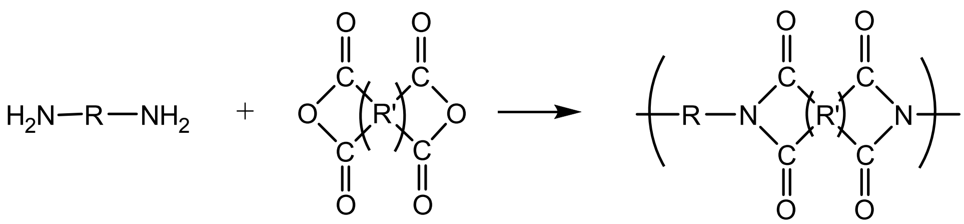
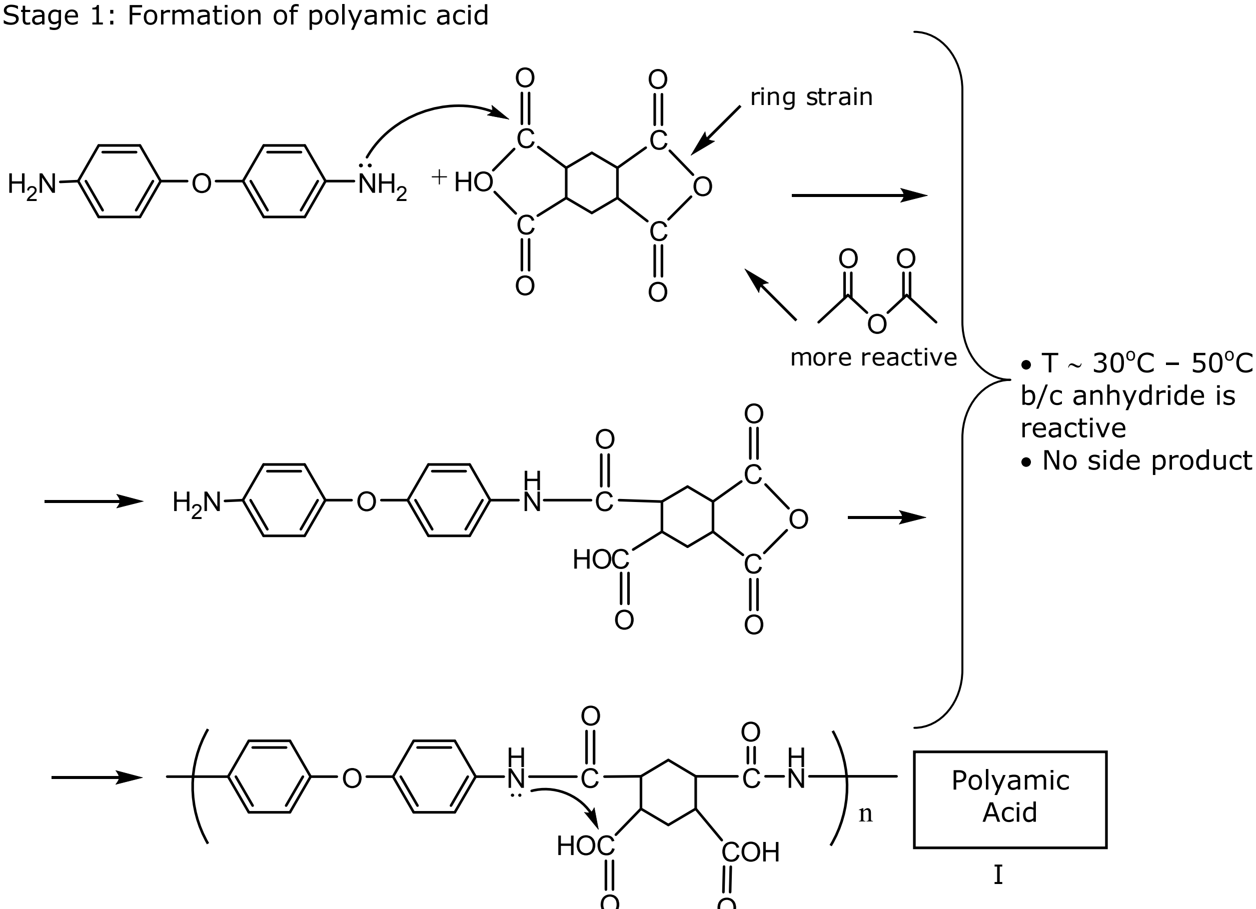
Lecture 7: Crosslinking and Branching, Network Formation and Gelation, Carothers Equation, Pn Approach

Polyimides



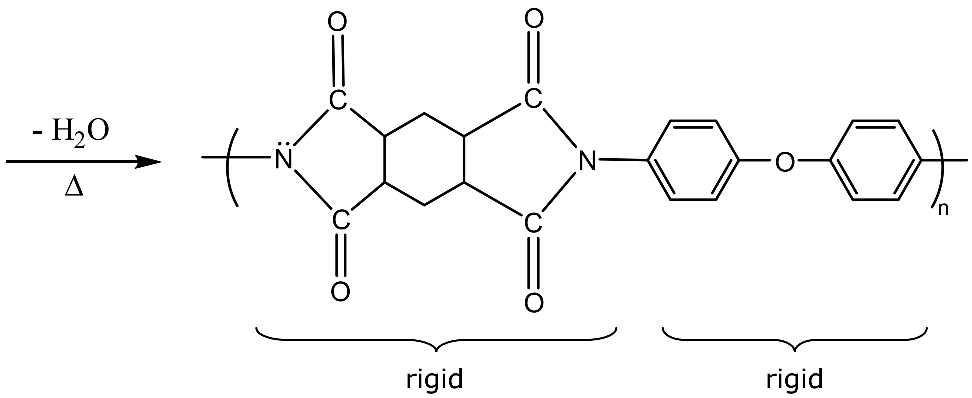
Staged formation of Polyimides

Stage 1: Formation of polyamic acid



• 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

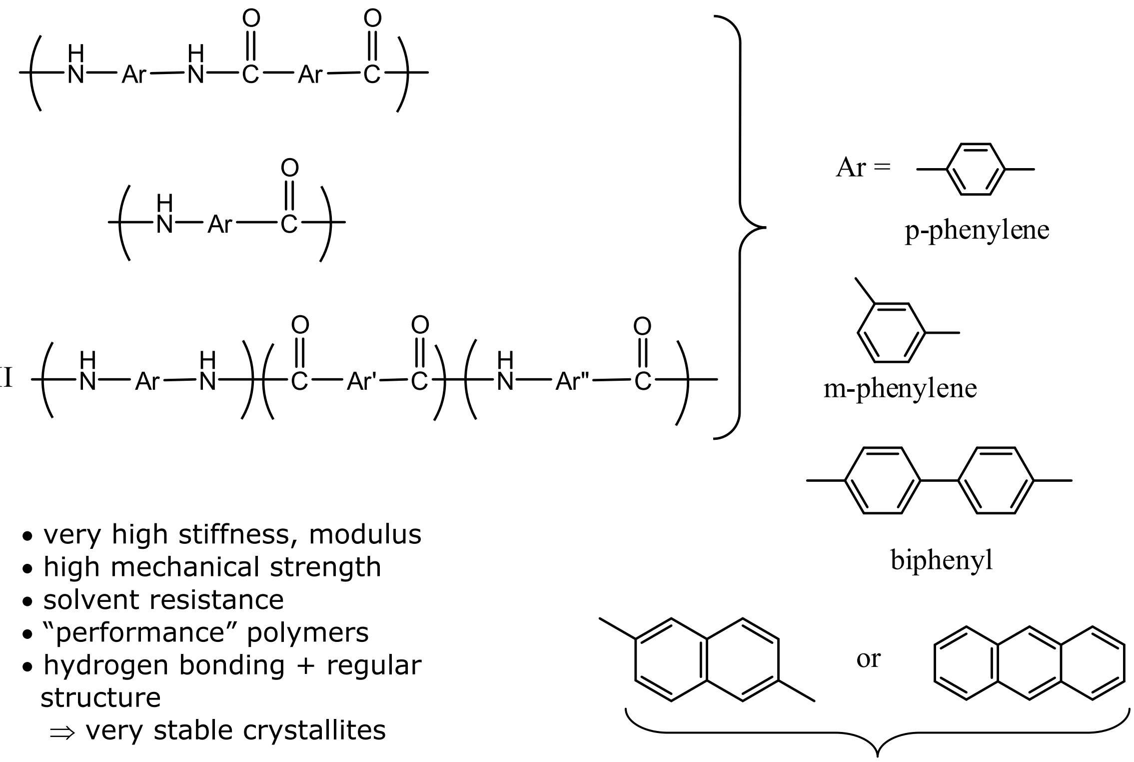
I 

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

Kapton®
Pyralin®
Vespel®

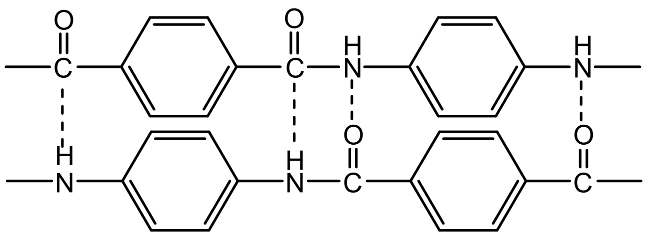
Aromatic Polyamides

"Wholly" aromatic

III 

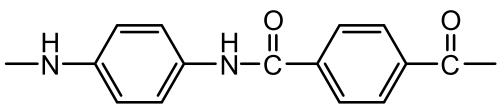
- very high stiffness, modulus
- high mechanical strength
- solvent resistance
- "performance" polymers
- hydrogen bonding + regular structure
  ⇒ very stable crystallites

"aramids"

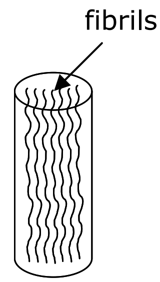


H-bonding
β sheets
⇒ semicrystalline
very high melting points
rigid backbones
⇒ liquid crystal phases in soln

Example:



Kevlar® (Dupont)



Compare to: high tensile steel

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

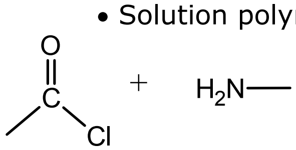
How to react? (making aramids)

- 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 } Not possible
  Remain phase separated from H_2O

- Solution polymerization:



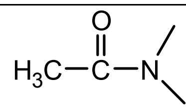
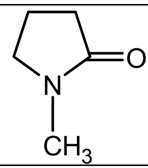
reactive groups

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

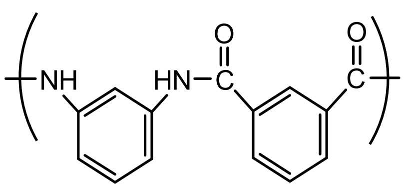
Often add LiCl or other Li salts to solvent

⇒ 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®: $T_m = 570^oC$
$T_g = ?$
$T_{deg} = 550^oC$ in N_2
$E_o = 6000 - 8000\ kg/mm^2$

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



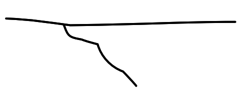
$T_m = 435^oC$
$T_g = 272^oC$
$E_o = 2000\ kg/mm^2$

Stretches out more

Branching and Network Formation

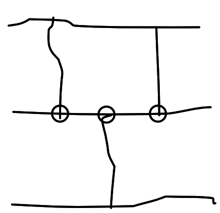
So far: difunctional monomers: f = 2

When monomer functionality f ≥ 3 ⇒



can form branches

\+



networks

- crosslinks are individual junctions
- networks are infinitely large

Examples:

1. a—b + a┬a (with a third a) → branches

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

3. a—a + b—b + b_f $\rightarrow$ branches, then crosslinks

4. a_f + b_f $\rightarrow$ branches, crosslinked networks