

Lecture 4: Common Processing Approaches, Near-equilibrium vs. Far from Equilibrium, Homogeneous Solution and Bulk Polymerizations

Acid catalyst [HA]

$$[a]_b kt = \frac{1}{1-\pi} - 1 = \bar{p}_n - 1$$

\bar{p}_n linear \uparrow with time

For self-catalyzed case:

$$\frac{1}{(1-\pi)^2} = \bar{p}_n^2 = 2[M]_b^2 kt + 1$$

$$\Rightarrow \bar{p}_n \uparrow \text{ with } \sqrt{t}$$

correlates with

Basic rate expression for acid catalyst:

$$R_p = k_3 K_{12} [HA] [COOH] [OH]$$

↓ decrease

Self-catalyzed:

$$R_p = k_3 K_{12,COOH} [COOH]^2 [OH]$$

↓

Slower reaction

Gets extremely slow at the end of the reaction

$-OH + -COOH \longrightarrow \begin{array}{c} O \\ \\ -C-O- \end{array}$	Polyester (k ~ 1)
$-NH_2 + -COOH \longrightarrow \begin{array}{c} O \quad H \\ \quad \\ -C-N- \end{array}$	Polyamide (k ~ 10) In some cases k ~ 100 (hungry polymer)

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 η 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)

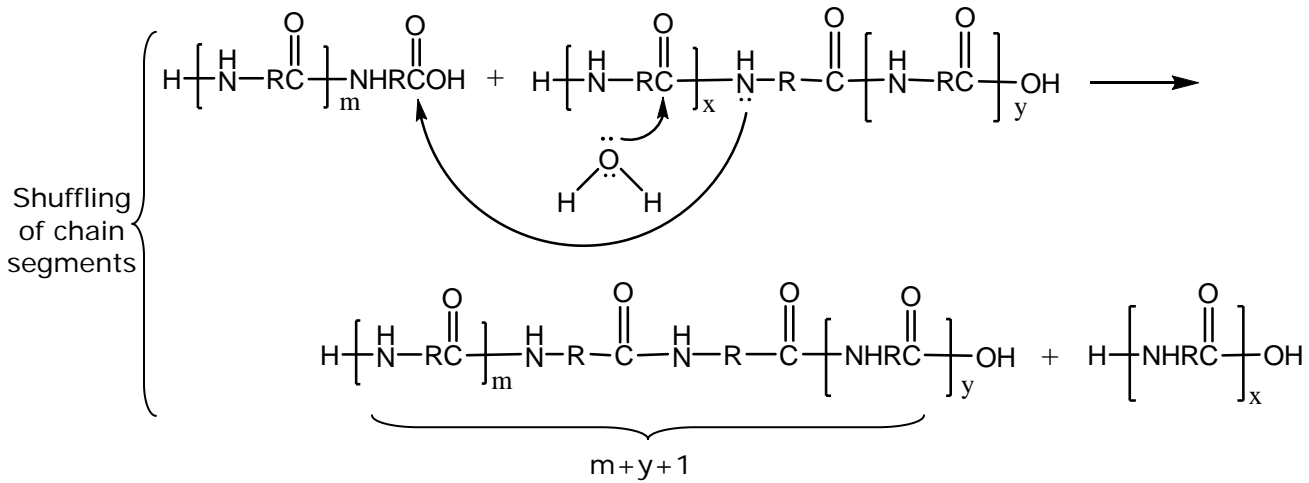
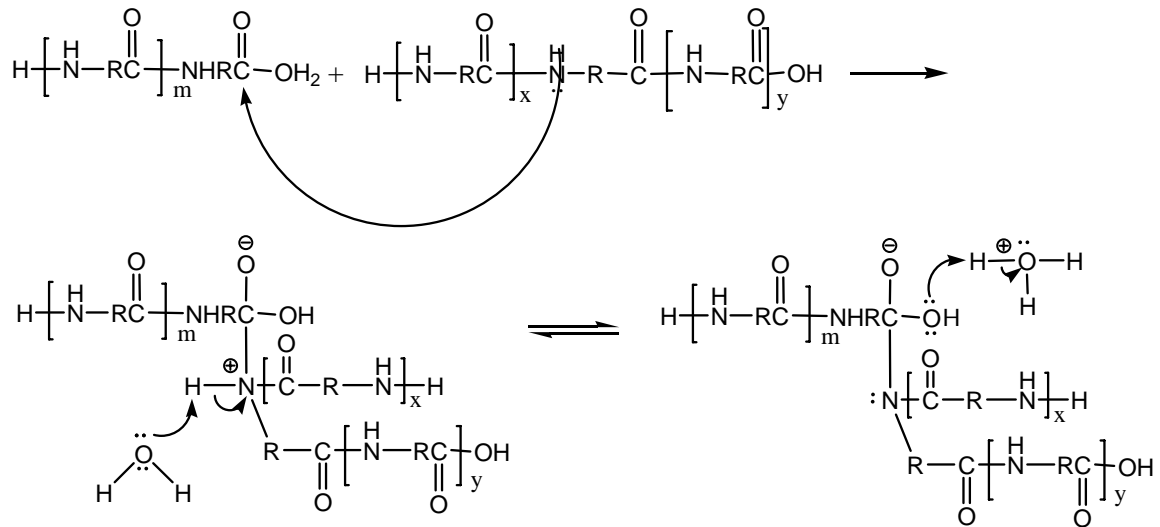


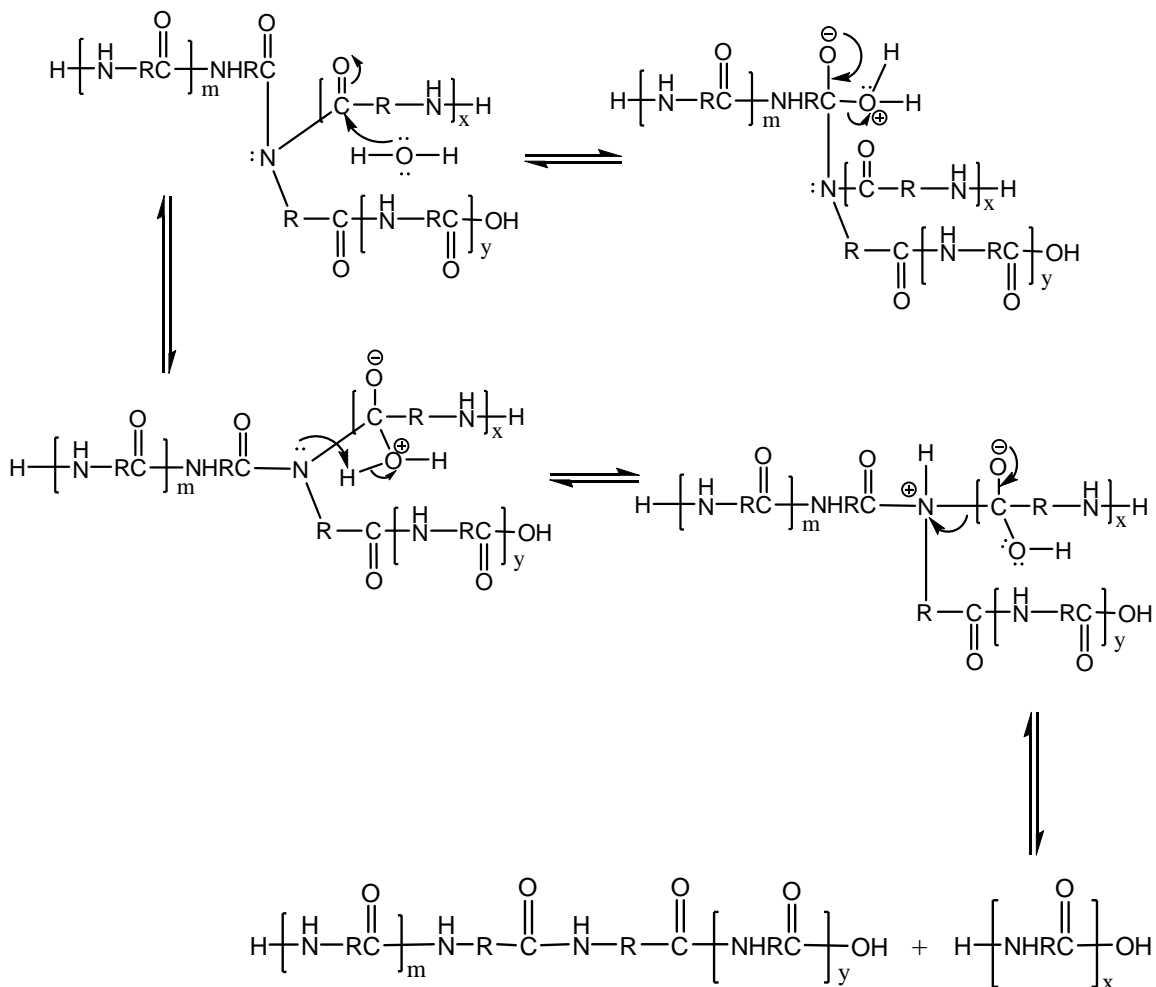
Illustration of shuffling of chain segments (redrawn below):



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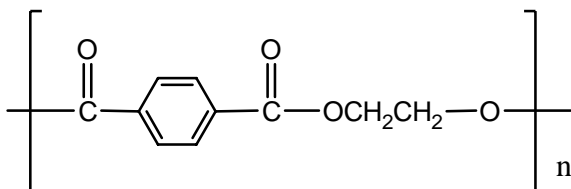
- If no removal of byproduct (H_2O)
 \Rightarrow No net change in MW
- Only if H_2O is removed during interchange will MW change (increase)
 \Rightarrow Can be used to increase MW in the final form of a product

Real Industrial Processes

Diacid + Diol → low MW polymers	}	Less need for high π
Crosslinked networks		

Making polyethylene terephthalate (PET) (polyester)

Trade names: Mylar®, Dacron®, Terylene®

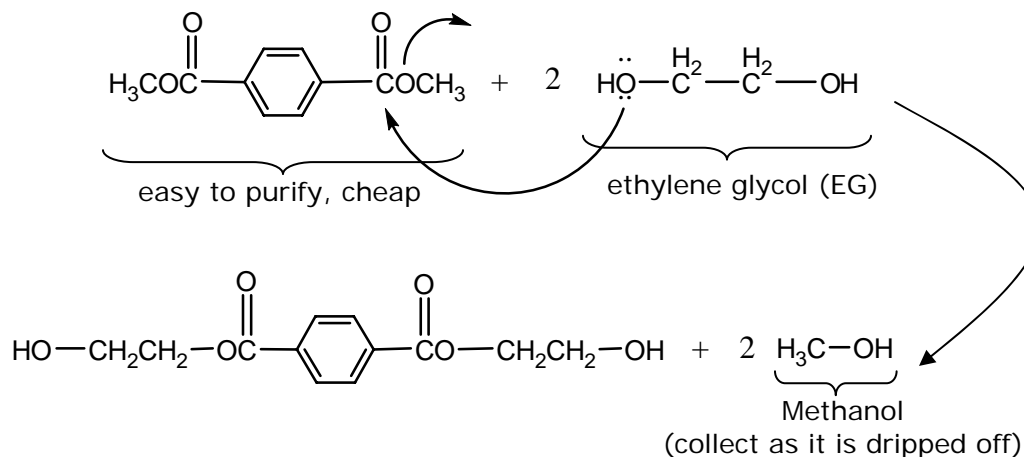


$T_m = 270^\circ\text{C}$	}	Ideal material for carpet, clothing, photographic substrates, Boil-in-Bag meals, PET Coke bottles
High mechanical strength (from aromatic group rigidity)		
Tough (flexibility in backbone)		
Partially crystalline (adds to toughness)		
⇒ \$9.5 billion/year		

$\text{HOC}-\text{C}_6\text{H}_4-\text{COH} + \text{HO}-\text{C}_2\text{H}_4-\text{OH}$	Need high MW
	Very slow
	Very expensive
	Instead...

2-Step Process

1. dimethyl terephthalate

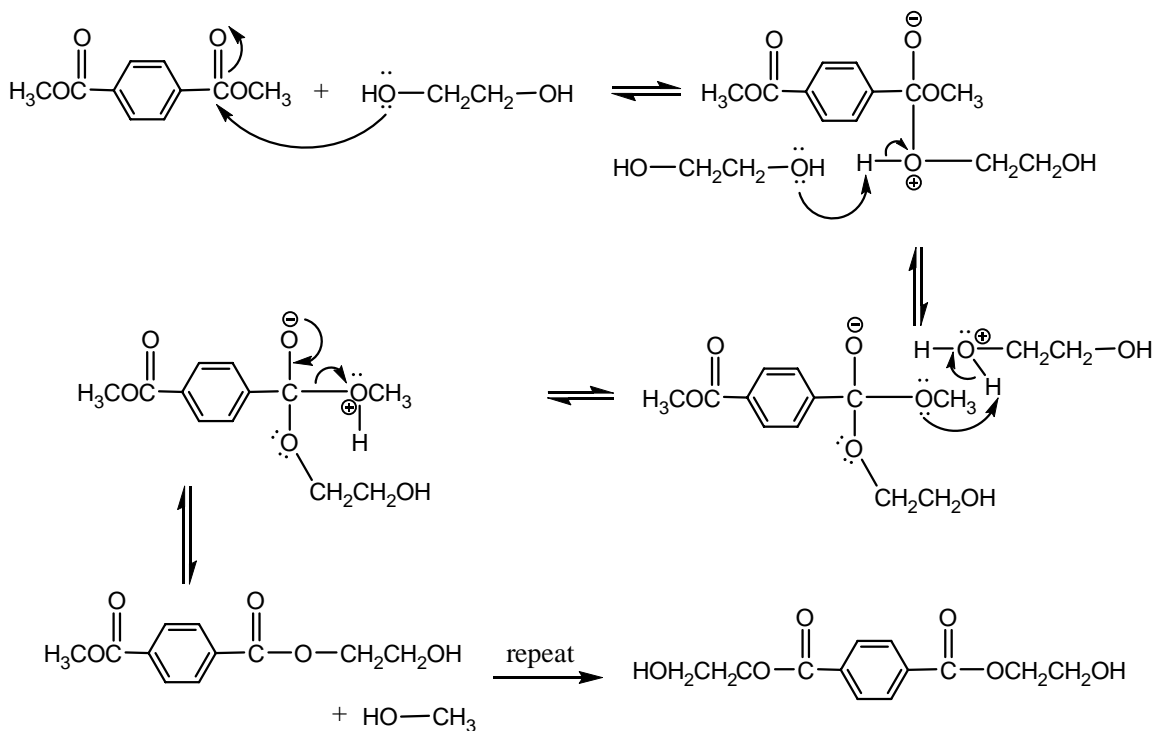


T ~ 150 – 210 °C

P ~ 1 atm

Done in "solvent" of excess ethylene glycol (increase rate of forward rxn)

Detailed mechanism for above reaction:

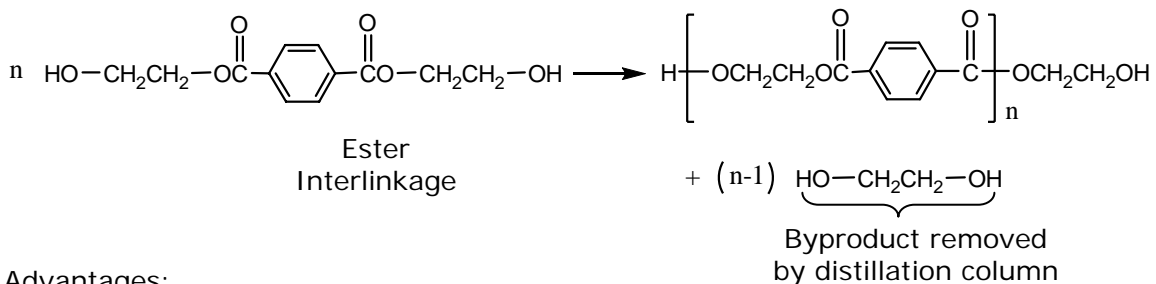


2. T = 270°C – 280°C (increase T)

Drip stops

P = 0.5 – 1 torr (create vacuum)

Drive off EG

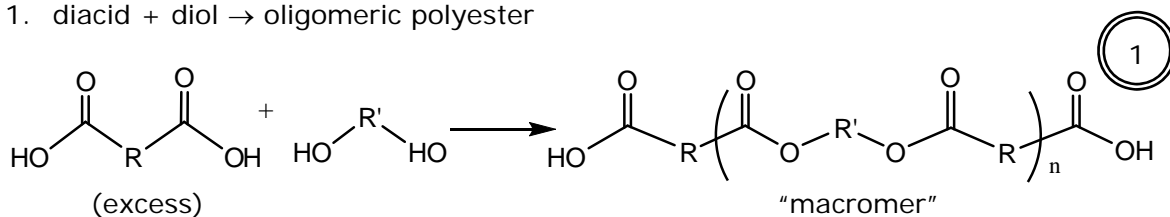


Advantages:

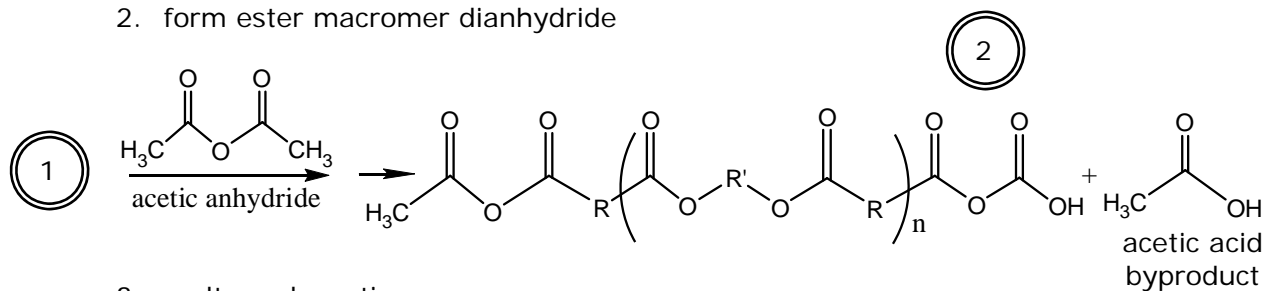
1. Stoichiometry balance not needed (only one monomer)
2. Dimethyl ester more easily purified
3. Ester interchange k (rate constant) is larger than k for acid + alcohol (better kinetics)
4. removal of ethylene glycol (EG) is cleaner than H₂O removal

Practical Example #2: Polyester anhydrides for Biodegradable polymer systems

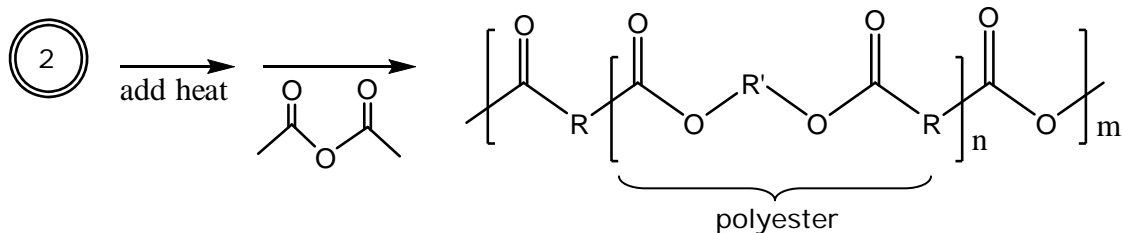
1. diacid + diol → oligomeric polyester



2. form ester macromer dianhydride



3. melt condensation



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