

## ***Biologically Relevant Polymer Presentation***

Definitions of Biologically Relevant Polymers:

- **Enzymatically degradable** – Polymer degrades through enzymatic breakdown in a biological (or ecological) environment (hydrolysis or oxidation catalyzed by enzyme).
- **Hydrolytically degradable** – Polymer undergoes hydrolytic degradation without assistance from enzyme under biologic conditions – often accelerated by pH or pH/temperature.
- **Bioresorbable or absorbable or resorbable** – Polymer breaks down into remnants that are natural products readily absorbed into the body, resulting in complete loss of original mass.
- **Biocompatible** – Polymer (*degradable or not*) does not cause a negative reaction or induce toxicity in the presence of or in contact with tissue, blood or organs

Erdmann, L and K. E. Urich. "Synthesis and Degradation Characteristics of Salicylic Acid-derived Poly(anhydride-esters)." *Biomaterials* 21, no. 19 (2000): 1941-1946.

Ikada, Y. and H. Tsuji. "Biodegradable Polyesters for Medical and Ecological Applications." *Macromolecular Rapid Communications* 21, no. 3 (2000): 117-132.

Poly  $\alpha$ -hydroxyacids are hydrolytically degradable (PLLA, PDLA, PGA, PLGA)

Poly(hydroxyalkanoates), poly(alkylene dicarboxylates) are enzymatically degradable

Polycondensation of traditional monomer yields low molecular weight oligomer

Polycondensation of cyclic monomer yields high molecular weight material

Hydrophobic, hydrophilic nature determined by R groups

For example,  $-\text{CH}_2-$  groups affect hydrophobicity and make the polymer more difficult to degrade in water

Stereochemistry affects crystallinity.

Enzymatic breakdown dependent on ability of enzyme to adsorb to the PE macromolecule at appropriate sites.

Aliphatic polyesters typically undergo enzymatic breakdown via esterases such as lipase (used in body to break down triacylglycerols to fatty acid and glycerol)

Aromatic polyesters are too hydrophobic and too rigid to allow binding by enzyme.

Lipases often ineffective on PEs with optically active center (PHB, PLLA, etc.) – PHA depolymerase effective in some cases, others require hydrolytic degradation or other enzymes.

Factors in degradation rate: hydrophobicity, stereochemistry, bulkiness of side groups, and crystallinity.

Manipulate with primary monomer structure, copolymerization.

PGA, PLLA, PDLLA, and PCL have moderate glass transition temperature.

Can create libraries of molecules:

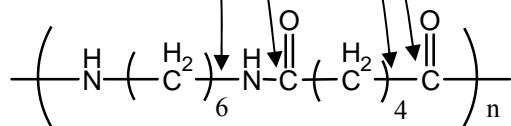
Anderson, D. G., D. M. Lynn, and R. Langer. "Semi-Automated Synthesis and Screening of a Large Library of Degradable Cationic Polymers for Gene Delivery." *Angew. Chem. Int. Ed.* 42 (2003): 3153-3158.

## Polyamides (Nylons)

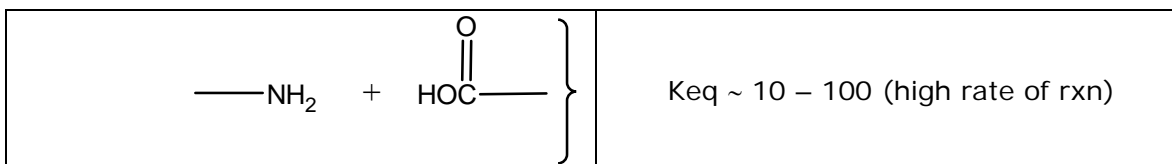
→ Coin phrase by Dupont

- Most common nylons:

Nylon 6,6:

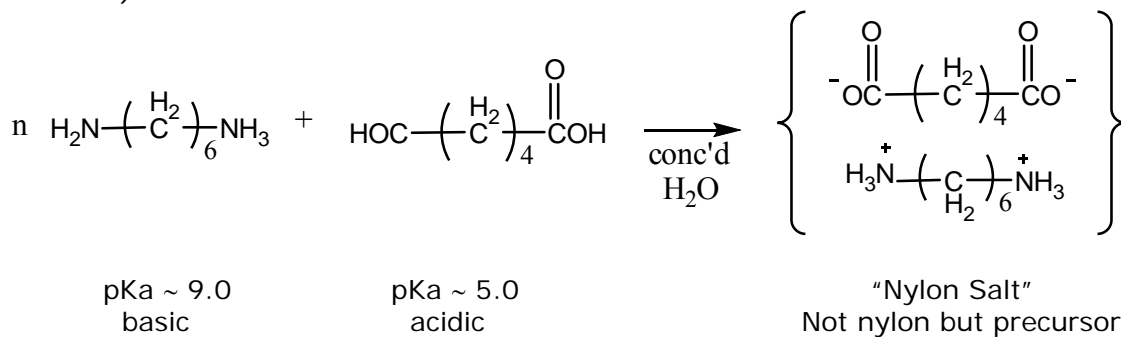


- aliphatic polyamides  
⇒ diamines + diacids



## Commercial Syntheses

1)



proton exchange  $\longrightarrow$  salt

- 50% wt concentration in H<sub>2</sub>O
- Adjust pH of solution by titrating acid/base monomer  
 $\Rightarrow$  pH = 7.0  $\rightarrow$  stoichiometry  $r = 1.0$
- If MW control desired, add monofunctional acid or amine

2) Salt solution concentration to a slurry

- a concentrated solution containing particles (concentrated suspension)

Raise T to  $\sim 210^\circ\text{C}$ , P = 250 psi (steam)

Rxn proceeds at moderate rates (water  $\rightarrow$  steam  $\rightarrow$  ...)

3) As  $\overline{p}_n \uparrow$ , go to next stage:

T  $\uparrow$  to  $275^\circ\text{C}$  (above  $T_m$  of Nylons)

P  $\downarrow$  to 1 atm  $\rightarrow$  reduces H<sub>2</sub>O

$\Rightarrow$  High MW with time/conversion

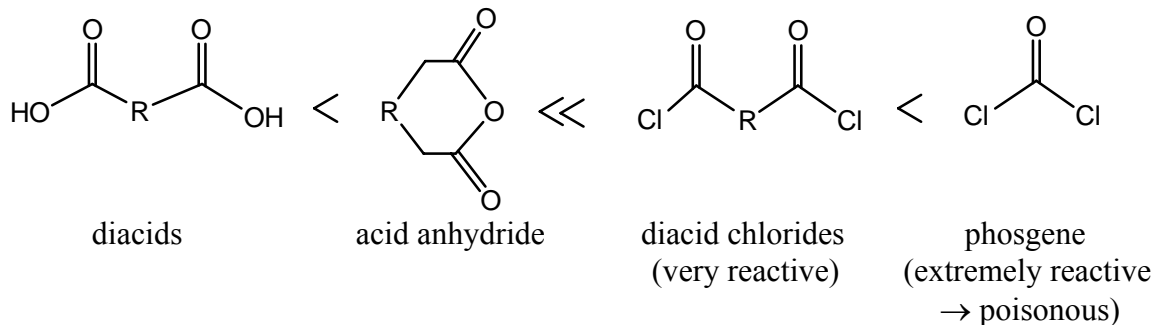
\*\* One way to make a polyamide

## Nylon6,6

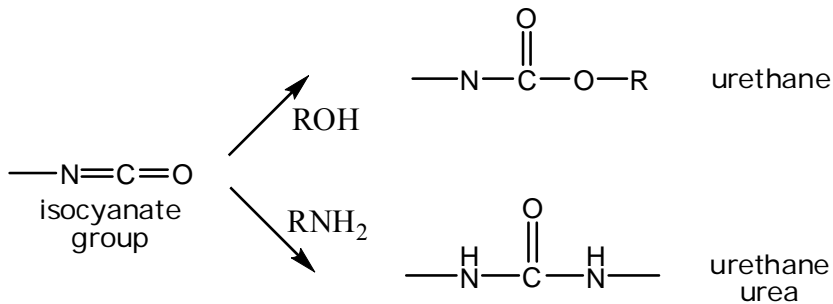
- 50% crystallinity
- form flexible fibers: crystalline structures are strong  
good H-bonding
- solvent resistance (Patagonia – clothing, carpets)

## Differences in Reactivity

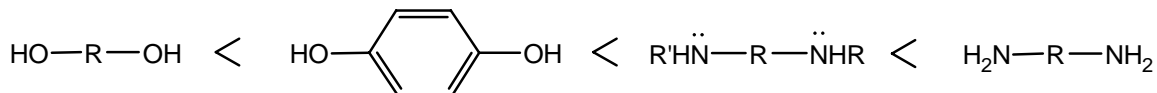
1.



2. Also very reactive



3.



R = alkyl

For highly reactive species:

Ex: diacid chloride + diamine  
       + diol }  $K_{\text{eq}} = 10^5 \sim 10^8$   
 can treat these as irreversible  
 → different reaction profiles and times

- Kinetics can become diffusion controlled (stirring becomes more important)
- Highly exothermic (high  $\Delta H$ )
- Need to consider heat transfer
- Short reaction times (relative to diol + diacid)

Most common:

