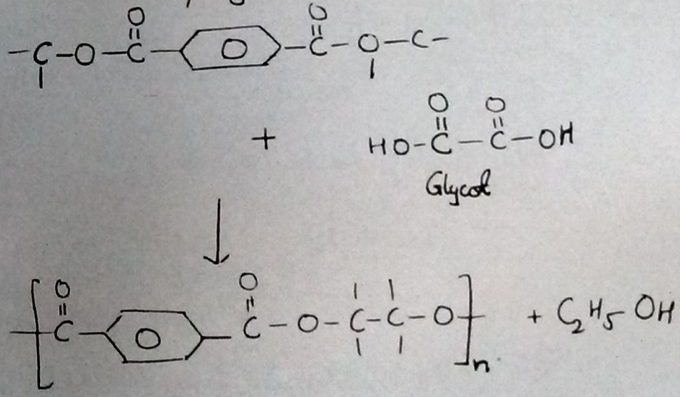


Termination

1) Combination

2) Disproportionation

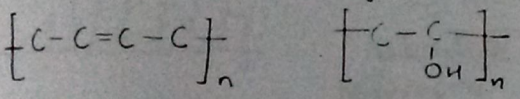
Condensation polymerisation



Calorimetry & Polymer

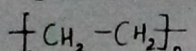
Polymer have broad band

Polymer Solubility & Viscosity



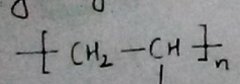
Poly Butadiene Poly Vinyl Alcohol

1. Poly Ethylene



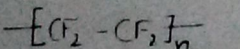
MP - 115-130°C
Annual production = 80 million tonnes (highest)

2. Poly Vinyl Chloride (PVC)



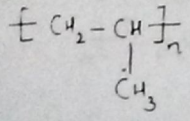
Rigid PVC → pipes
Flexible PVC → insulator
3rd most production

3. Poly Tetra Fluoro Ethylene (PTFE) [Teflon]



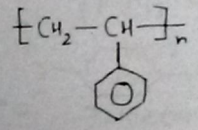
MP - 320°C
non sticky
low friction

4. Poly propylene



2nd highest production

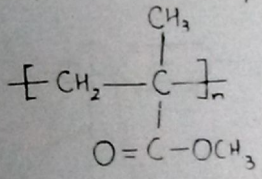
5. Poly styrene



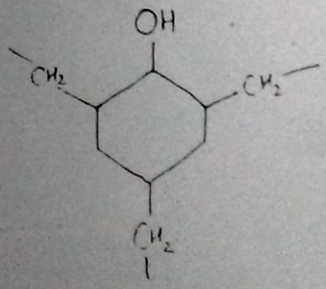
M.P. = 240°C
Textiles & Styrofoam

6. Polymethylmethacrylate (PMMA)

common name → plexiglass



7. Phenol formaldehyde (Bakelite)



first commercially available