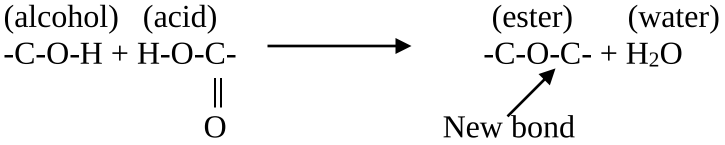
Step-growth polymerization forms polymers in a manner that is quite different from chain-growth polymerization. The mechanism requires that at least two different monomers participate in the reaction.[1] Before we consider the specific steps in step-growth polymerization, we'll first consider the necessary functional groups required in the monomers for the reaction(s) to occur.

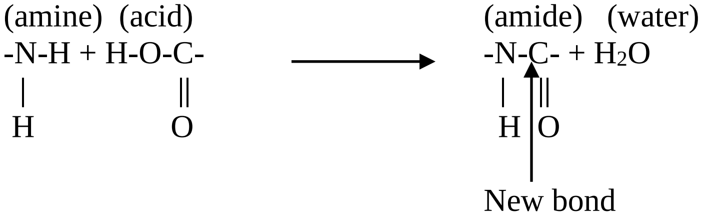
Each stage in step-growth polymerization involves a reaction between dissimilar chemical groups which are part of the monomer molecules.[2] The chemical groups are termed "functional groups" due to the fact they provide a specific attribute (functionality) that allows them to react together in a specific way to give the desired resin properties.

The most common type of reaction in forming resin via step-growth polymerization involves the formation of a new bond (covalent bond) between the two functional groups. Simultaneously, a by-product is produced from the reaction (sometimes water – which is why this polymerization is sometimes termed condensation polymerization). Let's illustrate this by looking at a generic alcohol and acid:



$$\overset{\text{(alcohol)}}{\text{-C-O-H}} + \overset{\text{(acid)}}{\text{H-O-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-}} \longrightarrow \overset{\text{(ester)}}{\text{-C-}\underset{\nearrow\,\text{New bond}}{\text{O}}\text{-C-}} + \overset{\text{(water)}}{H_2O}$$

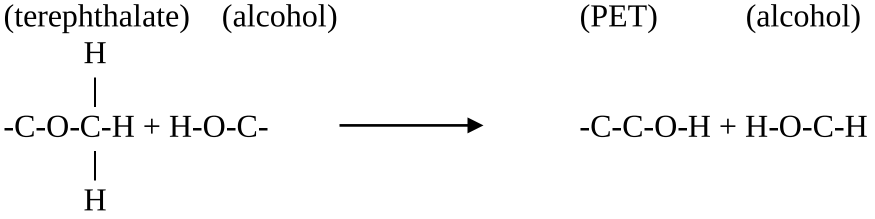
Two other types of monomers that combine via step-growth polymerization are an amine and an acid to form an amide:



$$\overset{\text{(amine)}}{\text{-}\underset{\underset{\text{H}}{|}}{\text{N}}\text{-H}} + \overset{\text{(acid)}}{\text{H-O-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-}} \longrightarrow \overset{\text{(amide)}}{\text{-}\underset{\underset{\text{H}}{|}}{\text{N}}\text{-}\underset{\underset{\text{O}}{\|}}{\text{C}}\text{-}} + \overset{\text{(water)}}{H_2O}$$

New bond

Water is not the only by-product that might be produced, however. Here's an example of a step-growth polymerization where an alcohol by-product is produced:



$$\overset{\text{(terephthalate)}}{\text{-C-O-}\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{H}}{|}}{\text{C}}}\text{-H}} + \overset{\text{(alcohol)}}{\text{H-O-C-}} \longrightarrow \overset{\text{(PET)}}{\text{-C-C-O-H}} + \overset{\text{(alcohol)}}{\text{H-O-C-H}}$$

A particular step-growth polymerization reaction of great historical and commercial significance is the polymerization of nylon. This reaction uses two symmetric bifunctional monomers (hexamethylene diamine and adipic acid). The resulting material is a polyamide, commonly known as nylon 6,6; the numerical designation in the name represents the number of carbons in each monomer.

Typical resins polymerized via step-growth include: acetals, nylons, polycarbonate, and polyesters.

Our next discussions will involve specific resins and how they perform both physically and mechanically. The resins to be presented have all been formed via the step-growth or chain-growth polymerization method; which in turn will have an effect on its strengths and weaknesses.

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[1] Askeland, Donald R., *The Science and Engineering of Materials*, PWS Publishing Company, 1994.

[2] Strong, A. Brent, *Plastics: Materials and Processing*, Prentice Hall, 2000.

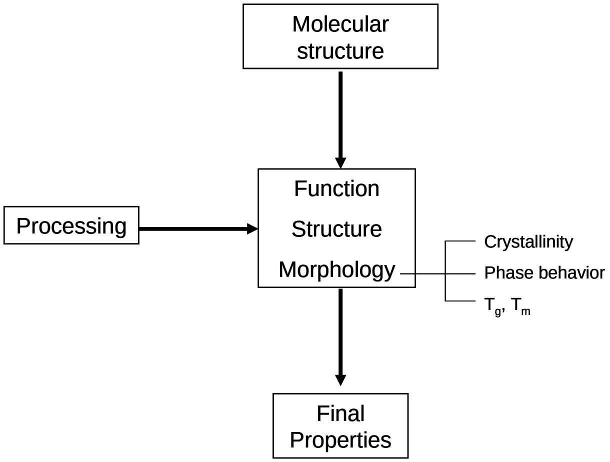
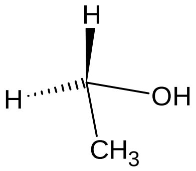


Figure 1: Processing and molecular structure of a polymer determines its function, structure, and morphology, which in turn determines its final properties

Diversity of Polymer Chains (two types):

A) Low molar mass (small) molecules

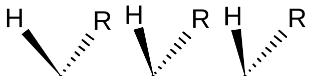
Example:



Synthesis determines molecular structure
One goal of synthesis is to avoid side reactions and achieve a pure product

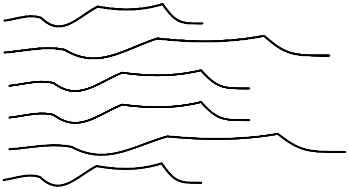
B) Polymer

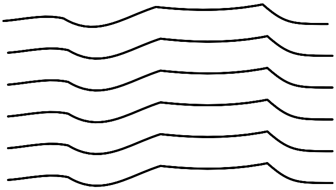
- Control molecular structure
- Control regularity of backbone
  - Ex: stereochemistry



abababab	regular copolymer
abbaaaba	random copolymer
aaaabbbb	block copolymer

- Control molecular weight
  - Impacts polydiversity:

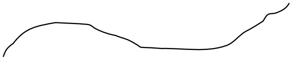




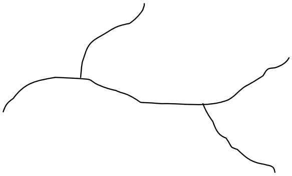
Polydisperse vs. Monodisperse

  - Overall molecular weight (MW) or mass
    - If a polymer has low MW, it acts like a fluid above T_g
    - If a polymer has high MW, it acts like a rubber above T_g
    - MW also determines mechanical properties, viscosity, rheology

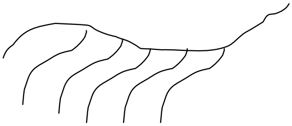
- Control architecture



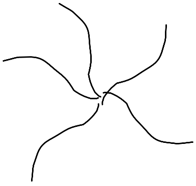
linear chain polymer



lightly branched polymer

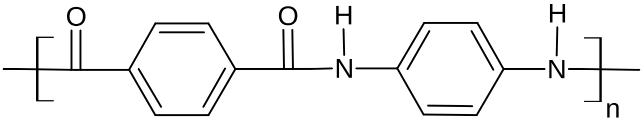


“combed” polymer

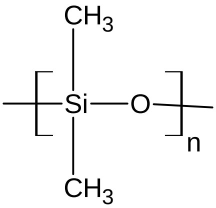


“star polymer”

- To gain a sense of rational design and synthesis
- To develop an intuition about the impact of a structure on property
- The following two examples demonstrate how structure determines the polymer's physical and chemical properties:
    - Ex 1: polyamides (Kevlar® by DuPont)



        - Kevlar®'s very low flexibility makes it a rigid structure
        - The hydrogen bonding enhances rigidity and makes it solvent-resistent
        - The long backbone gives it high mechanical strength
        - In fact, Kevlar® has a liquid crystalline structure
    - Ex 2: polydimethylsiloxane (PDMS)



        - The longer Si—O bond makes PDMS very flexible
        - CH_3 makes the polymer hydrophobic
        - $T_g \approx -100°C$

Goal 2: Apply knowledge to processes in industrial and commercial settings

- Determine which process is best for certain applications (Ex: there are ways to synthesize PDMS)
- There are variables in polymer approach, synthetic route, starting materials and/or catalysts, and solvent conditions

Goal 3: Awareness of new tools and approaches to materials design

- Less traditional approaches
- Functionalization of polymers
- Self-assembly approaches

N_i = number of molecules of MW=M_i

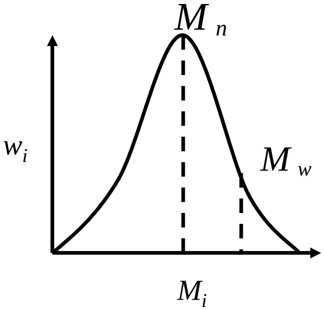
w_i = weight fraction of given system of chains with MW=M_i

$$w_i = \frac{N_i M_i}{\sum N_i M_i}$$

$\overline{M_n}$ = number average MW = $\dfrac{\text{total weight}}{\text{total \# molecules in sample}} = \dfrac{\sum N_i M_i}{\sum N_i}$

$\overline{M_w}$ = weight average MW = $\dfrac{\sum (N_i M_i) M_i}{\sum (N_i M_i)} = \dfrac{\sum N_i (M_i)^2}{\sum N_i M_i}$

The following graph shows the relationship between w_i *and* m_i:



Polydispersity can be measured by PDI (polydispersity index): $z = \dfrac{\overline{M_w}}{\overline{M_n}} \geq 1.0$.

z = 1.03 or 1.05 is considered close to monodisperse

- In chain growth, a monomer is activated and polymerization propagates by activating neighboring monomers. The process is very rapid and high MW polymers are achieved quickly.
- The following describes the chain growth reaction in which * represents the activated monomer M. This can be a free radical, negative charge, or positive charge:

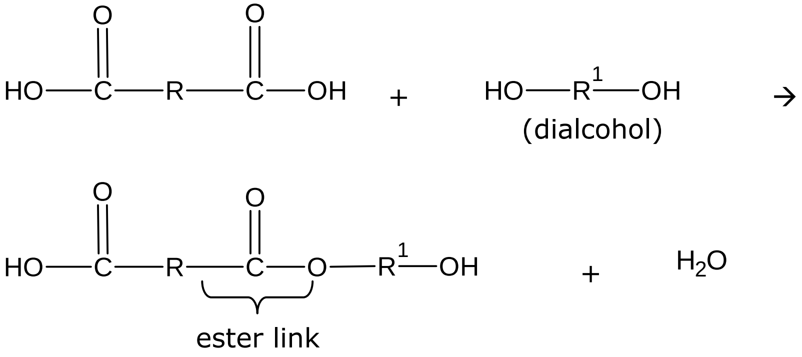
1. $R^* + M \rightarrow RM^*$
2. $RM^* + M \rightarrow RMM^*$
   …
   $RM_n^* + M \rightarrow RM_{n+1}^*$
3. Event that terminates

B) Step growth

- In chain growth, bifunctional monomers are added systematically to form covalent bonds. It generally involves 2 (or more) functional groups: “a” and “b.” Molecular weight increases “slowly” as dimers become trimers, which in turn become tetramers.
- Examples of polymers formed by chain growth: nylons, polyesters, polypeptides (proteins)
- [Handout] These are typical a and b groups:

a + b → c + d where c = covalent link
d = byproduct

1. a—a + b—b → a—c—b + d



$$HO-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-OH + HO-R^1-OH \rightarrow HO-\overset{\overset{O}{\|}}{C}-R-\underbrace{\overset{\overset{O}{\|}}{C}-O}_{\text{ester link}}-R^1-OH + H_2O$$

2. a—c—b + a—a → a—c—c—a

3. a—c—c—a + b—c—c—c—a → $a(c)_6a$ + d

Lecture 2: Molecular Weight Control, Molecular Weight Determination in Equilibrium Step Condensation Polymerizations, Interchange Reactions: Effects on Processing and Product, Application Example: Common Polyesters

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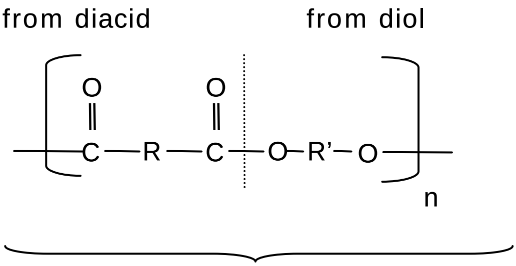
Step Growth Polymerization

2 functional groups: a,b → form new link c, may be a side product d

a—a + b—b → a—c—b +d

For example, if a—a is a diacid and b—b is a diol:



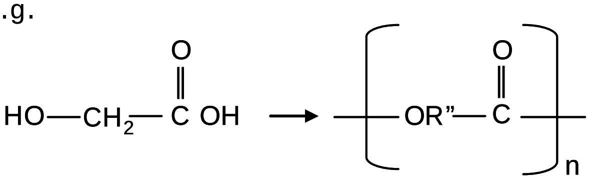
$$\underbrace{\left[-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-O-R'-O- \right]_n}$$

Polyester
(one repeat unit consists of 2 structural units)

Degree of polymerization ≡ number of monomer units or structural units incorporated in polymer chain
$= \overline{p_n}$

$$\overline{M_n} = \frac{\overline{p_n} \cdot M_u}{2}$$ where M_u = molecular weight (MW) of individual repeat units

Can also have a—b monomers:
e.g.



$$HO-CH_2-\overset{O}{\overset{\|}{C}}\,OH \longrightarrow \left[-OR''-\overset{O}{\overset{\|}{C}}- \right]_n$$

In this case:

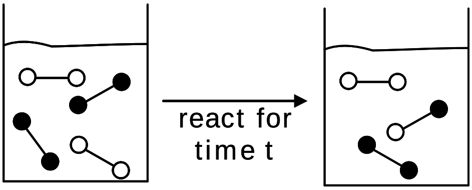
- R" = CH_2
- The repeat unit is the structural unit
  $\overline{M_n} = \overline{p_n} \cdot M_u$

How do you determine MW as a function of conversion?

$$\overline{p_n} = \frac{\text{total initial \# of monomer units}}{\text{total \# of molecules remaining}} = \frac{N_o}{N_{total}}$$

Simple thought experiment:

50 monomer units	25 a—a	○—○
	25 b—b	●—●



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

$$\overline{p_n} = \frac{50}{50-25} = 2$$

So π (conversion) can be related to $\overline{p_n}$.

$(Na)_o$ = initial # of a reactive group = 2 (# of a-a monomers)
$(Nb)_o$ = initial # of b reactive group = 2 (# of b-b monomers)

$$\pi_a = 1 - \frac{Na}{(Na)_o} \qquad \pi_b = 1 - \frac{Nb}{(Nb)_o}$$

Define $r \equiv \frac{(Na)_o}{(Nb)_o} \le 1$ Define: *a* is minority functional group

Stoichiometric ratio

Total # of functional groups initially present

$$N_o = (Na)_o + (Nb)_o = (Na)_o\left[1 + \frac{1}{r}\right]$$

At a given time t, have conversion π_a

$$N_t = \text{\# of functional groups at time t} = \underbrace{(Na)_o(1-\pi_a)}_{Na} + \underbrace{(Nb)_o - (Na)_o\pi_a}_{Nb}$$

$$\therefore \quad \boxed{\overline{p_n} = \frac{\frac{N_o}{2}}{\frac{N_t}{2}} = \frac{N_o}{N_t} = \frac{1+\frac{1}{r}}{1-2\pi_a+\frac{1}{r}} = \frac{1+r}{1-2\pi r+r}}$$

$\pi_a = \pi$ (assume referring to minority)

Simple case: r = 1.0 (perfect stoichiometry)

At	$\pi = 0.995^*$ →	$\overline{p_n} = 200$		↓
	$\pi = 0.99$ →	$\overline{p_n} = 100$	$\overline{p_n}$ drops fast	
	$\pi = 0.98$ →	$\overline{p_n} = 50$		
	$\pi = 0.90$ →	$\overline{p_n} = 10$	oligomer	

*Can take a long time. First 95% takes same time as last 2-3%.

Must ↑ π to get high MW $\quad \overline{p_n} = \frac{1}{1-\pi} \quad$ As π ↑, $\overline{p_n}$ explodes.

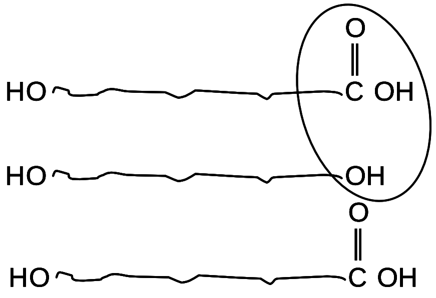
But, there is a problem:

Control of MW

How to control MW?

a) Control π (conversion)

Issue:

	T↑	MW changes when you ship it or store it.

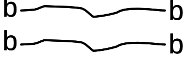
b) Control stoichiometry:

Assume: e.g. $\pi = 1.0$

$$\Rightarrow \overline{p_n} = \frac{1+\frac{1}{r}}{1-\frac{1}{r}} = \frac{1+r}{1-r}$$

Add excess of b—b

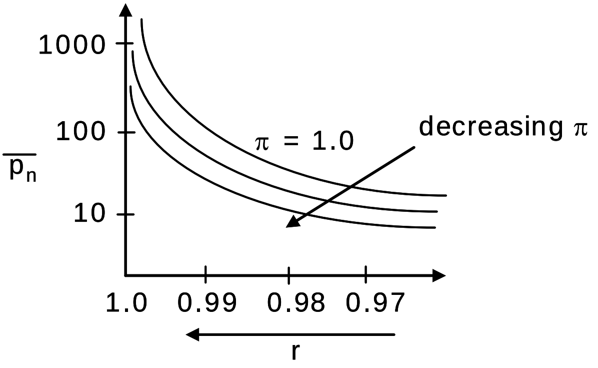
End up "capping" chains w/b groups

		b groups cannot react w/each other

e.g. 1% excess of b-b

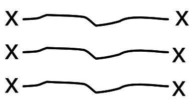
$\Rightarrow$ max $\overline{p_n} = 199$

Can intentionally cap w/alcohol or ester for certain applications.
Can use π, r to predict MW outcome of rxn.



Can also use monofunctional unit as an end capping agent:

\ a—a
b—b
b—x where x is a desired final group that can't react w/a or b
e.g. phenol

	• polyurethanes: longer chain molecules
	• surface groups

Here we redefine the ratio r:

Assume a—a b—b		$r = \dfrac{(Na)_o}{(Nb)_o + 2N_x}$		Caveat: $(Na)_o = (Nb)_o$ a—a b—b for this to work.
are in equal quantity		where N_x = # of b-x molecules		

Same expression if you're using a—b monomers.

MW Distribution as a Function of Conversion:

Assumptions: 1. Equal reactivities for all a,b functional groups.
Reactivities are the same for short a—a and long polymer (length independence) in viscous fluid.
2. Perfect stoichiometry: r = 1
3. For ease of explanation, use a-b monomer ($\pi_a = \pi_b$).

At a given time t, have conversion π

Probability that an a group has reacted: p = π

Probability that a molecule has x structural units = $\wp_x$

x structural units ⇒	(x-1) =	# of a groups reacted		Prob of this combination
	1	a group unreacted		

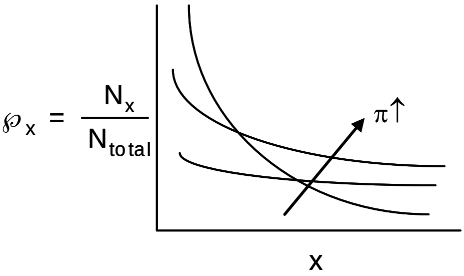
Prob of x-1 a groups reacted: p^{x-1}
Prob of unreacted a: $(1-\pi)$ or $(1-p)$

So, $\wp_x = p^{x-1}(1-p)$

$\wp_x$ = number fraction of chains with degree of polymerization x

$$\wp_x = \frac{\text{\# of x-length chains}}{\text{total \# of chains}} = \frac{N_x}{N_{total}} = \frac{N_x}{N_o\left(1-p\right)} = \frac{N_x}{\underbrace{N_o - N_o p}_{\text{Every time a molecule reacts lose } N_o p.}}$$

$N_x = \wp_x N_o(1-p)$



increase conversion → narrower and broader

Flory-Shulz Distribution: Some Monomer Always Present

$$\overline{p_n} = \frac{\sum\limits_x xN_x}{\sum\limits_x N_x} = \sum x\wp_x = \sum xp^{x-1}\left(1-p\right)$$

$$\sum p^{x-1} = \frac{1}{1-p}$$

$$\sum xp^{x-1} = \frac{1}{\left(1-p\right)^2}$$

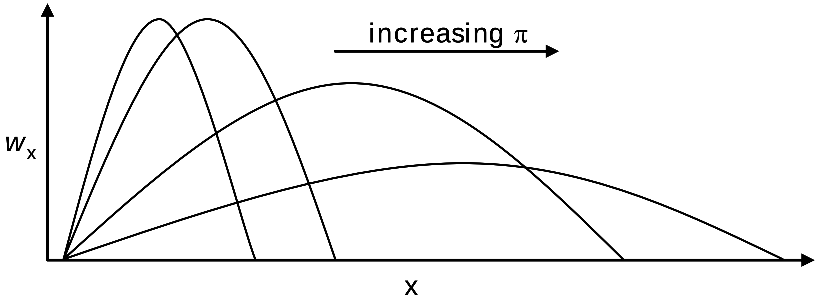
$$\overline{p_n} \Rightarrow \frac{1}{\left(1-p\right)}$$

Weight fraction: $w_x = \frac{xN_x}{N_o} = x\left(1-p\right)^2 p^{x-1}$

$$\underbrace{\overline{p_w} = \frac{1+p}{1-p}}_{\text{Result of using } \overline{p_w} \text{ expression and summations}} \text{ or } \frac{1+\pi}{1-\pi}$$

$$\text{PDI} = z = \frac{\overline{p_w}}{\overline{p_n}} = 1 + p = 1 + \pi$$

As $\pi \rightarrow 1.0$
$z \rightarrow 2.0$



Lecture 7: Crosslinking and Branching, Network Formation and Gelation, Carothers Equation, Pn Approach

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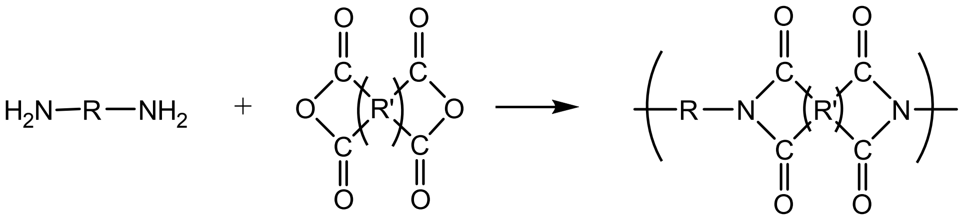
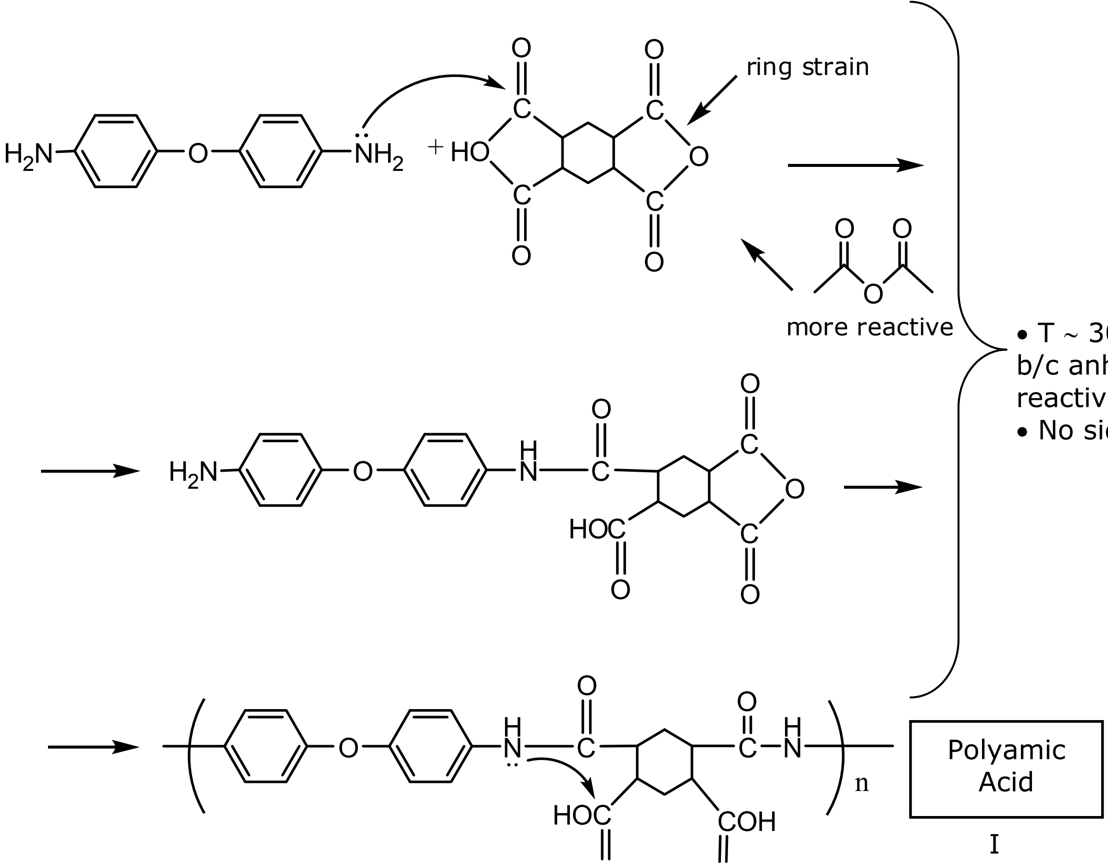
Polyimides



Staged formation of Polyimides

Stage 1: Formation of polyamic acid



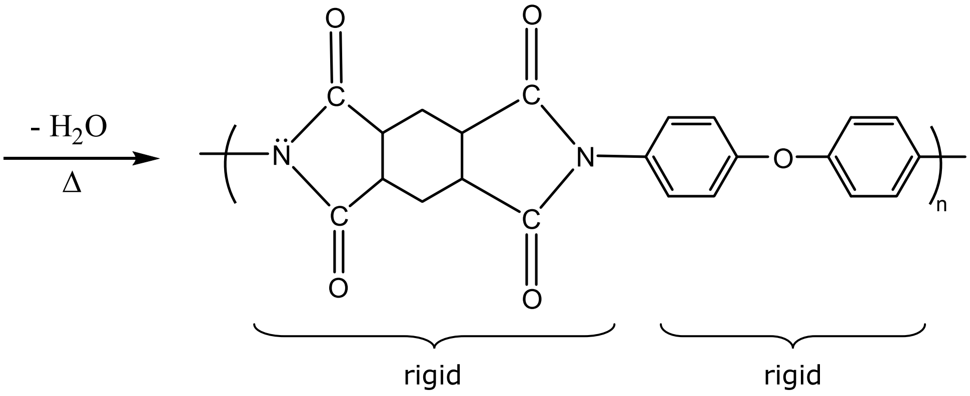
- T ~ 30°C – 50°C b/c anhydride is reactive
- No side product

- Can CAST polyamic acid or SPIN into final form
- Relatively soluble in many solvents

Stage 2: Cyclization

- reaction takes place in solid state or near solid state
- H_2O removal

I

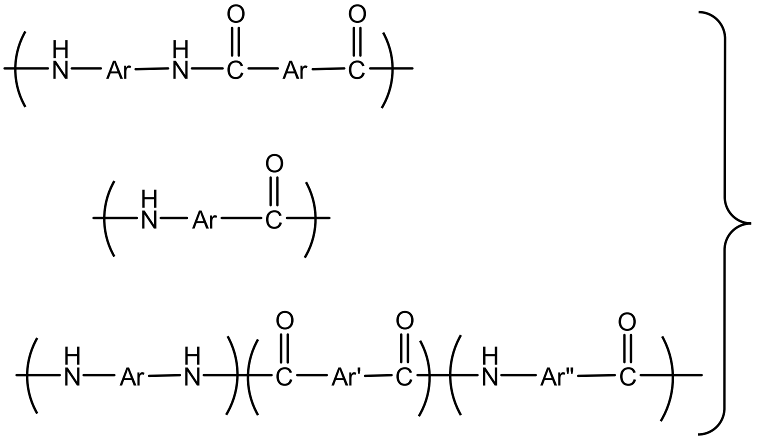


T > 150°C
Low P (vacuum)
Final product is intractable

Kapton®
Pyralin®
Vespel®

Aromatic Polyamides

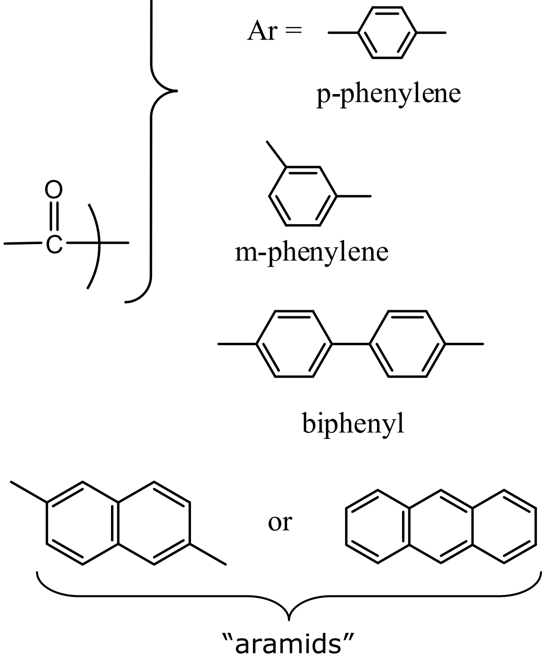
"Wholly" aromatic



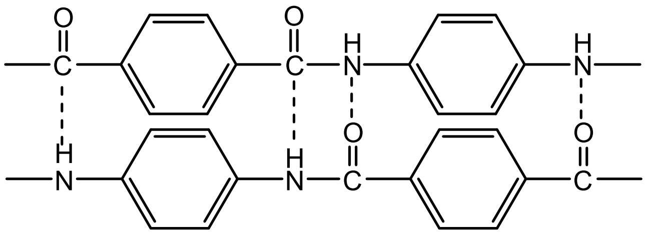
$$-\!\!\left(\overset{H}{N}-Ar-\overset{H}{N}-\overset{\overset{O}{\|}}{C}-Ar-\overset{\overset{O}{\|}}{C}\right)\!\!-$$

$$-\!\!\left(\overset{H}{N}-Ar-\overset{\overset{O}{\|}}{C}\right)\!\!-$$

III $$-\!\!\left(\overset{H}{N}-Ar-\overset{H}{N}\right)\!\!\left(\overset{\overset{O}{\|}}{C}-Ar'-\overset{\overset{O}{\|}}{C}\right)\!\!\left(\overset{H}{N}-Ar''-\overset{\overset{O}{\|}}{C}\right)\!\!-$$

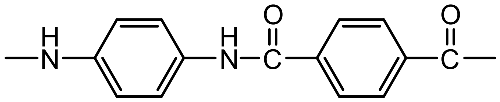


- very high stiffness, modulus
- high mechanical strength
- solvent resistance
- "performance" polymers
- hydrogen bonding + regular structure
  ⇒ very stable crystallites

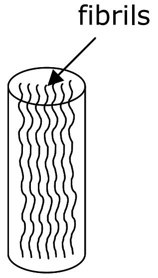


H-bonding
β sheets
⇒ semicrystalline
very high melting points
rigid backbones
⇒ liquid crystal phases in soln

Example:



Kevlar® (Dupont)



Compare to: high tensile steel

	Ultimate TS	ε at break	Energy at break	Weakness:
Kevlar 49	3.6 GPa	2.7%	25 MJ/m^3	Low compressive strength. (analogy: broom straws)
High tensile steel	1.5 GPa	0.8%	6 MJ/m^3	

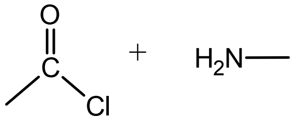
How to react? (making aramids)

- Bulk melt: T_m way too high!

- Interfacial polymerization: possible

Get product as precipitate at interface
Works for partially aromatic polyamides
Solvent: solvate low + mod MW's
Remain phase separated from H_2O
} Not possible

- Solution polymerization:

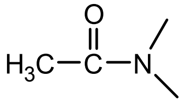
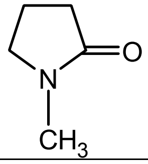


reactive groups

highly reactive – allows dilution

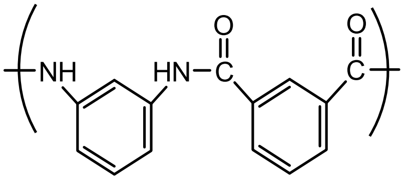
Reaction conditions:
T ~ 25°C – 50°C or lower
Add Li_2CO_3, Na_2CO_3, CaOH
Solvents: must be very polar, H-binding groups
Advantageous if also sol basic
⇒ neutralize HCl

Often add LiCl or other Li salts to solvent
⇒ aid in H-bond break-up

Common Solvents:	$CHCl_3$	↓	Less polar
	CH_2Cl_2		
	CH_3CN		
	$Cl\text{-}CH_2\text{-}Br$		
DMAc			
NMP			
DMSO			More polar

Kevlar®: T_m = 570°C
T_g = ?
T_{deg} = 550°C in N_2
E_o = 6000 – 8000 kg/mm^2

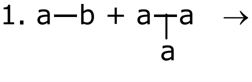
Slight Change: go from p (para) to m (meta) linkages



T_m = 435°C
T_g = 272°C
E_o =2000 kg/mm^2

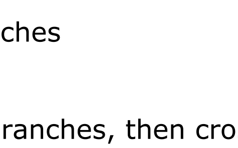
Stretches out more

Branching and Network Formation
So far: difunctional monomers: f = 2
When monomer functionality f ≥ 3 ⇒



can form branches

\+



networks

- crosslinks are individual junctions
- networks are infinitely large

Examples:

1. a—b + $\underset{\substack{| \\ a}}{a-a}$ → branches

2. a—b + a_f + b—b → branches, then crosslinks

3. a—a + b—b + b_f → branches, then crosslinks

4. a_f + b_f → branches, crosslinked networks

Examples of Step growth Polymers

Polyamides & Polyimides: $(-\overset{O}{\overset{\|}{C}}-NH-)$,
$\dashrightarrow -N<\begin{smallmatrix}CO-\\CO-\end{smallmatrix}$

* **Nylons:**
(1935) 6,6 $n\ NH_2-(CH_2)_6-NH_2 + n\ COOH-(CH_2)_4-COOH$
Hexamethylene diamine Adipic Acid
6C

$$\downarrow$$

$$-[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO-]_n + 2H_2O$$

Nylon 6,9 $H_2N-(CH_2)_6NH_2 + n\ COOH-(CH_2)_7COOH$
9C Azelaic acid

$$\downarrow$$

$$[NH-(CH_2)_6-NH_2-CO-(CH_2)_7CO]_n + 2H_2O$$

Nylon 6,10 sebacic acid $(COOH-(CH_2)_8COOH)$
10C

Nylon 6,12 dodecanedioic acid
12C

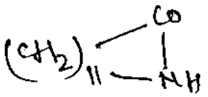
Nylon 11 $n\ H_2N-(CH_2)_{10}COOH$ (ω-aminoundecanoic acid)
11C.

Nylon 6

$\longrightarrow$ Nylon 6 $[(CH_2)_5CONH]_n$

6C caprolactum

Nylon12



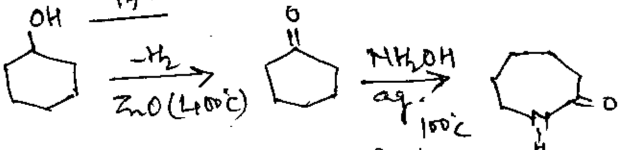
12C

Hexamethylene diamine

$$COOH-(CH_2)_4COOH \xrightarrow{NH_3} NC-(CH_2)_4CN \xrightarrow{H_2} \text{Hexamethylene diamine}$$

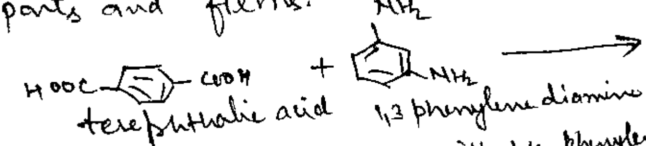
Adipic Acid Adiponitrile

Caprolactum:



Beckmann rearrangent

⇒ Nylons are strong and tough materials. Their mechanical properties depend on the degree of crystallinity. Because of good mechanical property & adoptability to both moulding and extrusion, nylons are often used for gears, bearing, & electrical mounting. They perform quietly and need little or no lubrication. Nylon resins are used as filaments, bristles, wire insulation, appliance parts and films.



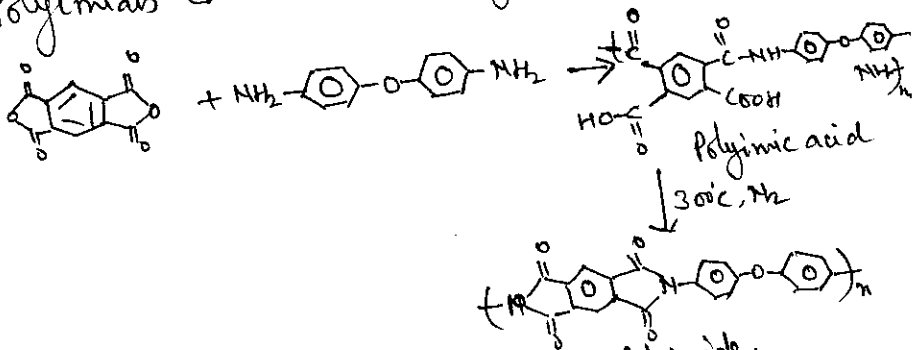
Kevlar polymer
High m.p.
390°c – 380°c.

or with 1,4-phenylene diamine (mp. 425°c).

or with

gives extraordinary strong materials (tensile strength / density) of the fibre is higher than that of any other continuous material fibrous.

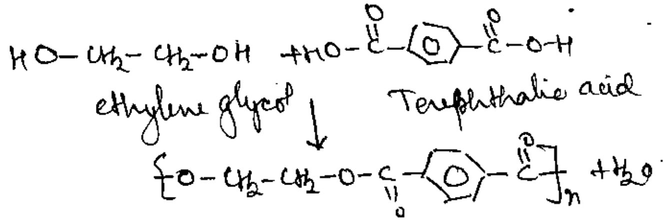
⇒ Polyimides can withstand high temperature (~428°C)



Polyimide.

Used in coating in supersonic aircraft materials.

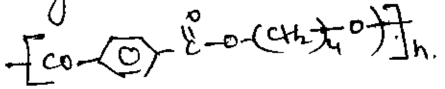
Polyesters:



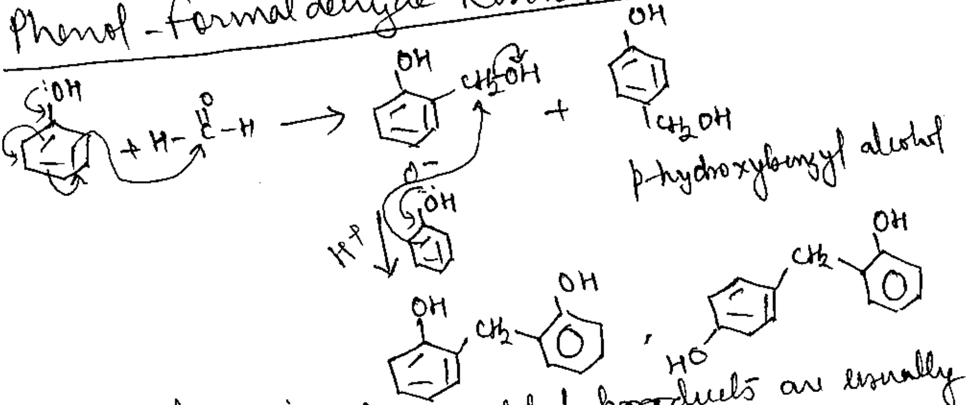
Terylene (PET)

However in the place of terephthalic acid, its dimethyl ester (dimethyl terephthalate, DMT) is used as the former is difficult to purify. This polycondensation is trans esterification and CH_3OH is the byproduct. PET mp = 265°c. resistant to heat, moisture and chemicals. good mechanical strength upto 175°c. Used in fiber (terycot is blend of terylene & cotton).

(PBT) Poly (butylene terephthalate)



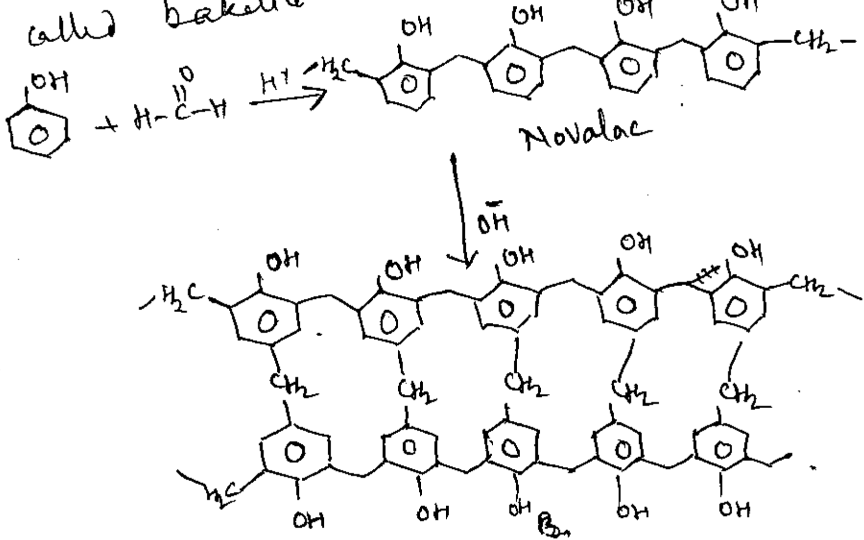
Phenol-formaldehyde Resin:



The phenolic resins for moulded products are usually prepared by a two stage process.

First stage is condensation of formaldehyde with slight excess of phenol in the presence of ~~slight~~ acid catalyst. This reaction produces linear thermoplastic polymer which is known as Novalac. Novalac contains no methylol groups.

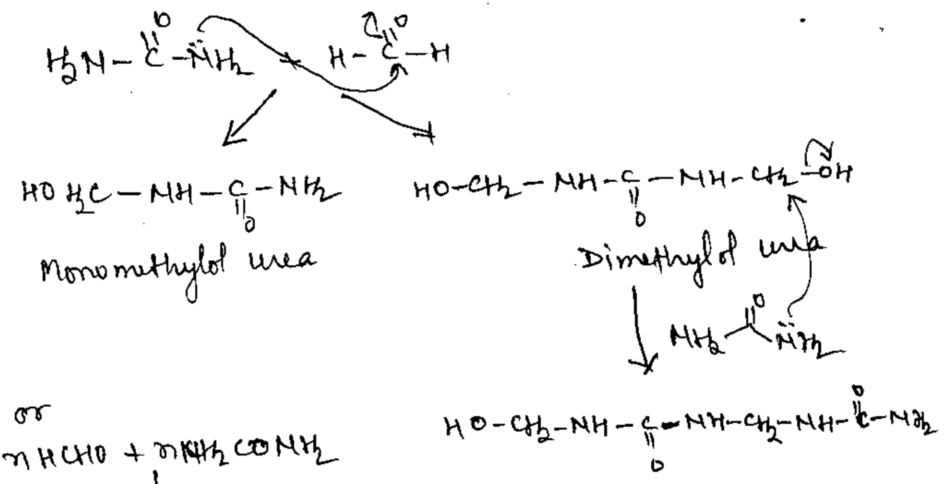
Second Stage : Reaction b/w Novalac and more formaldehyde in the presence of basic catalyst results in hard infusible thermoset resin called bakelite.



Novalac

Backelite.

Urea formaldehyde Resin: Urea reacts with formaldehyde under slightly alkaline or neutral conditions leading give resin.



$$H_2N-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 + H-\overset{O}{\overset{\|}{C}}-H$$

$$HOH_2C-NH-\underset{O}{\underset{\|}{C}}-NH_2$$

Monomethylol urea

$$HO-CH_2-NH-\underset{O}{\underset{\|}{C}}-NH-CH_2-\ddot{O}H$$

Dimethylol urea

$$\downarrow NH_2-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$$

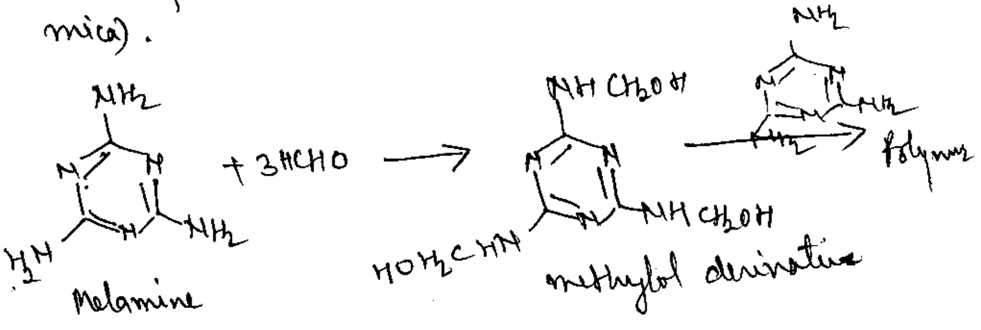
$$HO-CH_2-NH-\underset{O}{\underset{\|}{C}}-NH-CH_2-NH-\overset{O}{\overset{\|}{C}}-NH_2$$

or

$$n\,HCHO + n\,NH_2CONH_2 \xrightarrow{} H\left[NH-CO-NH-CH_2\right]_n OH$$

Melamine-formaldehyde Resin:-

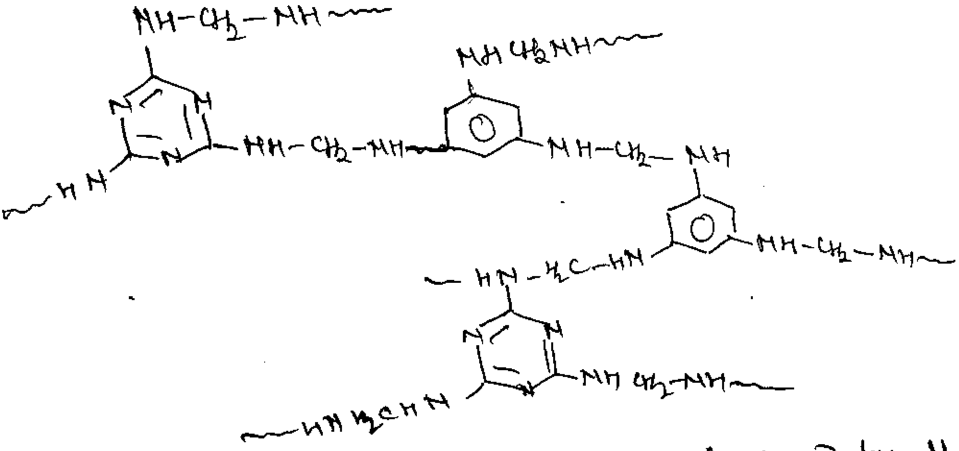
Melamine and formaldehyde react to give hexamethy-lol-melamine, which on heating in presence of acids gives cross linked polymer called melamine resin. It is resistant to heat and moisture and used in making dinnerware and decorative tablotops. (formica).



Melamine

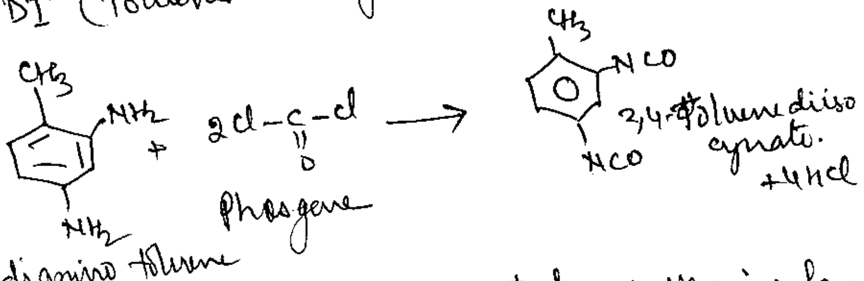
methylol derivative

methylol derivative is further condensed with melamine to give a ~~melamine~~ linear polymers and when it reacts with excess of formaldehyde gives ~~melamine~~ melamine-formaldehyde resin.



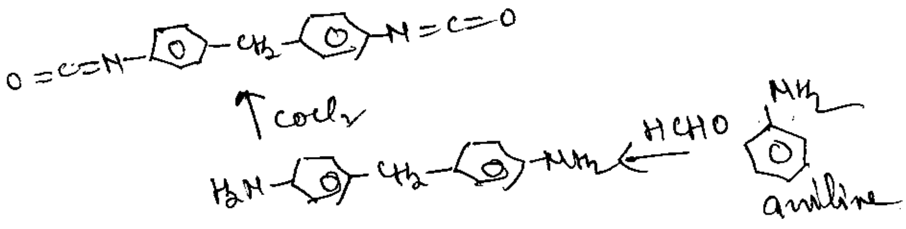
Polyurethane: (Polyisocyanate) are produced by the reaction of a diisocyanate with a compound containing atleast two active hydrogens, such as diol or diamine.

TDI (Toluene diisocyanate)

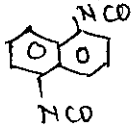


Resins can be produced in different forms varying from hard, glossy, solvent resistant coating, to abrasion and solvent resistant rubbers, fibers flexible and rigid foams.

* MDI (Diphenylmethane diisocyanate)



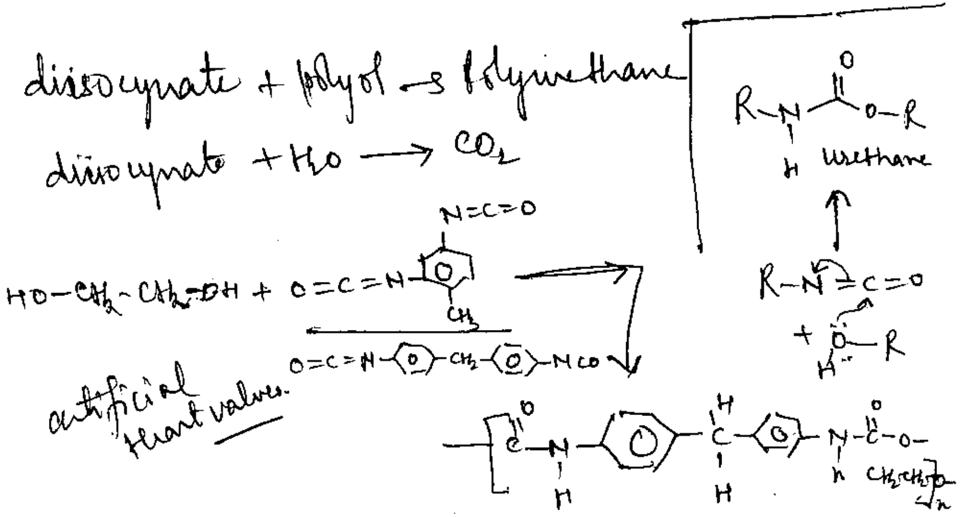
NDI (Naphthalene 1,5 - diisocyanate)



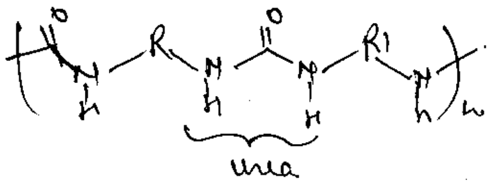
HDI (Hexamethylene diisocyanate

diisocyanate + polyol → Polyurethane

diisocyanate + H_2O → CO_2

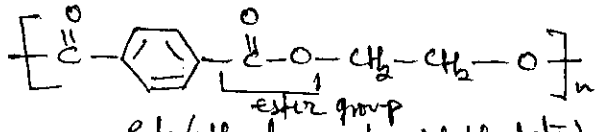


artificial heart valves.



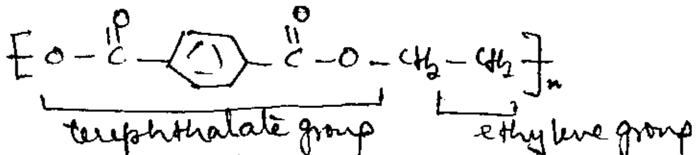
Polyurea

Polyesters:-



Poly(ethylene terephthalate)

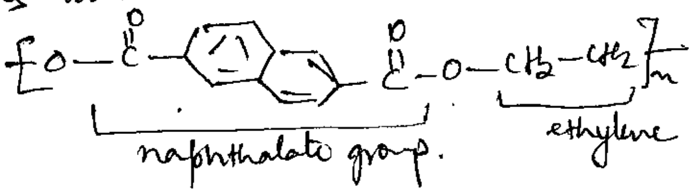
⇒ Polyesters hane have hydrocarbon backbones which contain ester linkages, hence the name.



⇒ The ester group in the polyester chain are polar, with the carbonyl oxygen atom having somewhat negative charge and the carbonyl carbon atom having a somewhat positive charge. The ⊕ve and ⊖ve charges of different ester groups are attracted to each other. This allows the esten groups of ~~nearly~~ nearby chains to line up with each other in crystal form, which is why they can form strong fibers. PET bottles. etc

⇒ The PET has too low a glass transition temperature, that is the temperature at which the PET becomes soft. Thats why hot items cannot be added into PET bottles because at high temperature PET becomes soft.

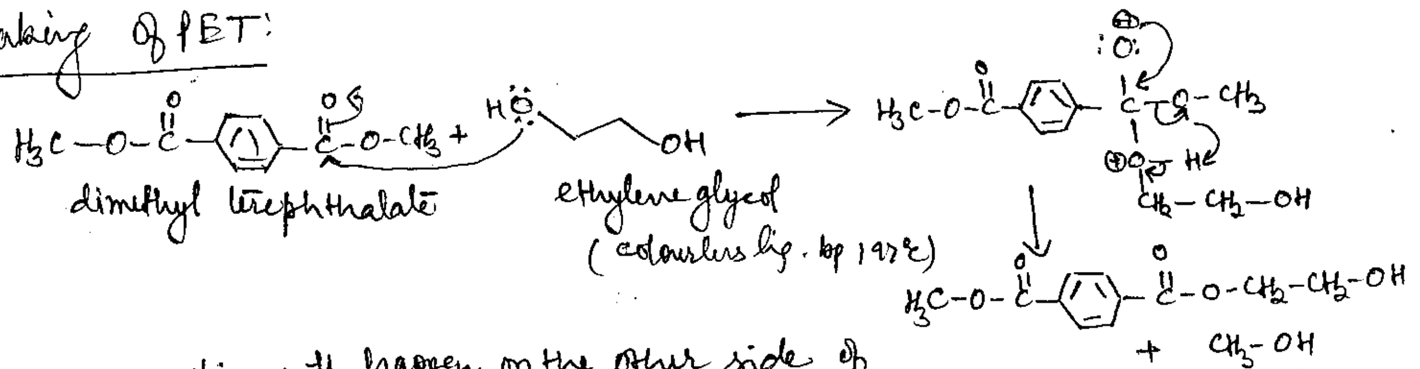
⇒ A new kind of polyester is also known which high temprature softness i.e. PEN (polyethylene naphthalate) or PEN. This can be used as a Jelly jars and returnable bottles



PEN.

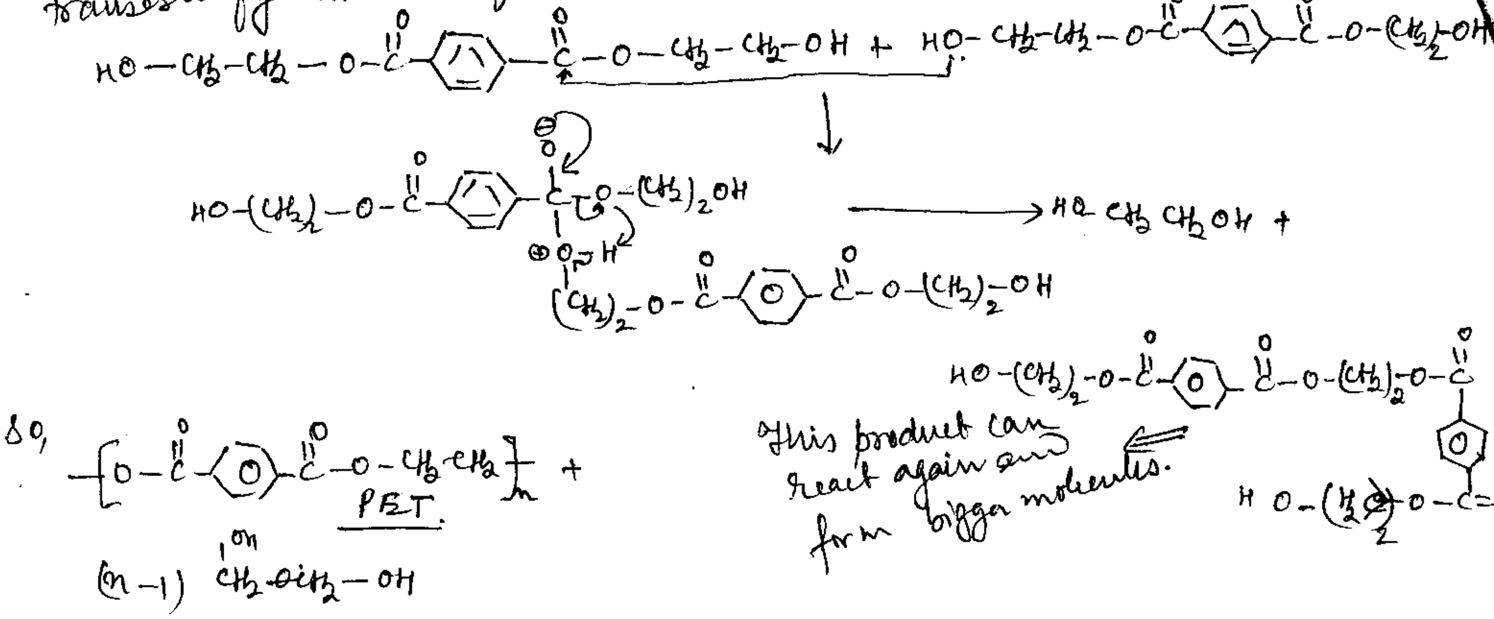
PEN has higher glass transition temperature than PET. That's the temperature at which a polymer gets soft. The glass transition temperature of PEN is high enough so that it can withstand the heat of both sterlizing bottle washing and hot strawberry jelly.

Making of PET:



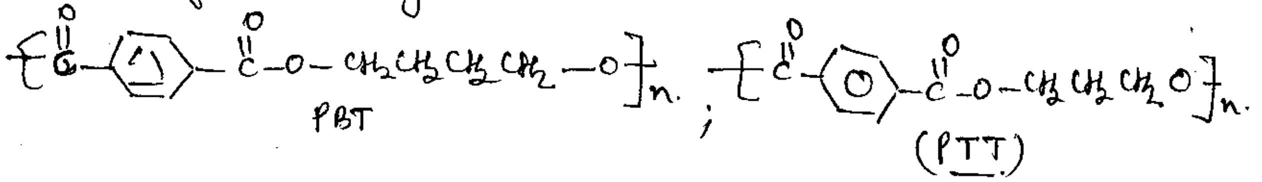
Same reaction will happen on the other side of the terephthalate, and this give us bis-(2-hydroxyethyl) terephthalate

It does some more reacting. But these reactions are easy to follow be
they're all transesterifications similar to the one you just saw. So, it c
transesterify with itself, as the picture beneath below



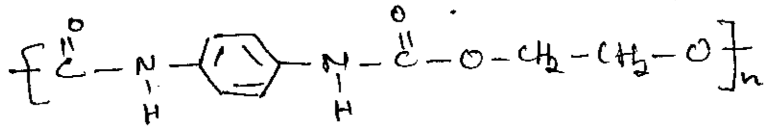
This product can react again and form bigger molecules.

⇒ There are two more polyesters on the market that related to PET. Polybutylene terephthalate) (PBT) and poly(trimethylene terephthalate). They are used for the same type of things as PET.



Properties:- PET is a colourless rigid substances, Because of its structure regularit the polymer readily crystallised and the physical properties of the bulk material are greatly affected by extent of crystallinity, which in turn is largely determined. The filaments are thus rapidly cooled and are largely amorphous and are weak. The filaments are then drawn at a temperature above the glass transition temperature (80°C) whereby molecular orientation and crystallinity and induced. Finally the filaments are heated at about 200°C under tension to give a dimensionally stable material of maximum crystallinity.

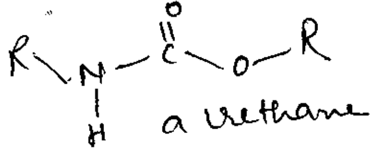
Poly(urethanes):



Poly(urethanes) are the most well known polymers used to make foams. If you ar sitting on a padded chair right now, the cushion is more than likely ma of polyurethane foam. Polyurethanes are more than foam. Much more than foam!

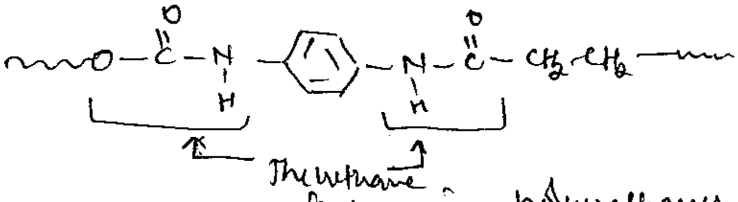
Polyurethanes are the single most versatile family of polymers there is. Polyurethanes can be elastomers, and they can be paints. They can be fibers, and they can be adhesives. They just pop up everywhere. A Wonderfully bizarre polyurethane is spandex.

Of course, polyurethanes are called polyurethanes because in their backbone they have a urethane linkage.



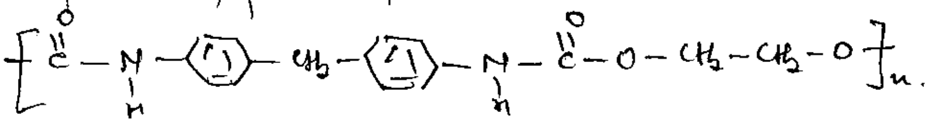
$R-NH-\overset{O}{\overset{\|}{C}}-O-R$

a urethane



The urethane linkage in a polyurethanes.

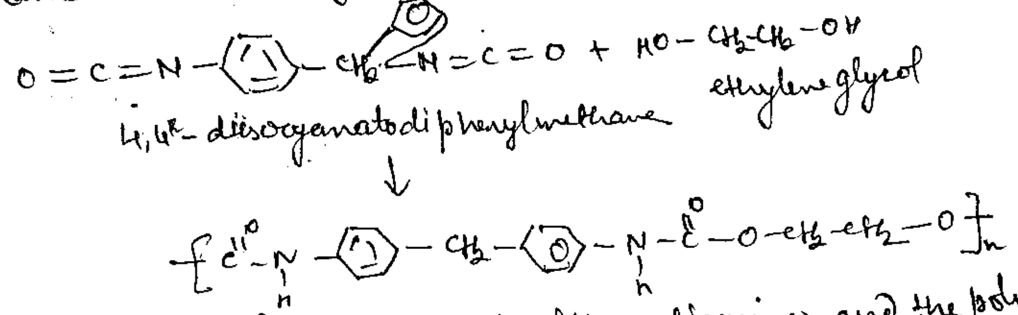
This is the simplest polyurethane, but polyurethane can be any polymer containg the urethane linkage in its backbone chain. More sophisticated polyurethanes are possible, for example:



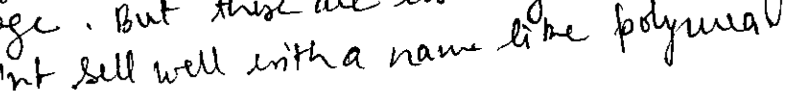
a more sophisticated polyurethane.

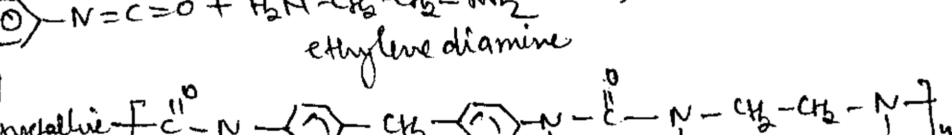
Preparation:-

Polyurethanes are made by reacting diisocyanates with dialcohols. To find ou how,



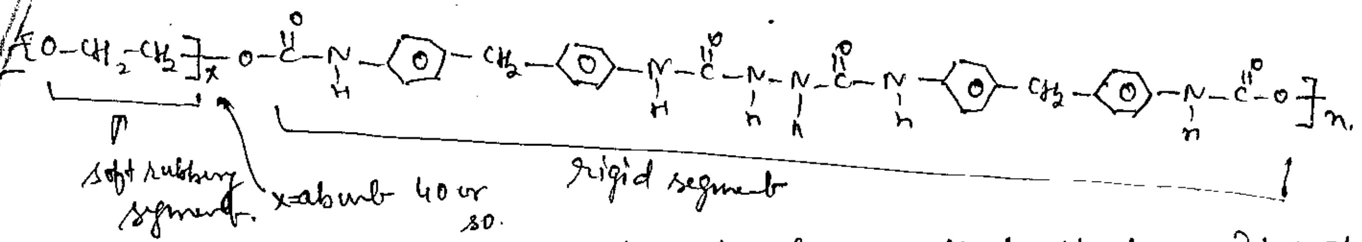
Sometimes, the dialcohol is replaced with a diamine, and the polymer we get i a polyurea, because it contains a urea linkage rather than a urethane linkage. But these are usually called polyurethanes, because they probab wouldn't sell well with a name like polyurea.





a polyurea.

Polyurethanes can hydrogen bond very well and thus can be very crystalline. for this Reason they are often used to make [illegible] with soft rubbery polymers. they are thermoplastic elastomers.



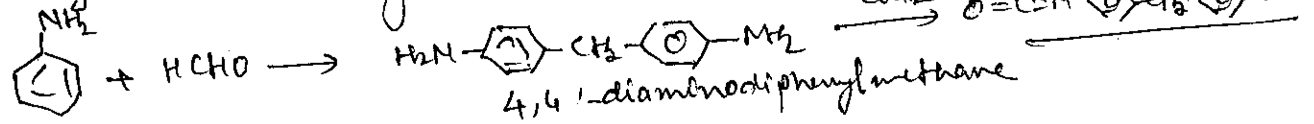
spandex has complicated structure, with both urea and urethane linkage in the backbone chain.

⇒ One unusual polyurethane thermoplastic elastomer is spandex, which DuPont sells under the trade name Lycra. It has both urea and urethane linkages in its backbone. What gives spandex its special properties is the fact that it has hard ~~structures~~ and soft blocks in its repeat unit. The short polymeric chain of polyglycol, usually about forty or so repeat units long, is soft and rubbery, the rest of the repeat unit, you know, the stretch with the urethane linkages, the urea linkages, and aromatic groups, is extremely rigid. This section is stiff enough that the rigid ~~seconds~~ sections from different chains clump together and align to form fibers. Of course, they are unusual fibers, as the fibrous domains formed by the stiff blocks are linked together by the rubbery soft sections. The result is a fiber that acts like an elastomer. This allows us to make fabric that stretches for exercise clothing and the like.

Generation of Isocyanates:

$$R'-NH_2 + COCl_2 \longrightarrow R-N=C=O + 2HCl$$

diphenylmethane diisocyanate:



$$H_2N(CH_2)_6NH_2 \xrightarrow{COCl_2} OCN-(CH_2)_6-NCO$$

$$R-N=C=O + R'OH \longrightarrow \underset{\text{a urethane}}{RNHCOOR'}$$

$$R-N=C=O + R'NH_2 \longrightarrow \underset{\text{a urea.}}{RNHCONHR'}$$

$$R-N=C=O + R'COOH \longrightarrow \underset{\text{a anhydride}}{[RNHCOOCOR']} \xrightarrow{-CO_2} \underset{\text{amide.}}{RNHCOR'}$$

$$R-N=C=O + H_2O \longrightarrow \underset{\text{carbamic acid}}{[R-NH-COOH]} \xrightarrow{-CO_2} RNH_2$$

$$R-N=C=O + R'NHCO-OR'' \longrightarrow \underset{\text{allophanate.}}{R-NH-CO-\overset{R'}{N}-CO-OR''}$$

with urea, phenols and amides also reacts.

$$R-N=C=O + R'NHCONHR'' \longrightarrow \underset{\text{biuret}}{RNH-CO-\overset{R'}{N}-\overset{O}{\overset{\|}{C}}-NHR''}$$

$$R-N=C=O + R'-NH-COR'' \longrightarrow \underset{\text{acylurea.}}{R-NH-CO-\underset{R'}{N}-COR''}$$

Properties of Polyester and Polyether foams:

Rigid polyurethane foams are closed-cell structures which are usu produced with a density of about 2 lb/ft³. Since the major interest in rigid foams has been the thermal ~~conductivity~~ insulation, the thermal conductivity of the foams is a physical property of some importance.

→ Solid polyurethane elastomers (as distinct from flexible foams) may be divided into three categories, namely

* cast, a millable and thermoplastic elastomers.

Other applications of Polyurethanes:

Surface coating

→ Air curing systems
→ Moisture curing system
→ Heat curing system.

Adhesives:

Several polyurethane type products are used as ~~ahe~~ adhesives. These general categories may be distinguished namely isocynate-polyol systems, soluble elastomers and polyisocynates.

→ The adhesive properties of the foregoing materials may be attributed to the polar nature of the polymers involved. Further, the isocynates present in the compositions may react with any active hydrogen present in the substrate or with the films of water which are often present on the surface of such materials as ceramics, glass and metals.