

Nylons *

Note Title

10/1/2007

History & Uses

Nylon is THE classic polycondensate, but not all nylons are polycondensates.

Went commercial in 1937

Wallace Carothers began in 1928 (DuPont)

First product = toothbrush bristles (1938)

The first crystalline plastic

Much higher service temperatures

Tough

Rigid

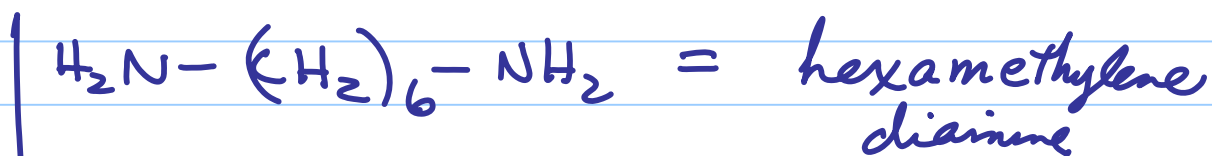
Lubrication-free

} bearings
gears

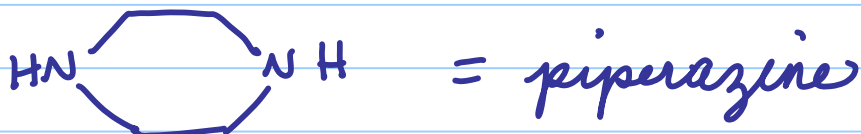
As we will see, there are many different nylons - generally, call them polyamides.

* Nylon Plastics, Melvin Kowen, Wiley, 1973.
Encyclopedia of Polym. Sci. "Polyamides"
Wikipedia (Nylon, caprolactam)

Some of The ingredients of "nylon"

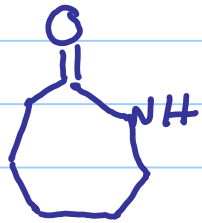


These give us nylon-66
↑ ↖ carbons from the diacid
↑ ↗ carbons from the diamine



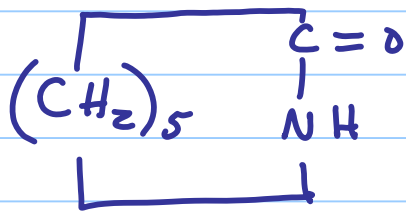
All these and more contribute to the AA BB chemistry covered earlier. The condensation chemistry of these is pretty obvious.

Here's something different, a 7-member ring



= caprolactam

too hard to draw, so do it like this

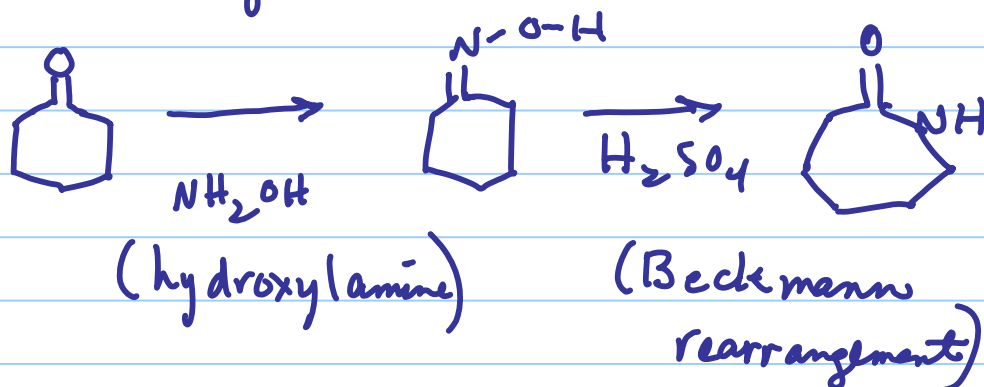


caproic acid = $CH_3(CH_2)_4COOH$



Smells like goats

Caprolactam production, one of several options.



Let us consider how to react these various monomers, remembering the limitations of polycondensation that prevent high conversions and high M_n .

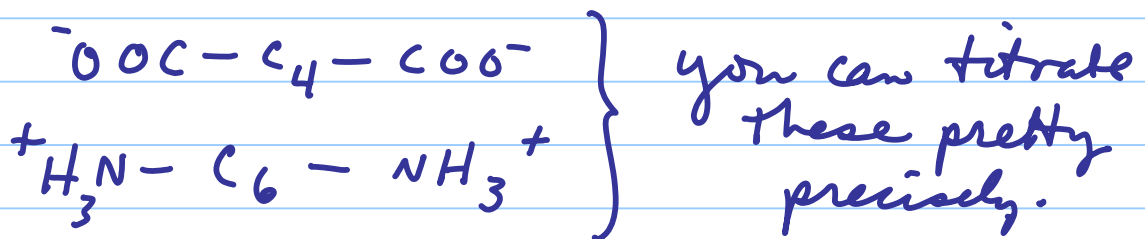
* How can we purify an AA-BB mixture?

* How will that lactam behave?

Nylon 66

In principle you could use not $\text{HOOC}-(\text{CH}_2)_4-\text{COOH}$ but a diester — e.g. $\text{CH}_3\text{OC}(=\text{O})-(\text{CH}_2)_4-\text{C}(=\text{O})\text{OCH}_3$

Using the acid directly, though provides a convenient way to self-adjust the stoichiometry through acid-base pairing.



You could also use a solvent like methanol, in which case the salt precipitates out!

Batch Reactor

salt solution loaded

concentrate to ~75%

transfer to pressure vessel (no O_2)

heat to 210°C (17 atm)

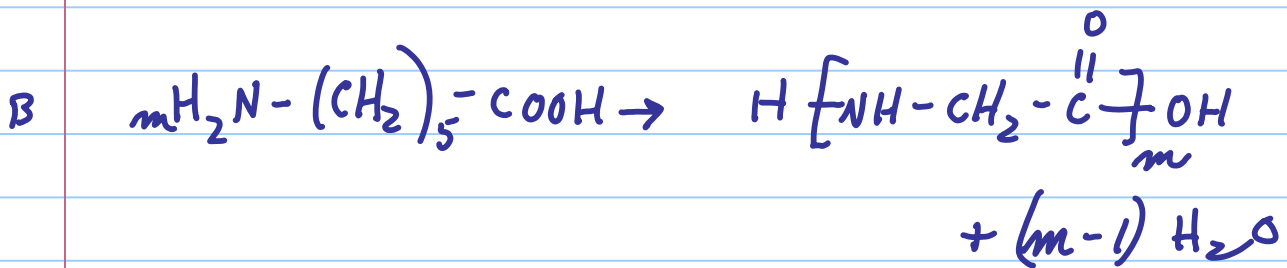
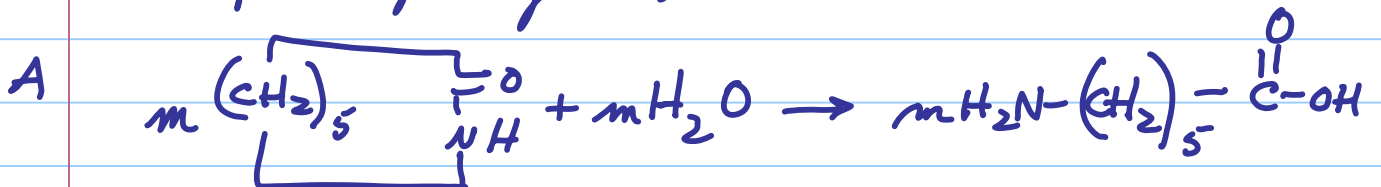
depressurize, raise to 280°C

apply vacuum to drive reaction.

Quench, chip, dry, bag, ship etc.

Nylon 6

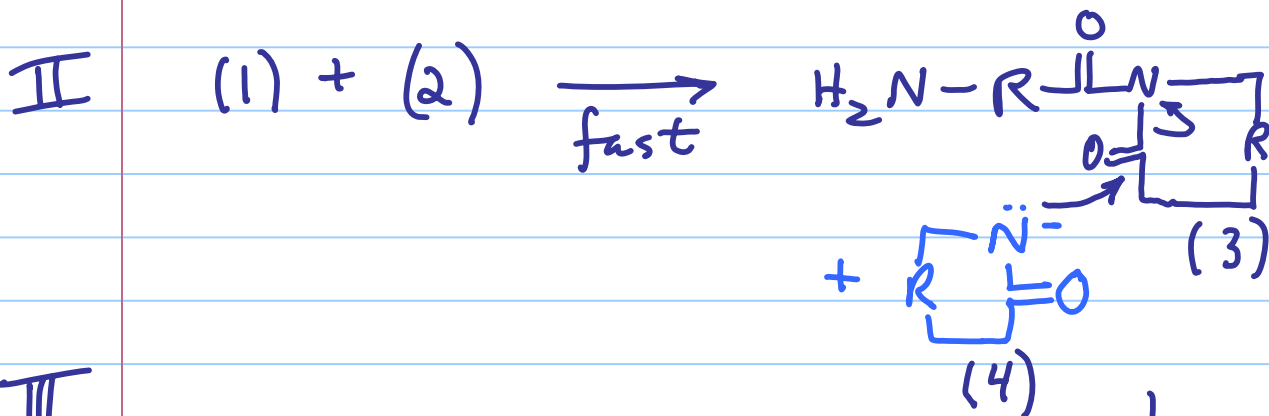
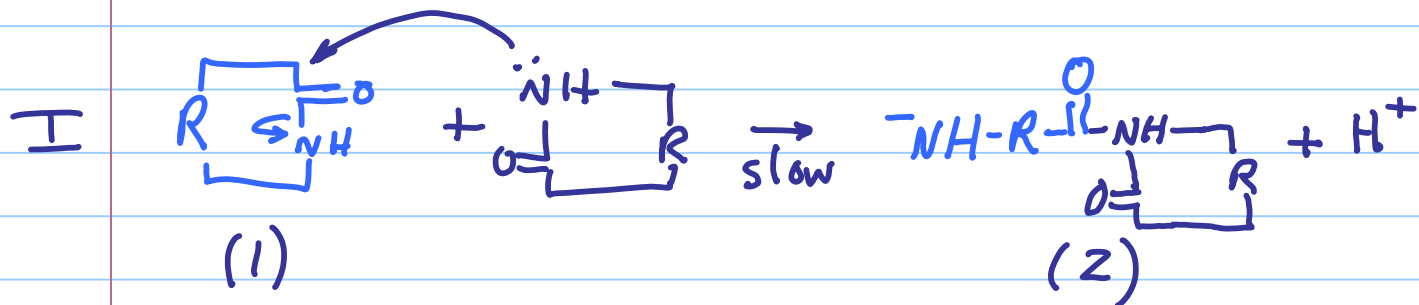
- obvious cure to the stoichiometry problem
- this is a complex polymerization
- it will suffice to consider the possibilities
- caprolactam does not polymerize if dry
- after hydrolysis, can condense



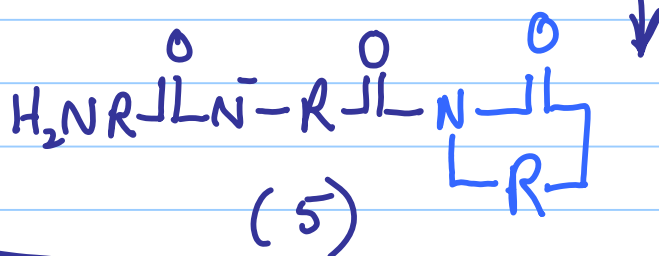
Rxn B is a condensation, but note that water went into the system for Rxn A.

- caprolactam can undergo additions and this dominates.

Let's see if we can get a plausible mechanism for this.



III



Names

(1) = lactam monomer

(2) = imide anion

(3) = neutral N-acyl lactam

(4) = lactam anion

Continue by covering that anion on (5) by abstraction of a proton from lactam monomer. Then insert the anion as in step III by reaction to the imide carbonyl to open the ring.

Base-catalyzed addition (BCA)

- Apparently, BCA is a viable option (see Encyclopedia of Polym. Sci "Polyamides")
- a metal hydride or other base is used to generate lactam anion (5)



The lactam anion reacts to lactam similar to the joining of two lactams in Rxn I above, which clearly benefits from added base to grab the putative H^+ .

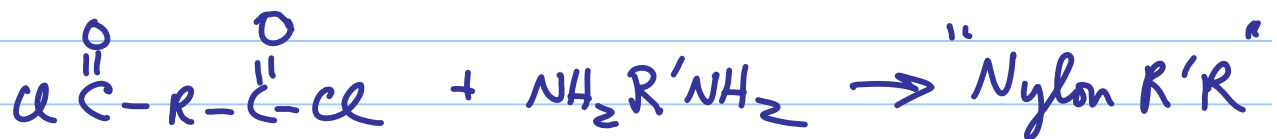
What should we expect for the MWD?
Well, it's an addition. There are not too many obvious termination rxns. Should we expect Poisson then?

Well... no, because the initiation isn't pulsed. Apparently formation of the N-acyl lactam is slow and smears the timing out.

Other Factors

Nylons contain unreacted monomer & various cyclic oligomers. Some are removed by vacuum and returned to the reactor (this has to broaden MWD, too).

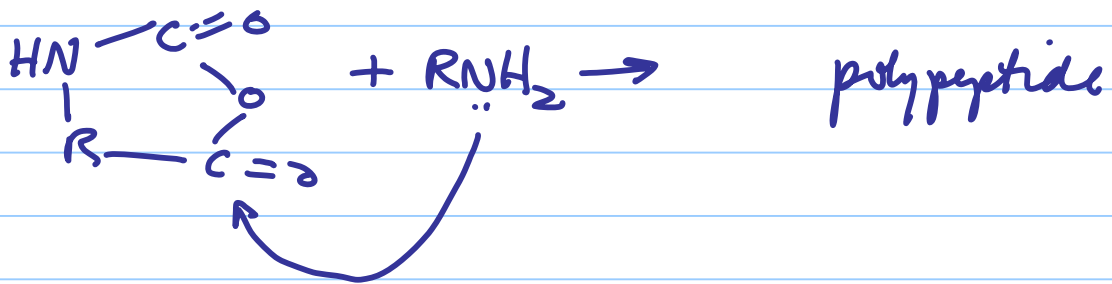
Interfacial polymerization of acid chlorides and diamines



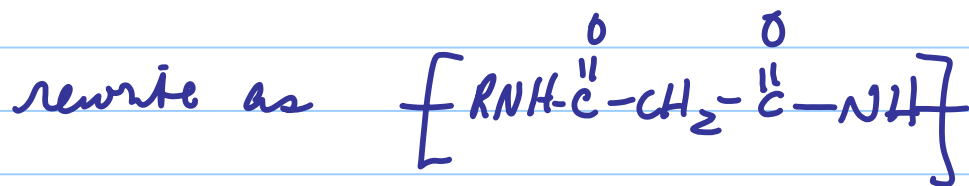
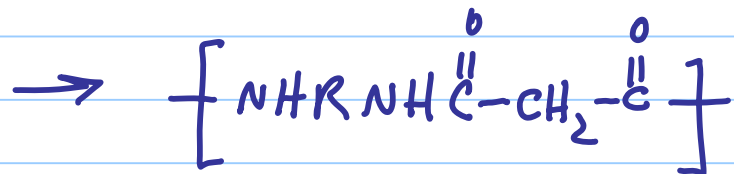
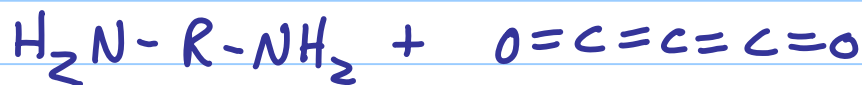
The acid chloride can be put in an organic solvent, immiscible with water that carries the diamine.

Other Polyamides

NCA ring opening to make polypeptides



Poly malonamide



$\text{O}=\text{C}=\text{C}=\text{C}=\text{O}$
carbon
suboxide

