Polyimides

\[
H_2N-R-NH_2 + O(C\{R\}C)O \rightarrow \left(\begin{array}{c}
R-N(\{\{R\}\})N \\
\end{array}\right)
\]

Staged formation of Polyimides

Stage 1: Formation of polyamic acid

- \( T \sim 30^\circ C - 50^\circ C \)
- b/c anhydride is more reactive
- No side product

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

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Stage 2: Cyclization
- reaction takes place in solid state or near solid state
- \( H_2O \) removal

\[
\begin{align*}
I \xrightarrow{-H_2O, \Delta} & \quad \text{rigid} \quad \text{rigid} \\
\end{align*}
\]

\( T > 150^\circ C \)
- Low P (vacuum)
- Final product is intractable

**Kapton®**
- Pyralin®
- Vespel®

**Aromatic Polyamides**
- "Wholly" aromatic

\[
\begin{align*}
\text{Ar} &= & \quad \text{p-phenylene} \\
\text{m-phenylene} & \quad \text{biphenyl} \\
\text{or} & \quad \text{"aramids"} \\
\end{align*}
\]
- very high stiffness, modulus
- high mechanical strength
- solvent resistance
- "performance" polymers
- hydrogen bonding + regular structure
  \( \Rightarrow \) very stable crystallites
Example:

\[
\begin{align*}
\text{Kevlar® (Dupont)} & \\
\end{align*}
\]

Compare to: high tensile steel

<table>
<thead>
<tr>
<th></th>
<th>Ultimate TS</th>
<th>E at break</th>
<th>Energy at break</th>
<th>Weakness: Low compressive strength. (analogy: broom straws)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar 49</td>
<td>3.6 GPa</td>
<td>2.7%</td>
<td>25 MJ/m³</td>
<td></td>
</tr>
<tr>
<td>High tensile steel</td>
<td>1.5 GPa</td>
<td>0.8%</td>
<td>6 MJ/m³</td>
<td></td>
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</tbody>
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How to react? (making aramids)

- Bulk melt: T_m way too high!
- Interfacial polymerization: possible

\[
\begin{align*}
\text{Get product as precipitate at interface} \\
\text{Works for partially aromatic polyamides} \\
\text{Solvent: solvate low + mod MW’s} \\
\text{Remain phase separated from H}_2\text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{Not possible} \\
\end{align*}
\]

- Solution polymerization:

\[
\begin{align*}
\text{highly reactive – allows dilution} \\
\end{align*}
\]

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
- \( \Rightarrow \) neutralize HCl
Often add LiCl or other Li salts to solvent ⇒ aid in H-bond break-up

<table>
<thead>
<tr>
<th>Common Solvents:</th>
<th>CHCl₃</th>
<th>Less polar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH₂Cl₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃CN</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cl-CH₂-Br</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>DMAC</th>
<th>![DMAC structure]</th>
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<table>
<thead>
<tr>
<th>NMP</th>
<th>![NMP structure]</th>
</tr>
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<table>
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<tr>
<th>DMSO</th>
<th>More polar</th>
</tr>
</thead>
</table>

Kevlar®:
- $T_m = 570^\circ$C
- $T_g = ?$
- $T_{deg} = 550^\circ$C in N₂
- $E_o = 6000 - 8000$ kg/mm²

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

$$\left(\text{NH} \quad \text{HN} \quad \text{C} \quad \text{O} \quad \text{O}\right)$$
- $T_m = 435^\circ$C
- $T_g = 272^\circ$C
- $E_o = 2000$ kg/mm²
- Stretches out more

Branching and Network Formation
- So far: difunctional monomers: $f = 2$
- When monomer functionality $f \geq 3 \Rightarrow$
- can form branches
- networks
  - crosslinks are individual junctions
  - networks are infinitely large

Examples:
1. $a-b + a \quad a \quad \rightarrow \quad \text{branches}$
2. $a-b + a + b-b \quad \rightarrow \quad \text{branches, then crosslinks}$

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
3. \(a-a + b-b + b_f \rightarrow \) branches, then crosslinks

4. \(a_f + b_f \rightarrow \) branches, crosslinked networks