STEP GROWTH POLYMERIZATION

(or polyamides)

Typical examples are Nylons, polyesters, polypeptides.

Molecular weight increases slowly as dimers become trimers, which in turn become tetramers.

$HO-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH + HO-R'-OH \longrightarrow HO-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-OH + H_2O$ (ester link)

HO − R − H   HOOC − R'

↓

hydrolysis (Stoichiometric necessary)

$HO-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH$

↓

a − c − c − a

+

b − c − c − c − c − a →

$a(C_6)a + H_2O$

Characteristic:

- Release of small molecules
- Gradual growth of molecular weight
- Successive condensation reactions, "coupling".
- Relatively slow rxn
- Stoichiometric concerns.

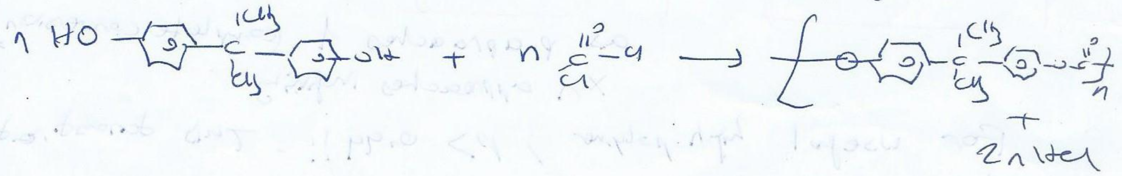
Polyester = carboxylic acid + alcohol

Polyamides = carboxylic acid + amine

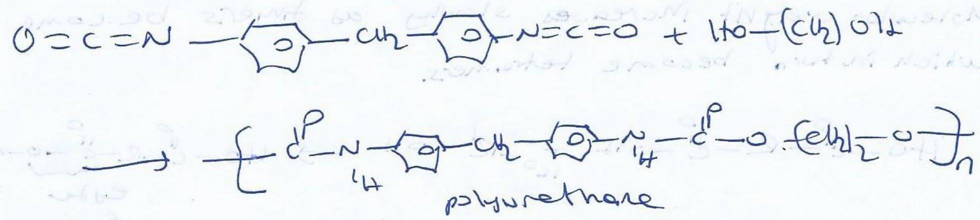
polyethers = dehydration of diols

polysiloxanes = condensation of silanols (SiOH)

Polycarbonate



Some condensation polymerization proceeds without liberating small molecules. This type of condensation polymerization is called polyaddition polymerization.



Carothers' Theory

How do you determine MW as a function of conversion

$X_n = \frac{N_0}{N}$ where X_n = number average degree of polymerization

N_0 = number of molecules present initially

N = number of molecules present after time t

p = extent of reaction at time t

$= \frac{\text{number of functional groups that have reacted}}{\text{number of functional groups present initially}} = \frac{N_0 - N}{N_0}$

= probability that any functional group present initially has reacted

$p \to 0.995 \to \bar{X}_n = 200$

$p \to 0.999 \to X_n \to 1000$

$$\frac{N_0}{N} = \frac{1}{1-p} \Rightarrow X_n = \frac{1}{1-p}$$ (Carothers equation)

as p approaches 1 (complete conversion), X_n approaches infinity

For useful high polymer, $p > 0.99$!! - This demonstrates need for purity, efficiency, stoichiometry.

$$M_n = M_0 X_n$$

where $M_0 = \frac{\text{molar mass of repeat unit}}{\text{number of monomer units in repeat unit (usually 1 or 2)}}$

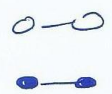
5-2 Determining MW as a Function of Conversion

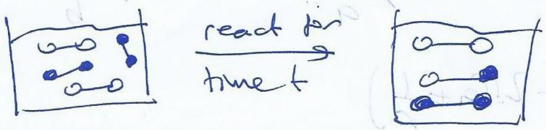
How do you determine MW as a function of conversion?

$$\bar{P}_n \; (X_n) = \frac{\text{total initial \# of monomer units}}{\text{total \# of molecules remaining}} = \frac{N_0}{N_{total}}$$

Simple thought experiment

50 monomer units: 25 a–a, 25 b–b





$$X_n = \frac{1}{1-p}$$

p = 0.9 → 0.99 → 0.999: X_n change

$$p = \frac{N_0 - N}{N_0}$$

$M_n = X_n \cdot M_0$ (molar mass of repeat unit)

If have 50% conversion ⇒ 25 a+b reactions
⇒ lose molecule w/each reaction (2 molecules become 1)

$X_n = \frac{1}{1-p}$ Carothers eqn

$$\bar{P}_n = \frac{50}{50-25} = 2 \qquad \left(\frac{N_0 - N}{N_0} = \frac{1}{2}\right)$$

(50, π (conversion) can be related to $\bar{P}_n$.

$(N_a)_0$ = initial # of a reactive groups = 2

$(N_b)_0$ = initial # of b reactive groups = 2

$$\pi_a = 1 - \frac{N_a}{(N_a)_0} \qquad \pi_b = 1 - \frac{N_b}{(N_b)_0}$$

Define $r \equiv \frac{(N_a)_0}{(N_b)_0} \leq 1$
→ stoichiometric ratio

Define: a is minority functional group

Total # of functional groups initially present

$$N_0 = (N_a)_0 + (N_b)_0 = (N_a)_0 \left[1 + \frac{1}{r}\right]$$

At a given time t, have conversion π_a

N_t = # of functional groups at time t

$$= \underbrace{(N_a)_0 (1-\pi_a)}_{N_a} + \underbrace{(N_b)_0 - (N_a)_0 \pi_a}_{N_b}$$

$$N_t = (N_a)_0 \left(1 - 2\pi_a + \frac{1}{r}\right)$$

$$\Rightarrow \bar{P}_n = \frac{1+r}{1-2\pi r+r} \quad \pi_a = \pi \text{ (assume referring to minority)}$$

smaller number of part or part representing less than half of the whole

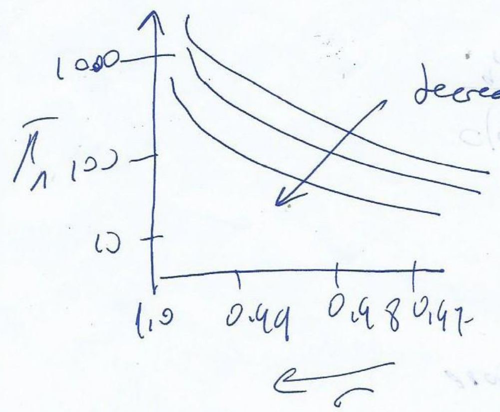
Simple case : $r = 1.0$ (perfect stoichiometry)

At $\pi = 0.995 \longrightarrow \bar{P}_n = 200$

$\pi = 0.99 \longrightarrow \bar{P}_n = 100$

$\pi = 0.98 \longrightarrow \bar{P}_n = 50$

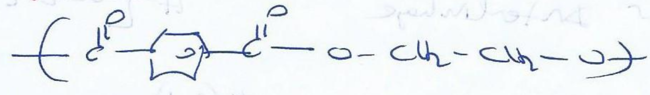
$\pi = 0.90 \longrightarrow \bar{P}_n = 10$ oligomer



Real Industrial Processes

Diacid + Diol → low MW polymers } less need
crosslinked networks } for high π

Making PET (Trade Names Mylar, Dacron, Terylene)

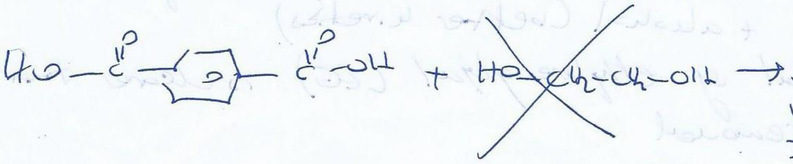


$T_m = 270°C$

high mechanical strength (from aromatic group rigidity)
Tough (flexibility in backbone)
Partially crystalline (adds to toughness)

} Ideal material for carpet, clothing, photographic substrates, Boil-in-bag meals, PET coke bottles

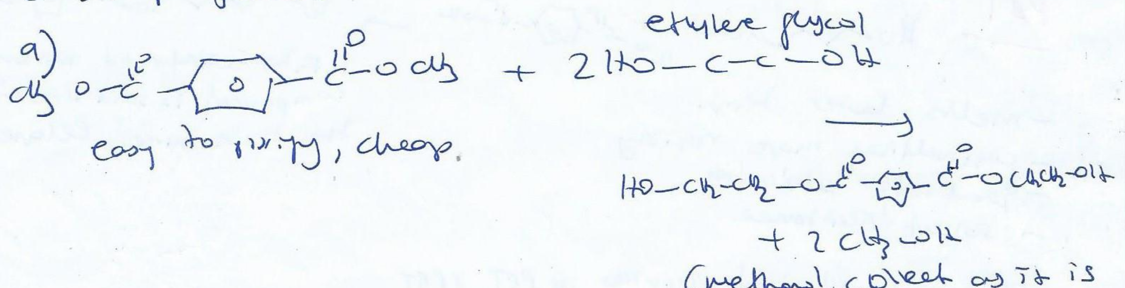
⇒ $ 9.5 billion/year



→ need high MW
very slow
Very inexpensive
Instead;

2-step process

a)



easy to purify, cheap.

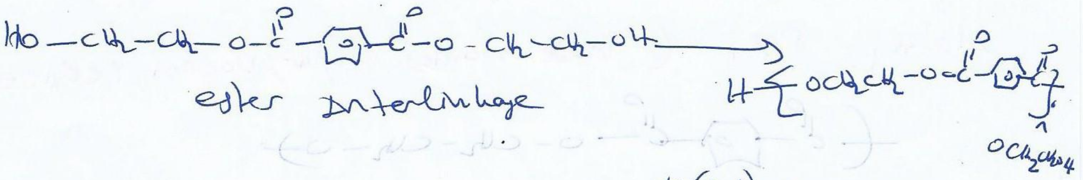
(methanol, collect as it is dripped off)

$T \sim 150-215°C$
1 atm

(3) T = 270 – 280 °C (increase T)

P = 0.5 – 1 torr (create vacuum)

Drive off EG



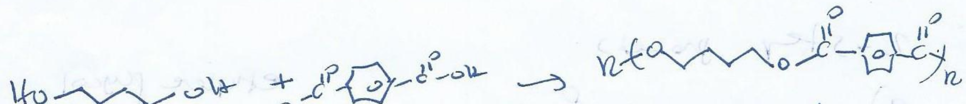
+ (n−1) HO–CH$_2$CH$_2$–OH

by product removed by distillation column

Advantages

1. Stoichiometry balance not needed (only one monomer)
2. Dimethyl ester more easily purified.
3. Ester interchange k (rate constant) is larger than k for acid + alcohol (better kinetics)
4. Removal of ethylene glycol (EG) is cleaner than H_2O removal

PBT



Fiber-reinforced molding compound is sold under the trade name Celanex.

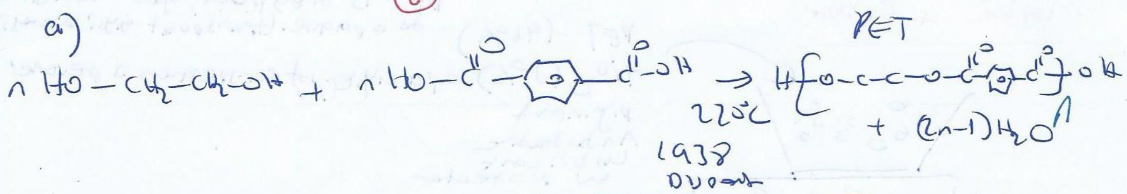
- melts lower temp.
- crystallizes more rapidly
- good self lubrication
- solvent resistance

General physical properties of PET & PBT

	PET	PBT
Heat deflection temp. (1,820 kPa; °C)	100	65
maximum resistance to continuous heat (°C)	100	60
crystalline melting point (°C)		
Coefficient of linear expansion (cm/cm °C, 10^{-5})	6,5	7.0
Compression strength (kPa)	$8,6\times10^4$	$7,5\times10^4$
Flexural " (kPa)	$1,1\times10^5$	9.6×10^4
Impact " (Izod)	26	53
Tensile "	$6,2\times10^4$	$5,5\times10^4$
ultimate elongation (%)	100	100
Density (g/mL)	1,35	1,35

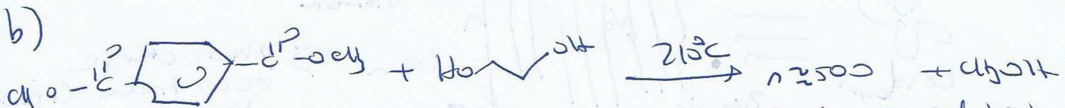
(6)

a)



PET is widely known as the fiber Dacron. It is highly crystalline, $T_m = 265°C$.

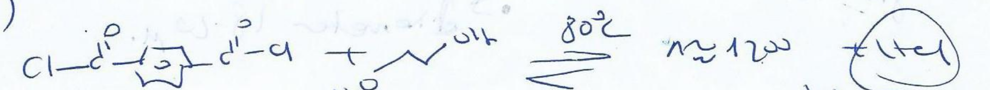
b)



essentially you get high molecular weight you remove byproducts more easily than water

]C], Dupont 1942

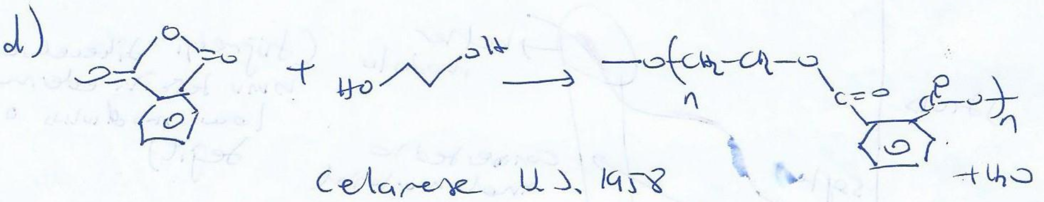
c)



titrate with base.

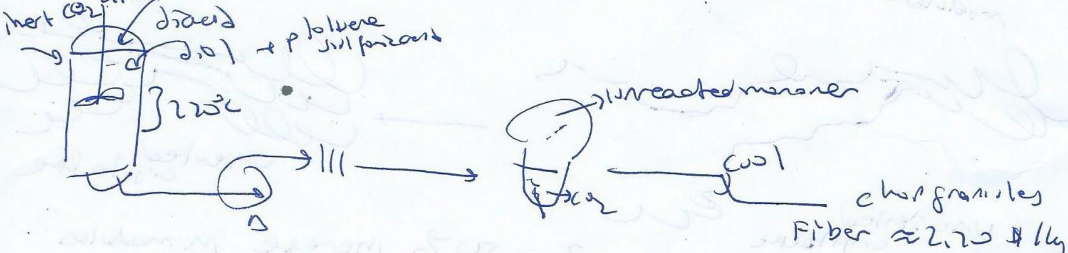
Hoesch, 1950

d)



Celanese U.S. 1958

PET (film, fiber, granules) produced 4×10^7 kg/year.



Fiber ≈ 2.20 $/kg
granule 1.40 $/kg

There is no chemistry between fibre and granules. It is just mechanical techniques

Make a Fiber

PET is transparent, you should do opaque. (transparent giysi istemeyiz)

PET (96%)

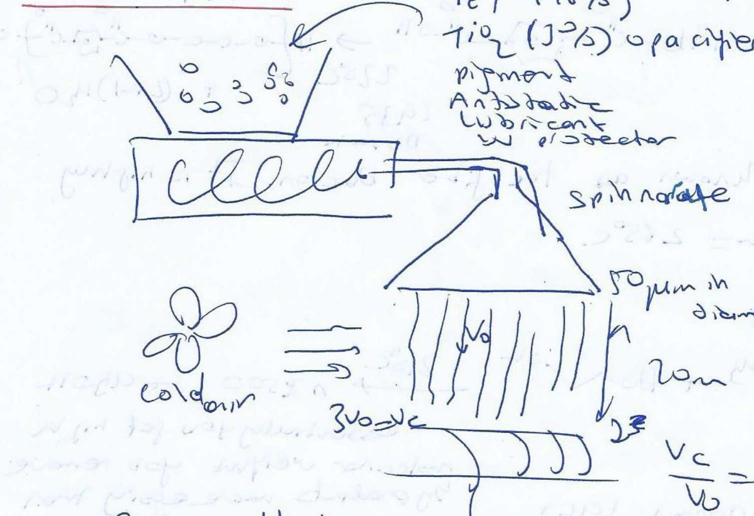
TiO_2 (3%) opacifier, transparency is prevented

pigment

Antistatic

Lubricant

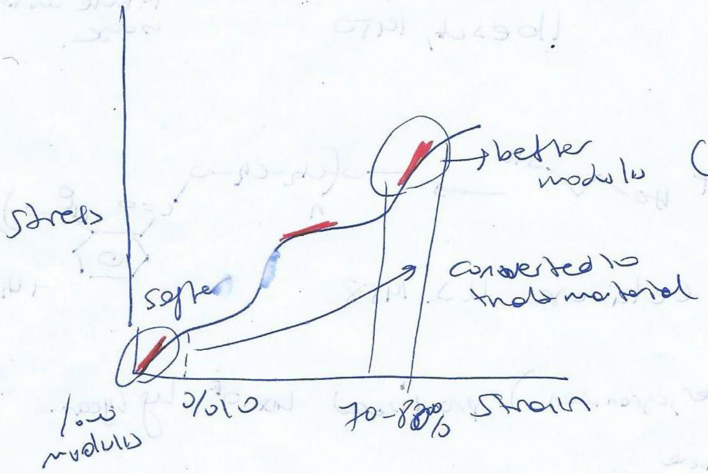
UV protector



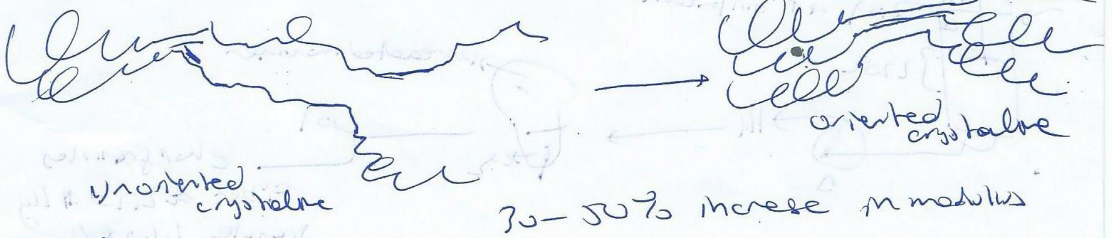
$\frac{V_c}{V_o}$ = Draw ratio

3 Vo altında manufacturer yok, fakat üstünde olan 4, 2, 4 gibi ver.

diameter 18-20 μ.



(düğmeyi düzeceksem bunu tercih ederim low modulus olanı değil)



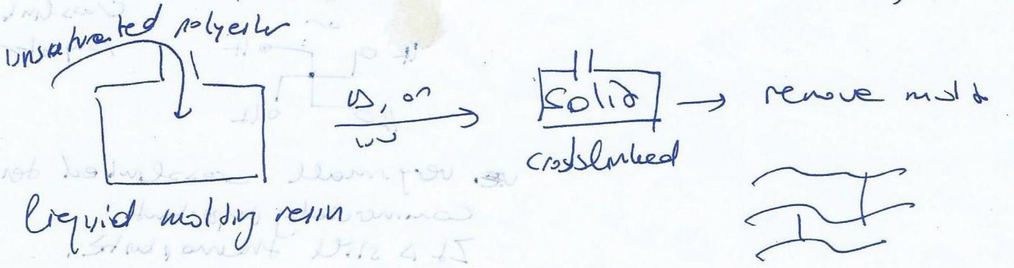
30-50% increase in modulus

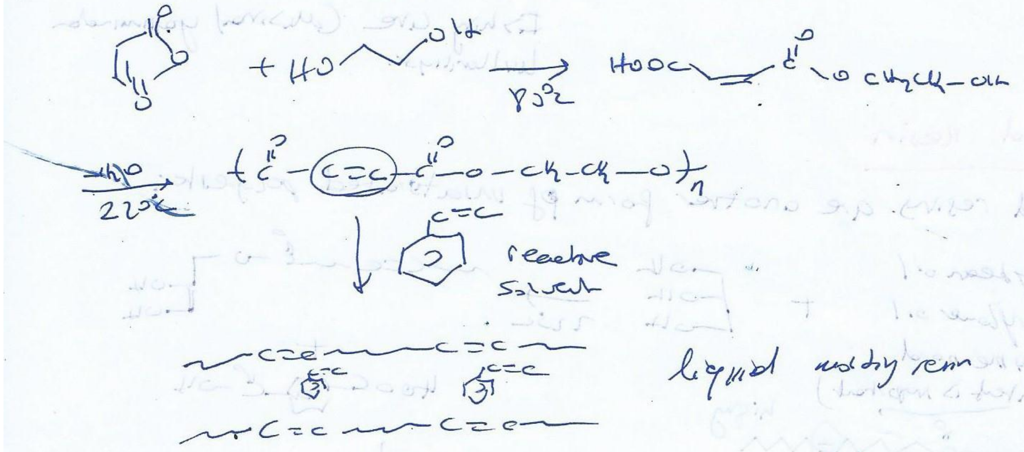
(annealing is also increase crystallinity)

(amorph region chains too irregular to permit regular packing)

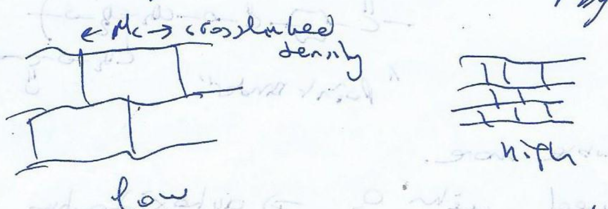
UNSATURATED POLYESTER

(electrical box) (natural gas box)
elektrik kutusu, doğalgaz kutusu, banyo küveti?, filtreler



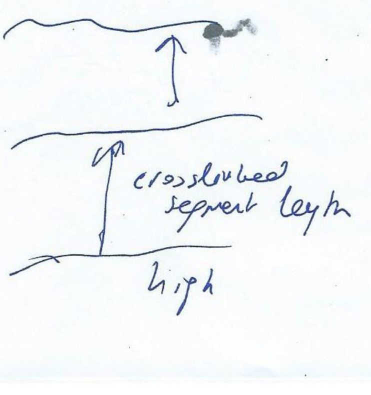


— no by product in the process (you can't needed to remove any by product)



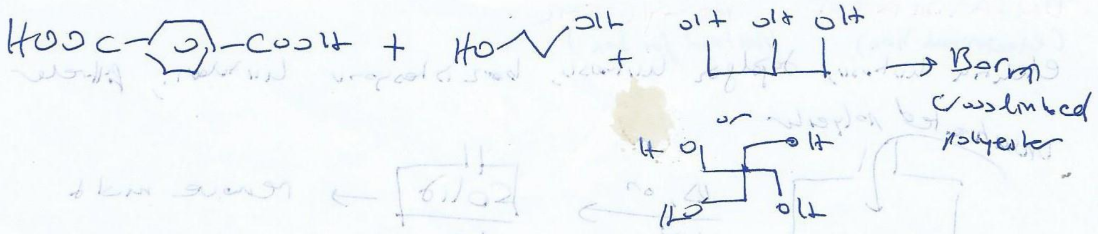
(lower modulus, more flexible)

(generally higher modulus, but they are brittle)



— using catalyst
— molecule
— styrene

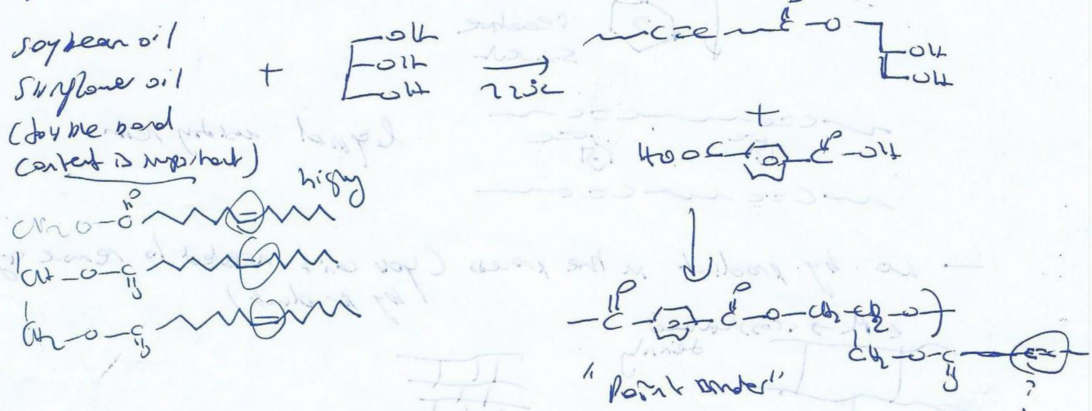
} affect the x-linked density.



ve. very small crosslinked density
commercially important
It is still thermoplastic.
Fishing line (misina) yapımında kullanılıyor.

Alkyd resin

Alkyd resins are another form of unsaturated polyesters



→ After drying no soluble more.
get x-linked with O_2. ⇒ autoxidation

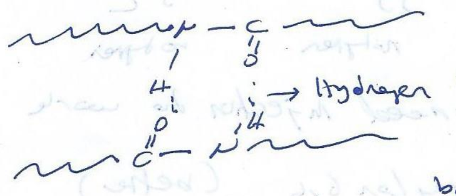
Polyamides (Nylon)

Nylon (DuPont, 1938, Carrothers)

$-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-$ Amide

$-O-\overset{O}{\overset{\|}{C}}-$ ester

New York City, 1940 first sale in open hour a million pairs sold



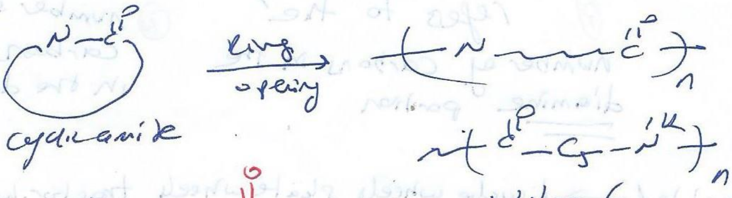
Many hydrogen bonding occur between long polymer chains. So, you will get pretty strong reversible structure. Increasing temp. break up hydrogen bonding but when it is cooled it is reformed.

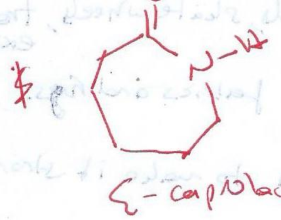
$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH + H_2N-(CH_2)_6-NH_2 \longrightarrow -(\overset{O}{\overset{\|}{C}}-C_4-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-C_6-\overset{H}{N})-$

$Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-Cl$ → interfacial polymerization

(parachute) Nylon 6,6

Nylon paraşütte kullanıldı II. Dünya savaşında, ipek çok pahalı. 1938'de ayrıca kadın çorabı olarak da kullanılmış.





ε-caprolactam

Nylon	6-6	6	6-10	6-11
(density) ρ	1,14	1,13	1,09	1,09
melting point	264	215	215	185
Tensile strength	11000	11000	8500	5500
Impact	1,5	3	2.0	1.8
Softening temp.	78	80	55	52
compressive strength	1x10^5	9,7x10^4	not given	not given

You need low melting point, you need injection to work under extrude. ⇒ nylon 6 > nylon 6,6 (better)

Nylon density is higher than 1.0 !! Generally polymers density is lower i.e polystyrene, polyester. This is because of H-bonding.

$$\{ \overset{H}{N}-(CH_2)_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}} \}_n$$

Nylon 6,10

6 → refers to the number of carbons in the diamine portion

10 → number of carbons in the diacid.

Nylon 66 → molded ⇒ bicycle wheels, skate wheels, tractor hood extensions

→ Fiber ⇒ clothing, fabrics and rugs.

Polyester is blended with the nylon to make it stronger

The properties of polyamides are improved by the formation of polyether blocks and by blending with thermoplastics such as EPDM, PET, PBT and TPE.

Nylon 6,6 is the dominant nylon in the United States, while Nylon 6 is the dominant nylon in Europe.

Nylons are generally semicrystalline, meaning they have a good amount of order.

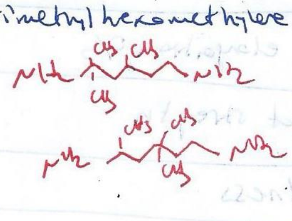
Nylons are also "lubrication free" ⇒ they do not need a lubricant for easy mobility so that they can be used as mechanical bearings and gears without the need for periodic lubrication.

In general, more crystalline nylons are used as fibers. while, less crystalline nylons materials are more used as plastics.

The amount of crystallinity is controlled through a variety of means, including introduction of bulky groups and asymmetric units, rapid cooling of nonaligned melts, and introduction of plasticizing materials.

⇒ Grace and Company developed Trogamid T ⇒ amorphous transparent nylon

⇒ from condensation of  ⊕ mixture of 2,2,4- and 2,4,4- trimethylhexamethylene diamine



Advantages – Disadvantages of Polyamide

Advantages

Tough, strong, impact resistant
Low coefficient friction
Abrasion resistance
High temperature resistance
Good solvent resistance
Resistant to bases
Lubrication free

Disadvantage

* High moisture absorption with dimensional instability – loss of up to 30% of tensile strength and 50% of tensile modulus (max. allowance moisture content %0,1 – %0,2)
* Subject to attack by strong acid and oxidizing agent
* Requires UV stabilization
* High shrinkage in molded sections
* Electrical and mechanical properties influenced by moisture content

Properties of Reinforced Nylon

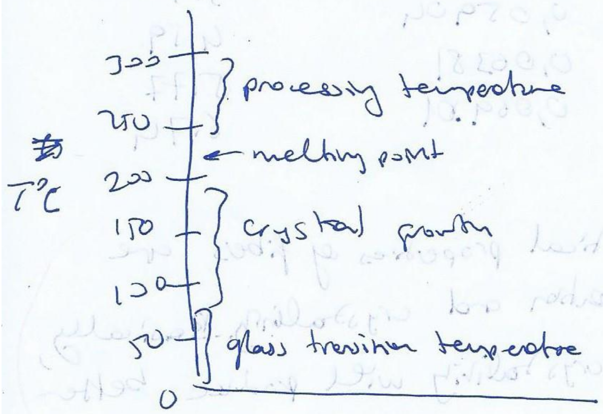
	Nylon 6,6	Nylon 6,6 with %30 short glass	Nylon 6,6 with %30 carbon fibre
Density	1,13–1,15	1,4	1,06–1,10
Crystallinity	30%–50%	30%–50%	30%–50%
Tensile strength, psi	14,000	28,000	32,000
Tensile modulus	230k–550k	1300k	3300k
Tensile elongation, %	15–80%	3%	4%
Impact strength	0,55–1,00	1,6–4,5	1,5
Hardness	R120	R120	R120
Cost $/lb	1,40	1,70	7,70

③

Too high moisture content result in:

* bubbles / foaming in the melt
* holes in the film
* bubbles collapse
* hydrolytic breakdown

Low moisture act as plasticizer in Nylon 6 during melting. All nylons absorb moisture. The extent of moisture absorption depends on temperature, crystallinity, and humidity. Moisture below 0.2 %, so pellets should be dried before manufacturing.



Effect of Resin Drying Temperature on Zero Melt Viscosity

Drying temperature °C	MW exponent
5	3.8
110	4.6-5.4

$\eta = k(MW)^{a}$

35% of total nylon produced is used in the automobile industry.

Fiber Formation

Polymer viscosity → a function of molecular weight.

$M_n \approx 14{,}000-20{,}000$ for textile fiber production

Two step melt spinning, comprised of spinning and drawing, is considered to be the conventional method to manufacture nylon filaments.

Elastic modulus, moisture sorption, tenacity and elongation at break are affected by drawing.

Table 1. Effect of Drawing on Birefringence and Elastic modulus

Draw Ratio (V_c / V_0)	Birefringence	Elastic modulus
1	0,00832	1,97
2	0,[illegible]3297	2,74
3	0,05523	3,70
4	0,05904	4,59
5	0,06381	5,77
60	0,06901	6,74

[illegible] lines — fiber follow up? Draw ratio ↑

> Birefringence = The resolution or splitting of a light wave into two unequally reflected waves by an optically anisotropic medium such as calcite or quartz (double refraction) related with light diffraction

Mechanical, thermal and optical properties of fibers are strongly affected by orientation and crystallinity. Basically, higher fiber orientation and crystallinity will produce better properties.

Dyeability: The dyeing efficiency of nylon fibers is enhanced due to the end groups $-COOH$ and $-NH_2$, which exhibit polar and hydrophilic characteristics.

Degradation ~ $COOH$ and ~NH_2 end groups sensitive to: light, heat, oxygen, acids and alkali.

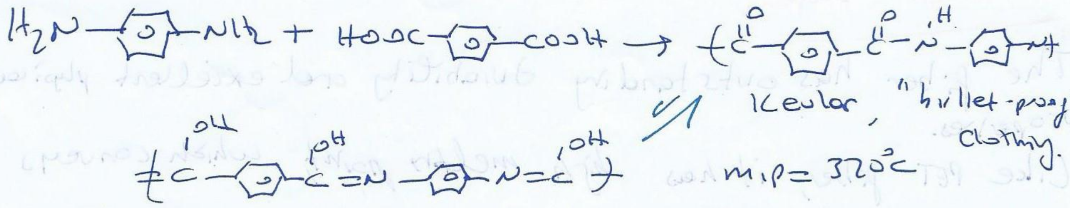
When exposed to elevated temperatures, unmodified nylons undergo molecular weight degradation, which result in loss of mechanical properties. The degradation is highly time / temperature dependent. By adding heat stabilizer, nylon can be used at elevated temperature for long-term performance.

Adding carbon black can reduce the radiation degradation (dokuma mamy kumas) 4

Nonwoven Usage

The fiber has outstanding durability and excellent physical properties.
Like PET fiber, it has high melting point, which conveys good high-temperature performance.
The fiber is more sensitive than PET, despite this fact nylon is not considered a comfortable fiber in contact with the skin.
Its toughness makes it a major fiber of choice in carpets, including needle punched floor-covering products.
Because of its relatively high cost, nylon has somewhat limited use in nonwoven products.
It is used as a blending fibeer in some cases, because it conveys excellent tear strength. The resiliency (flexible) and wrinkle (kırışık) recovery performance of a nonwoven produced from nylon is not as excellent as that from PET fiber.

Aromatic Polyamides



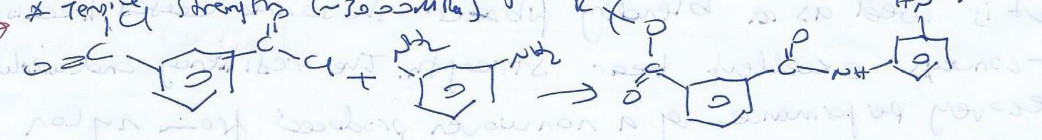
Kevlar, "bullet-proof" clothing.

m.p = 320°C

Enol (conjugation) ⇒ makes kevlar extremely strong polymer. continuously conjugated and without destroying the aromaticity

M.p. is very high, It bring problem in the process. Uzun zaman Kevlar parcalar metal Iler gibi calısılır

- ⇢ * Kevlar ~~kis~~ very low flexibility makes it a rigid structure
- * The H-bonding enhances rigidity and makes it solvent resistant
- * The long backbone gives it high mechanical strength
- * kevlar has a liquid crystalline structure.
- ⇢ * By weight it has higher strength and modulus than steel
- ⇢ * Tensile strength (~3000 MPa)



Nomex

Race car drivers → clothes, cork, shoes } flame retardant nomex

~~Military~~ Military wear flight suits → ''

Space shuttle parts.

General Physical Properties of a Typical Aramid

Heat deflection temperature (1,820 kPa, °C)	260
Maximum resistance to continuous heat (°C)	150
Crystalline melting point (°C)	>370
Coefficient of linear expansion (cm/cm °C, 10^{-5})	2.6
Compressive strength (kPa)	2×10^5
Flexural " (kPa)	1.7×10^5
Impact " (Izod: cm-N/cm of notch)	75
Tensile " (kPa)	1.2×10^5
Ultimate elongation (%)	5
Density (g/mL)	1.2