Acid catalyst [HA]

\[
[a]_0 k t = \frac{1}{1 - \pi} - 1 = \overline{p_n} - 1
\]

\(\overline{p_n}\) linear \(\uparrow\) with time

For self-catalyzed case:

\[
\frac{1}{(1 - \pi)^2} = \overline{p_n}^2 = 2[M_H^+ k t + 1]
\]

\(\Rightarrow \overline{p_n} \uparrow\) with \(\sqrt{t}\)

Basic rate expression for acid catalyst:

\[
R_p = k_j K_{12}[HA][COOH][OH]
\]

\(R_p \downarrow\) decrease

Self-catalyzed:

\[
R_p = k_j K_{12,COOH}[COOH]^2[OH]
\]

Slower reaction

Gets extremely slow at the end of the reaction

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Product</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{-OH} + \text{--COOH} \rightarrow \text{--C--O})</td>
<td>Polyester ((k \sim 1))</td>
<td></td>
</tr>
<tr>
<td>(\text{-NH}_2 + \text{--COOH} \rightarrow \text{--C--N})</td>
<td>Polyamide ((k \sim 10))</td>
<td></td>
</tr>
</tbody>
</table>

Typical process conditions for near equilibrium step growth:

- **High T**
  - to increase \(k\) (\(k \uparrow\) with \(T \uparrow\))
  - to aid in byproduct removal
- **Bulk or mass polymerization** (no solvent)
  - if the reactants are miscible (forming 1 uniform, mixed phase), get highest concentrations possible
  - no need for separations step (remove solvent)
  - viscosity \(\eta\) low enough to process until high MW
  - product can be directly processed into final form
- **Solvents**
  - may be needed to solubilize two monomers (reactants)
- could allow higher T to be approached without scorching polymer
- carrier (dilutant) for viscous media (exp for high MW)

**Interchange Reactions in Near-Equilibrium Polymerization**

\((k \sim 1-10)\)

Ex: polyamide (but same thing happens in polyester)

```
\begin{align*}
\text{Shuffling of chain segments} & \quad \text{Illustration of shuffling of chain segments (redrawn below):} \\
\text{Continued on next page}
\end{align*}
```
• If no removal of byproduct (H$_2$O)
  $\Rightarrow$ No net change in MW
• Only if H$_2$O is removed during interchange will MW change (increase)
  $\Rightarrow$ Can be used to increase MW in the final form of a product
**Real Industrial Processes**

| Diacid + Diol → low MW polymers | Crosslinked networks | Less need for high $\pi$ |

**Making polyethylene terephthalate (PET) (polyester)**

Trade names: Mylar®, Dacron®, Terylene®

\[
\begin{align*}
\text{O} & \quad \text{O} \\
\text{C} & \quad \text{C} \quad \text{OCH}_2\text{CH}_2 \quad \text{O} \\
\end{align*}
\]

$n$

$T_m = 270^\circ\text{C}$

<table>
<thead>
<tr>
<th>High mechanical strength (from aromatic group rigidity)</th>
<th>Ideal material for carpet, clothing, photographic substrates, Boil-in-Bag meals, PET Coke bottles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tough (flexibility in backbone)</td>
<td>Partially crystalline (adds to toughness)</td>
</tr>
<tr>
<td>$\Rightarrow$ $9.5$ billion/year</td>
<td></td>
</tr>
</tbody>
</table>

**2-Step Process**

1. dimethyl terephthalate

\[
\begin{align*}
\text{H}_3\text{CO}_2\text{C} & \quad \text{COCH}_3 \\
\end{align*}
\]

easy to purify, cheap

\[
\begin{align*}
\text{HO} & \quad \text{C} \quad \text{C} \quad \text{OH} \\
\end{align*}
\]

ethylene glycol (EG)

\[
\begin{align*}
\text{HO} & \quad \text{CH}_2\text{CH}_2 \quad \text{O} \\
\end{align*}
\]

Methanol (collect as it is dripped off)
T \sim 150 – 210 \, ^\circ \text{C} \\
P \sim 1 \, \text{atm} \\
Done in “solvent” of excess ethylene glycol (increase rate of forward rxn) 

Detailed mechanism for above reaction:

\[ \begin{align*}
\text{H}_3\text{COCOCH}_3 + \text{HO-CH}_2\text{CH}_2\text{OH} & \rightleftharpoons \text{H}_3\text{COCOCOCH}_3 \\
& \quad \text{HO-CH}_2\text{CH}_2\text{OH} \quad \text{H}_3\text{COCOCH}_3 \\
& \quad \text{HO-CH}_2\text{CH}_2\text{OH} \\
\text{H}_3\text{COCOCOCH}_3 + \text{HO-CH}_3 & \rightarrow \text{HOCH}_2\text{CO-OCOCOCH}_3 \quad \text{repeat}
\end{align*} \]

2. \( T = 270^\circ\text{C} - 280^\circ\text{C} \) (increase \( T \)) 
   Drip stops 
   \( P = 0.5 - 1 \) torr (create vacuum) 
   Drive off EG 

\[ \begin{align*}
n \text{HO-CH}_2\text{CH}_2\text{CO-OCOCOCH}_3 & \rightarrow \left[ \text{HOCH}_2\text{CO-OCOCOCH}_3 \right]_n \\
& \quad + (n-1) \text{HO-CH}_2\text{CH}_2\text{OH} \\
\text{Ester Interlinkage} & \quad \text{Byproduct removed by distillation column}
\end{align*} \]

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 \( \text{H}_2\text{O} \) removal
Practical Example #2: Polyester anhydrides for Biodegradable polymer systems

1. diacid + diol → oligomeric polyester

\[
\text{HO} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{O} \quad \text{R'} \quad \text{O} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{OH} \\
\text{excess}
\]

→

\[
\text{HO} \quad \text{R} \quad \text{O} \quad \text{R'} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{ OH} \\
\text{“macromer”}
\]

2. form ester macromer dianhydride

\[
\text{H}_3\text{C} \quad \text{O} \quad \text{O} \quad \text{H}_3\text{C} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{R'} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{OH} \\
\text{acetic anhydride}
\]

→

\[
\text{H}_3\text{C} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{R'} \quad \text{O} \quad \text{R} \quad \text{O} \quad \text{OH} \\
\text{acetic acid byproduct}
\]

3. melt condensation

- ester groups: relatively hydrolysable
- anhydride groups: can be even more hydrolytically susceptible
⇒ degradable polymer
⇒ alkyl esters, acids