Step-Growth Polymerization

16:160:509 – Polymer Chemistry

Lecture 3 to 4

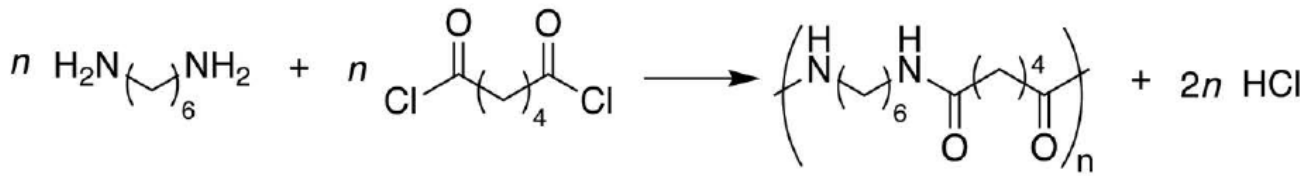
RUTGERS
School of Arts and Sciences
DEPARTMENT OF CHEMISTRY
AND CHEMICAL BIOLOGY

Two Basic Types of Polymerization

How do we put many monomers together in a row?

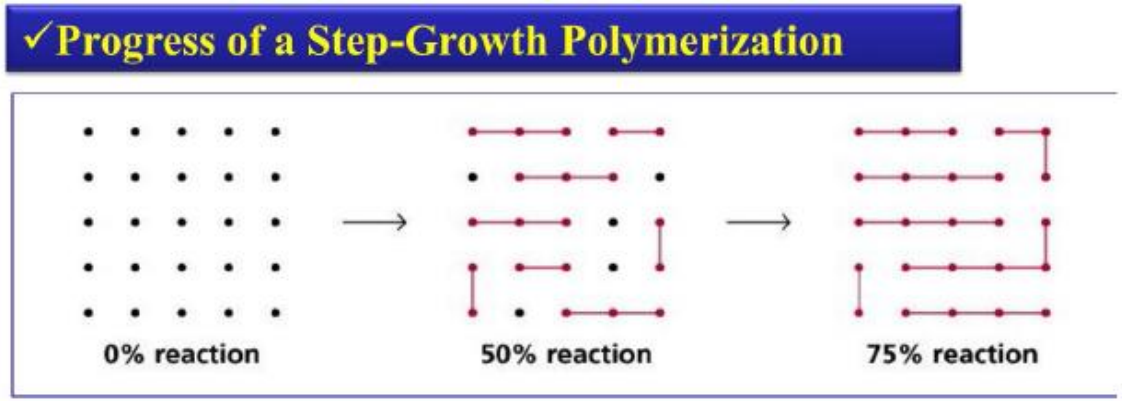
- **Step-Growth Polymerization** (usually referred to as "**polycondensation**")

  Bi-functional or multifunctional monomers react to form first dimers, then trimers, longer oligomers and eventually long chain polymers



Poly(hexamethylene adipamide), nylon 6,6

Monomer + monomer ⟶ dimer
Dimer + monomer ⟶ trimer
Dimer + dimer ⟶ tetramer
Trimer + monomer ⟶ tetramer
Trimer + dimer ⟶ pentamer
Trimer + trimer ⟶ hexamer
Tetramer + monomer ⟶ pentamer
Tetramer + dimer ⟶ hexamer
Tetramer + trimer ⟶ heptamer
Tetramer + tetramer ⟶ octamer
etc.

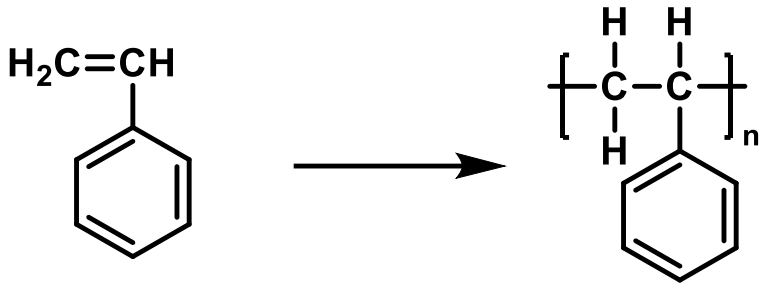


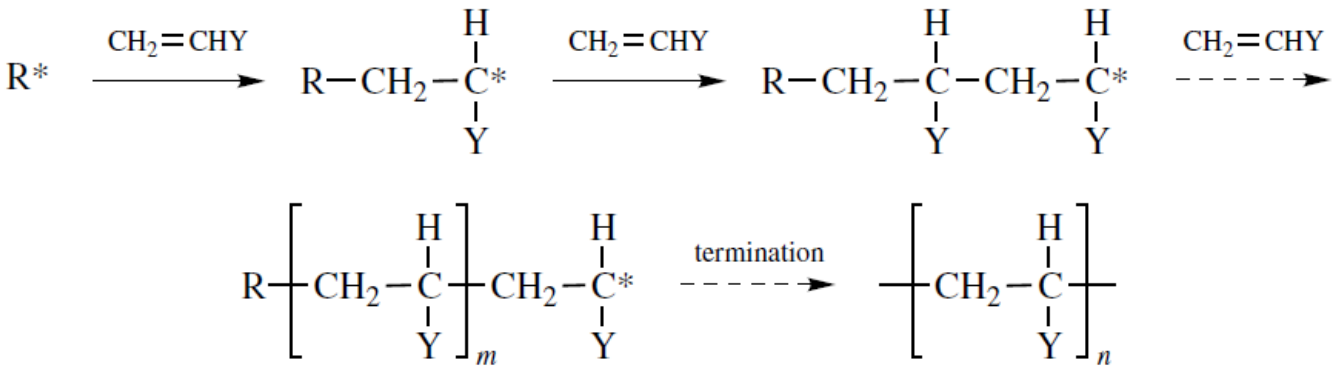
Two Basic Types of Polymerization

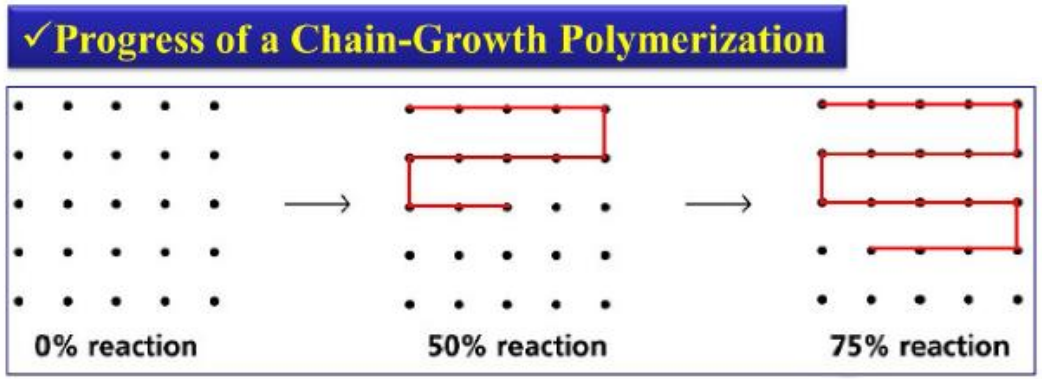
How do we put many monomers together in a row?

- **Chain-Growth Polymerization** (usually referred to as "**addition polymerization**")

Monomer molecules add onto the active site on a growing polymer chain one at a time.







Equal Reactivity of Functional Groups

- Before we proceed, we need to mention one important concept: *the reactivity of a functional group is independent of the size of the molecule to which it is attached*.
- In the case of step-growth polymerization, this means the reactivity of functional groups on monomer, dimer, trimer, etc., is the same. As you will see, this greatly simplifies our analysis of the reaction kinetics.
- See page 46 in Lodge for a detailed theoretical treatment.

Molecular Size (x)	$k \times 10^4$ for $H(CH_2)_xCO_2H$
1	22.1
2	15.3
3	7.5
4	7.5
5	7.4
6	
8	7.5
9	7.4
11	7.6
13	7.5
15	7.7
17	7.7

Rate constants for esterification (25°C) in homologous compounds

Molecular Weight Control in Step-Growth Polymerization

Scenario 1: step-growth polymerization of bifunctional monomers A—A and B—B

- In the feeding stock, the numbers of A and B functional groups are given by $N_{A,0}$ and $N_{B,0}$, respectively
- Define stoichiometric ratio r as $N_{A,0}/N_{B,0}$. A and B are chosen such that B—B is in excess (i.e., $r \leq 1$)
- Define the extent of reaction p as the fraction of the limiting groups (A groups) that have reacted at a particular time
- Define the degree of polymerization as the number of monomers (not the number of repeat units) in the chains (i.e., a tetramer A-a-b-b-a-a-b-B has a DP of 4)

Calculate the number-average degree of polymerization X_n

The total # of monomers (reacted + unreacted) is given by $\frac{N_{A,0}+N_{B,0}}{2} = \frac{N_{A,0}}{2}\left(1+\frac{1}{r}\right)$

At a given p, # of unreacted A group is $N_A = N_{A,0}(1-p)$

# of unreacted B group is $N_B = N_{B,0} - N_{A,0}\cdot p = N_{A,0}\left(\frac{1}{r}-p\right)$

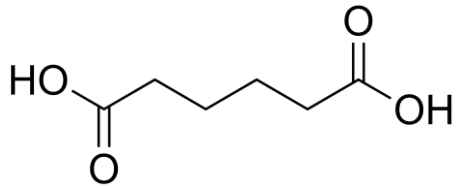
Note each polymer (regardless of lengths) has two unreacted groups at two termini

$$\#\text{ of polymers} = \frac{N_A+N_B}{2} = \frac{N_{A,0}}{2}\left(1+\frac{1}{r}-2p\right)$$

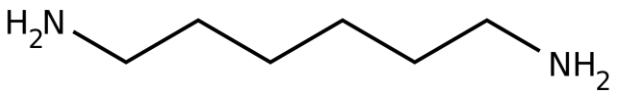
$$X_n = \frac{\text{total \# of monomers}}{\#\text{ of polymers}} = \frac{\frac{N_{A,0}}{2}\left(1+\frac{1}{r}\right)}{\frac{N_{A,0}}{2}\left(1+\frac{1}{r}-2p\right)} = \frac{1+r}{1+r-2rp}$$

Molecular Weight Control in Step-Growth Polymerization

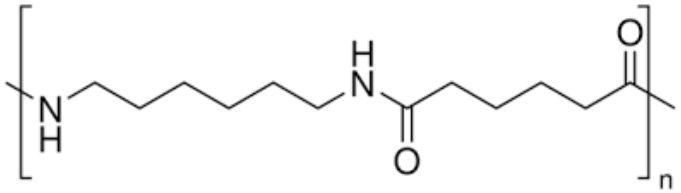
Calculate the feed ratio of adipic acid and hexamethylene diamine that should be employed to obtain a polyamide of approximately 15,000 molecular weight at 99.5% conversion. Do the same calculation for a 19,000 molecular weight polymer.



adipic acid (M = 146 g/mol)



hexamethylene diamine (M = 116 g/mol)



Nylon 6,6

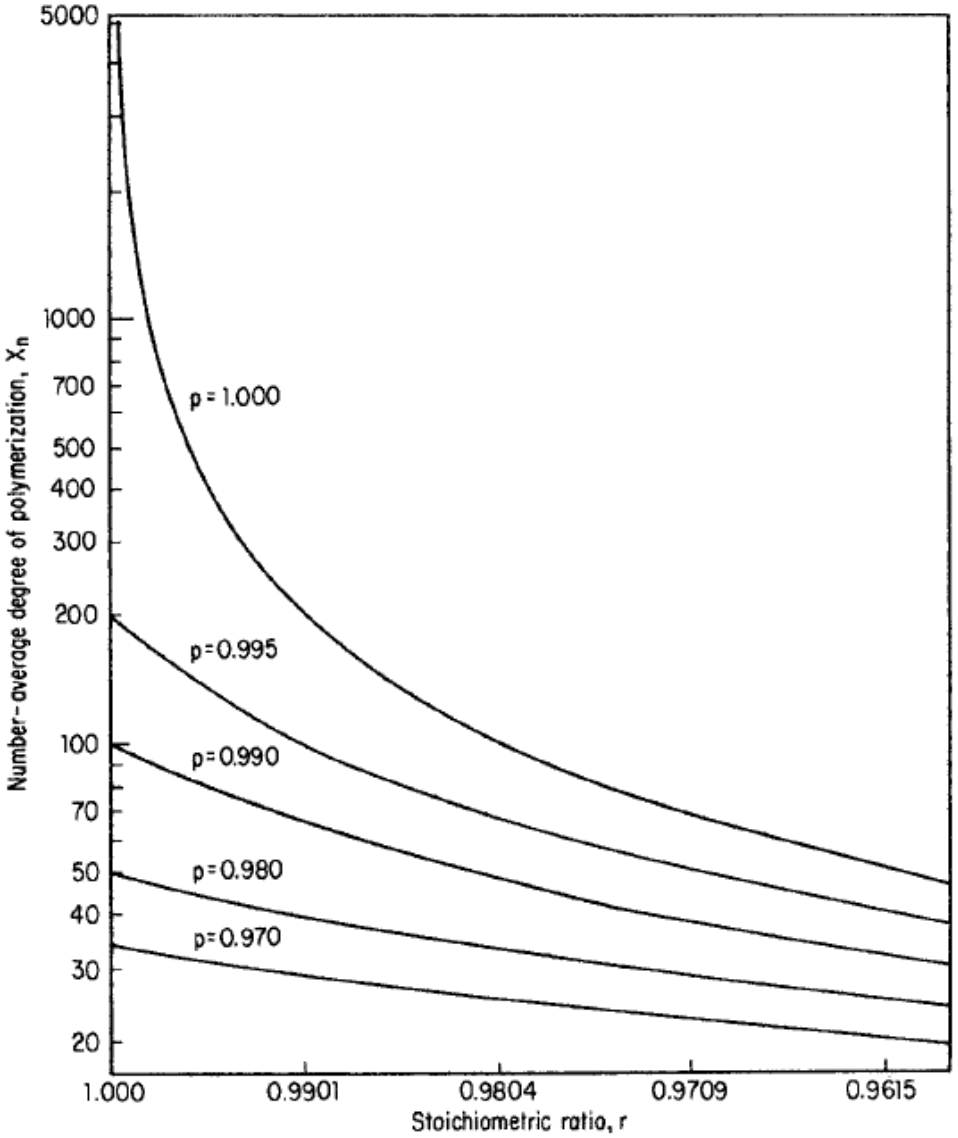
$$X_n = \frac{15000}{146+116-2\times 18} \times 2 = 132.7 \qquad \frac{1+r}{1+r-2r\times 0.995} = 132.7 \qquad r = 0.9949$$

Assuming hexamethylene diamine is used in excess, what is the identity of the end groups of this product?

A-A + excess B-B, all chains end with B groups.

In this case, B = NH_2, so all end groups are amino groups.

Molecular Weight Control in Step-Growth Polymerization



$$X_n = \frac{1 + r}{1 + r - 2rp}$$

Some values of X_n calculated for values of r and p close to unity

r	$p = 0.95$	$p = 0.97$	$p = 0.99$	$p = 1.00$
0.95	13.5	18.2	28.3	39.0
0.97	15.5	22.3	39.9	65.7
0.99	18.3	28.7	66.8	199
1.00	20.0	33.3	100	∞

It is difficult to achieve high molecular weight using step-growth polymerization:

- p has to be close to 1—requires very high conversion.
- r has to be close to 1—requires precise stoichiometric control plus very pure monomer stocks.

Molecular Weight Control in Step-Growth Polymerization

Scenario 2: step-growth polymerization of A—B type monomers

Calculate the number-average degree of polymerization X_n

Total # of monomers (reacted + unreacted) = $N_{A,0} = N_{B,0}$

At a given p, # of unreacted A groups, $N_A = N_{A,0}(1-p)$

# of unreacted B groups, $N_B = N_{B,0} - N_{A,0} \times p = N_{A,0}(1-p)$

Each polymer has two unreacted groups at two termini

$$\#\text{ of polymers} = \frac{N_A + N_B}{2} = N_{A,0}(1-p)$$

$$X_n = \frac{\#\text{ of monomers}}{\#\text{ of polymers}} = \frac{N_{A,0}}{N_{A,0}(1-p)} = \frac{1}{1-p}$$

The above expression is equal to $X_n = \frac{1+r}{1+r-2rp}$ when $r = 1$

($r = 1$ is inherent for A-B type monomers)

Molecular Weight Control in Step-Growth Polymerization

Scenario 3: step-growth polymerization of an equimolar mixture A—A and B—B by the addition of small amounts of a monofunctional reactant B—O (O is unreactive).

In the manufacturing of polymers, our goal is not necessarily to make the highest molecular-weight polymers possible. Rather, we often need to target a particular range of molecular weights. In step-growth polymerization of A—A and B—B, the most widely used approach is to maintain equimolar stoichiometry between A—A and B—B, and then tune r by adding a monofunctional reactant B—O.

A–A + B–B (excess) → B~~B ← still potentially reactive (unstable polymer)

A–A + B–B + B–O → O~~O ← unreactive (stable polymer)

We have the following # of molecules at the beginning of the rxn

A–A: $\frac{N_{A,0}}{2}$ B–B: $\frac{N_{B,0}}{2}$ B–O: $N_{B',0}$ $N_{A,0} = N_{B,0}$

Each monofunctional B–O acts as an (excess) B–B in terms of MW control

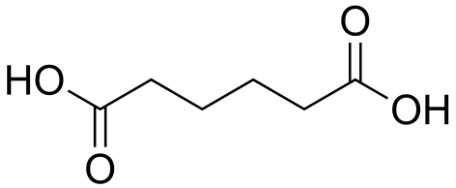
So it follows the same expression of X_n in Scenario 1, with r defined as

$$r = \frac{N_{A,0}}{N_{B,0} + 2N_{B',0}}$$

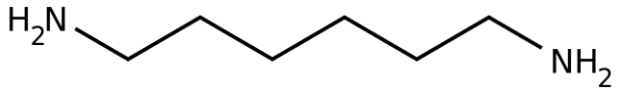
Note that the above discussion only applies to an equimolar mixture of A—A and B—B. Other situations require equations that will be discussed in Lecture 18.

Molecular Weight Control in Step-Growth Polymerization

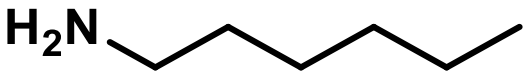
100 mol of adipic acid and 100 mol of hexamethylene diamine are used to synthesize Nylon 6,6. To target a number-average molecular weight of 20,000 g/mol, hexylamine (a monofunctional amine) is used. Calculate how much hexylamine (in mol) is needed to achieve the desired molecular weight at a conversion of 99.9%.



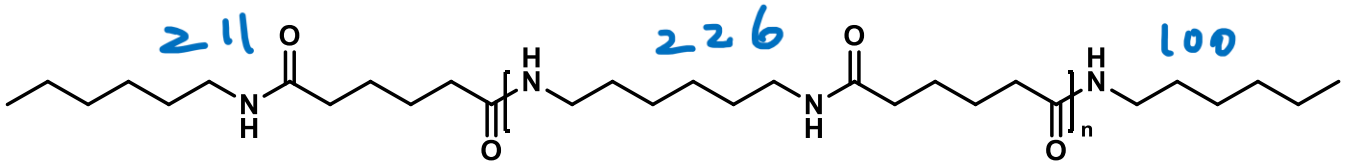
adipic acid (M = 146 g/mol)



hexamethylene diamine (M = 116 g/mol)



hexylamine (M = 101 g/mol)



$n = \frac{20000 - 211 - 100}{226} \approx 87$ $X_n = 3 + 87 \times 2 = 177$

$X_n = \frac{1+r}{1+r-2rp}$, solve for $X_n = 177$, $p = 0.999$, we have $r = 0.9907$

$r = \frac{N_{A,0}}{N_{B,0} + 2N_{B',0}} = \frac{200}{200 + 2N_{B',0}}$ solve for $r = 0.9907$, we have

$N_{B',0} = 0.939$ mol

Molecular Weight Distribution in Step-Growth Polymerization

What does the **molecular weight distribution** look like in step-growth polymerization? For simplicity, let's consider the step-growth polymerization of A—B type monomers (the derivation applies equally to stoichiometric A—A plus B—B types of step polymerizations).

At a given time, the probability a single A group has reacted is equal to p (the extent of rxn)

For an i-mer, it has one A group unreacted and $i-1$ A groups that have reacted

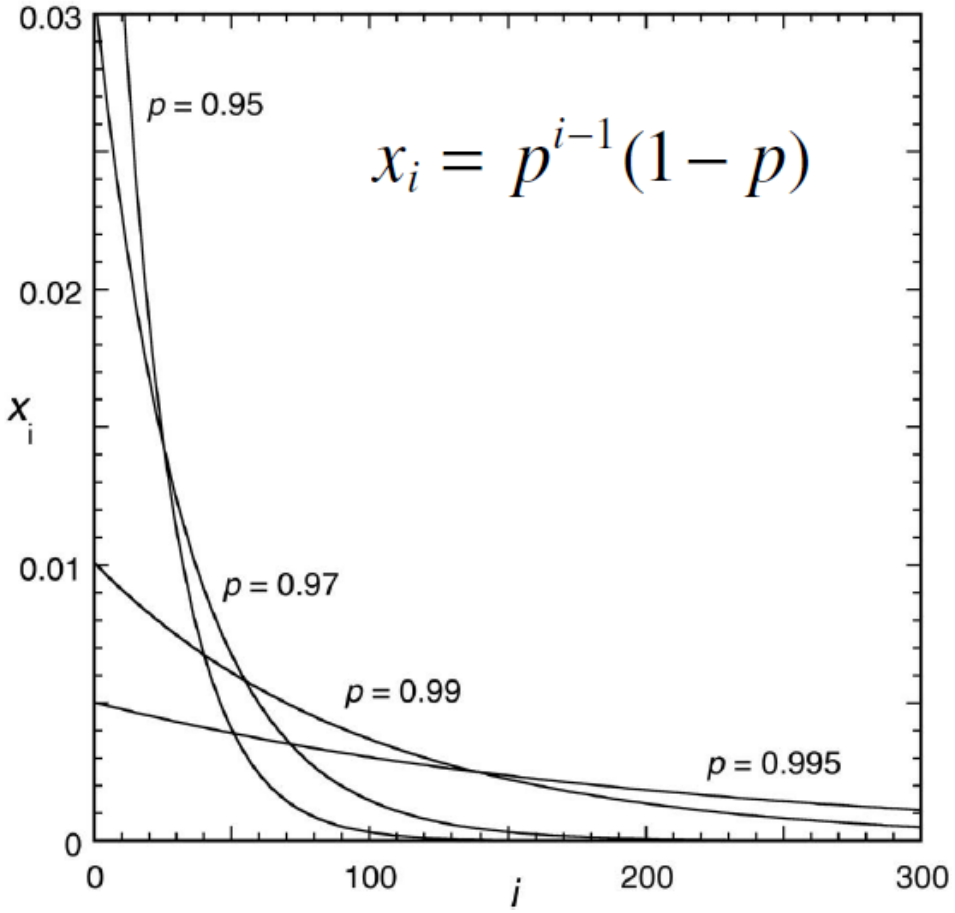
Therefore, the probability that a random chosen polymer is i-mer is $(1-p)\cdot p^{i-1}$

By definition, this probability is the number fraction of an i-mer

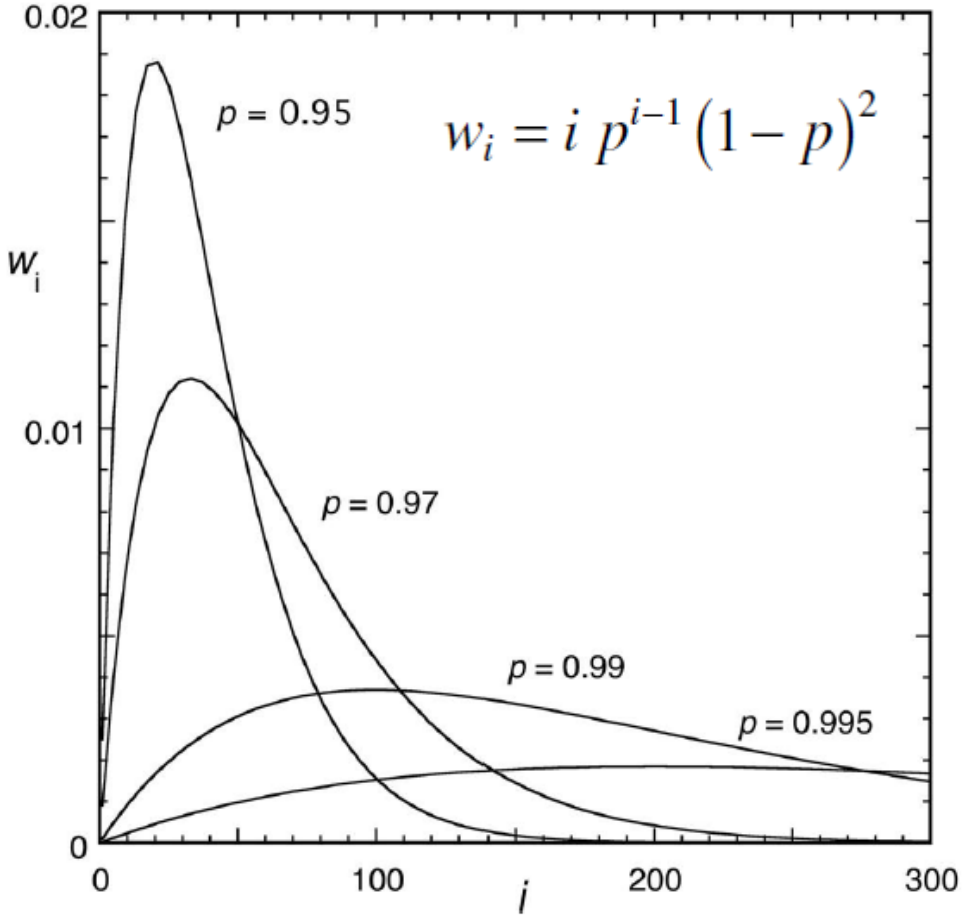
$x_i = p^{i-1}(1-p)$ $\Rightarrow$ known as most probable (or Flory-Schulz) distribution

$$w_i = \frac{x_i \cdot i}{\sum x_i \cdot i} = \frac{i \cdot p^{i-1}(1-p)}{\sum i\, p^{i-1}(1-p)} = \frac{i \cdot p^{i-1}(1-p)}{\frac{1}{1-p}} = i \cdot p^{i-1}(1-p)^2$$

Molecular Weight Distribution in Step-Growth Polymerization



Mole fraction of *i*-mer



Weight fraction of *i*-mer

What Else Can We Learn from the Molecular Weight Distribution?

See Page 640 in Lodge for the math used here

$$X_n = \sum x_i \cdot i = \sum p^{i-1}(1-p) \cdot i = (1-p) \sum i \cdot p^{i-1} = (1-p) \times \frac{1}{(1-p)^2} = \frac{1}{1-p}$$

We've got the same result by simply calculating the average

$$X_w = \frac{\sum x_i \cdot i^2}{\sum x_i \cdot i} = \frac{\sum p^{i-1}(1-p) \cdot i^2}{\frac{1}{1-p}} = \frac{(1-p) \times \frac{1+p}{(1-p)^3}}{\frac{1}{1-p}} = \frac{1+p}{1-p}$$

$$Đ = \frac{X_w}{X_n} = 1 + p$$

- The dispersity goes to 2.0 (quite broad) as the conversion reaches 100%.
- An inherent limitation of step-growth polymerization: it is impossible to achieve high molecular weight and narrow dispersity at the same time.

Kinetics of Step-Growth Polymerization

What we have just derived gives us a good idea of what will happen at a given conversion *p*, but it does not tell us how long it takes to reach that conversion.

We consider the simplest case: a step-growth polymerization driven by the reaction between stoichiometric A and B groups. The reaction is carried out with an external catalyst, such that it follows second-order kinetics with a rate constant *k*.

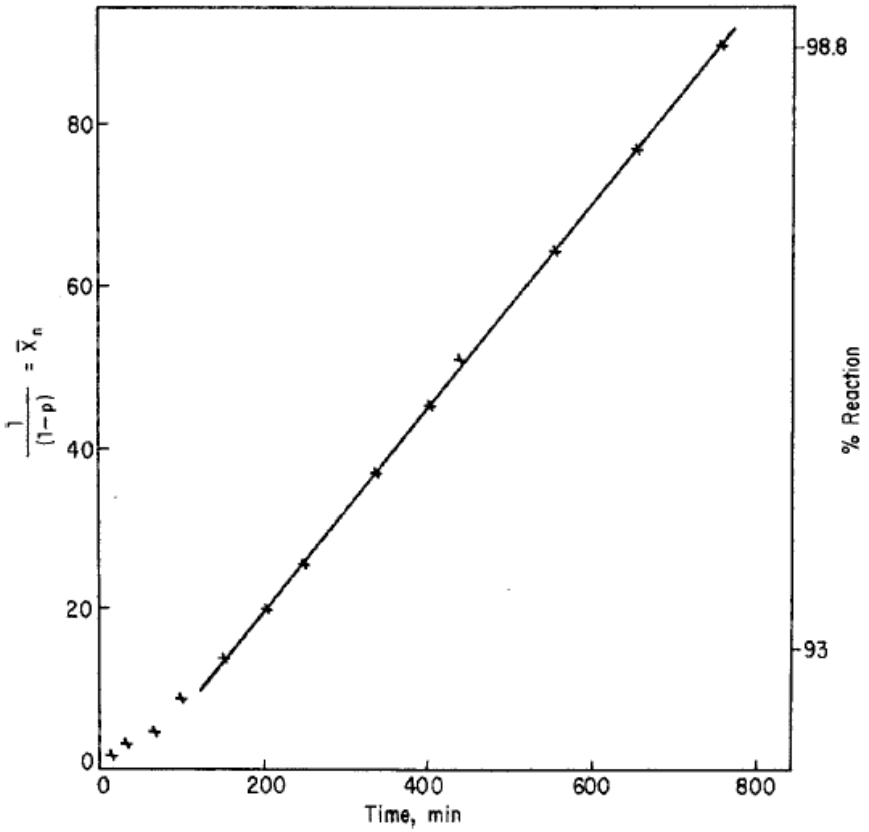
$$\sim A + B \sim \rightarrow \sim a\text{-}b \sim$$

$$-\frac{d[A]}{dt} = k[A][B] = k[A]^2$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]_0(1-p)} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{1-p} = X_n = k t [A]_0 + 1$$



Self-catalyzed step-growth polymerization shows different and slower kinetics. See Page 54 in Lodge.

Kinetics of Step-Growth Polymerization

Show that the time required to go from p = 0.98 to p = 0.99 is very close to the time required to reach p = 0.98 from the start of polymerization for the external acid-catalyzed polymerization of an equimolar mixture of a diol and a diacid.

$$\frac{1}{1-p} = k[A]_0 t + 1$$

From $p=0$ to $p=0.98$: $\frac{1}{1-0.98} = k[A]_0 t + 1$ $\quad t_{0\to 0.98} = \frac{49}{k[A]_0}$

From $p=0$ to $p=0.99$: $\frac{1}{1-0.99} = k[A]_0 t + 1$ $\quad t_{0\to 0.99} = \frac{99}{k[A]_0}$

From $p=0.98$ to $p=0.99$: $\quad t_{0.98\to 0.99} = \frac{99}{k[A]_0} - \frac{49}{k[A]_0} = \frac{50}{k[A]_0}$

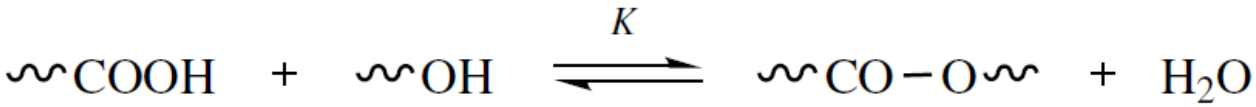
How about the time required to go from p = 0.99 to p= 0.995?

From $p=0$ to $p=0.995$ $\quad \frac{1}{1-0.995} = k[A]_0 t + 1$ $\quad t_{0\to 0.995} = \frac{199}{k[A]_0}$

From $p=0.99$ to $p=0.995$ $\quad t_{0.99\to 0.995} = \frac{100}{k[A]_0}$

Equilibrium Considerations

Our kinetic analysis assumes the reaction is irreversible. However, many reactions used in step-growth polymerization reach equilibrium, especially at high conversion. Let's consider the following reaction (used to make polyesters) run in a closed system (i.e., with no removal of the water byproduct).



Assume $r = 1$, at conversion p

$[H_2O] = [\sim \overset{O}{\overset{\|}{C}} - O \sim] = p \cdot [COOH]_0$ $\quad [\sim COOH] = [\sim OH] = (1-p)[COOH]_0$

$$K_{eq} = \frac{[H_2O]\cdot[\sim \overset{O}{\overset{\|}{C}} - O \sim]}{[\sim COOH]\cdot[\sim OH]} = \frac{p^2[COOH]_0^2}{(1-p)^2[COOH]_0^2} = \frac{p^2}{(1-p)^2} = (X_N - 1)^2$$

$$X_N = K_{eq}^{\frac{1}{2}} + 1$$

Polyester (COOH + OH): $K_{eq} = 1 \sim 10$ $\quad X_N \approx 2\text{-}5$

Polyamide (COOH + NH_2): $K_{eq} = 10^2 \sim 10^3$ $\quad X_N \approx 10\text{-}40$

To overcome this limit, we often need an open, driven system to remove the byproduct

Equilibrium Considerations

The polymerization between equimolar amounts of a diol and a diacid proceeds with an equilibrium constant of 20. What will be the expected degree of polymerization and extent of reaction if the reaction is carried out in a closed system without removal of the by-product water?

$$X_N = K_{eq}^{\frac{1}{2}} + 1 = 20^{\frac{1}{2}} + 1 = 5.47$$

$$p = 1 - \frac{1}{X_N} = 1 - \frac{1}{5.47} = 0.817$$

To what level must [H_2O] be lowered in order to obtain a degree of polymerization of 200 if the initial concentration of carboxyl groups is 2 M?

$$K_{eq} = \frac{[H_2O] \cdot [\sim C(=O)-O-]}{[-COOH] \cdot [-OH]} = \frac{[H_2O] \cdot p \cdot [COOH]_0}{(1-p)^2 [COOH]_0^2}$$

$$p = 1 - \frac{1}{X_N} = 1 - \frac{1}{200} = 0.995$$

$$[H_2O] = \frac{K_{eq}(1-p)^2[COOH]}{p} = \frac{20 \times (1-0.995)^2 \times 2}{0.995} = 0.001\ M$$

Three Methods for Performing Step-Growth Polymerization

1. Bulk polymerization

- Well suited for step polymerization because the viscosity (molecular weight) remains relatively low throughout most of the polymerization process.
- Works well for reactions with a small K_{eq}, where heating or vacuum is needed to remove byproducts.
- No need for product separation—direct processing of final products possible
- Limitations:
    1. Not suitable for highly exothermic reactions.
    2. The required heating might lead to undesired side reactions.

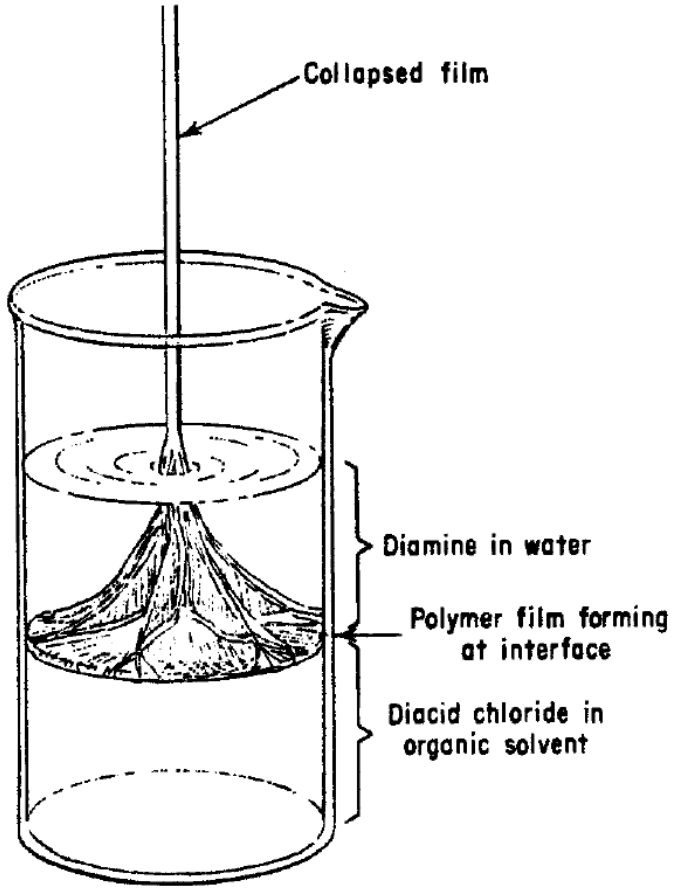
2. Solution polymerization

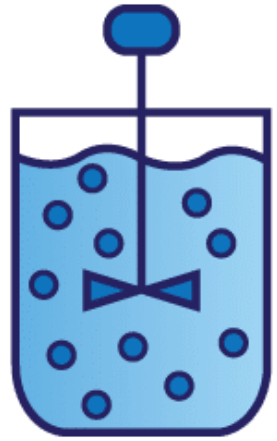
- Good mixing is easy to achieve in solution due to low viscosity.
- Heat dissipation is easy in solution, which is beneficial for highly exothermic reactions.
- Works well for reactions with a large K_{eq}.
- Limitations:
    1. Solvents need to be removed after polymerization.
    2. To prevent premature precipitation, solvents with good solubility for polymers are needed but are often difficult to find.

Three Methods for Performing Step-Growth Polymerization

3. Interfacial polymerization

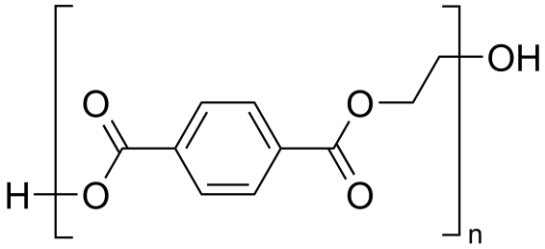
- High-molecular-weight polymers are formed at the interface regardless of the overall percent conversion based on the bulk amounts of the two reactants.
- The reaction is diffusion-controlled, so there is no need to control stoichiometry externally.
- Limitations:
  1. It works well only for reactions that have a high kinetic constant (R_p >> diffusion).
  2. One monomer needs to be water-soluble while the other must not.
  3. Many practical considerations that often limit the design of a good interfacial polymerization process.





Stirred interfacial polymerization: A-rich phase is dispersed as tiny droplets in B-rich phase through high-speed mechanical mixing.

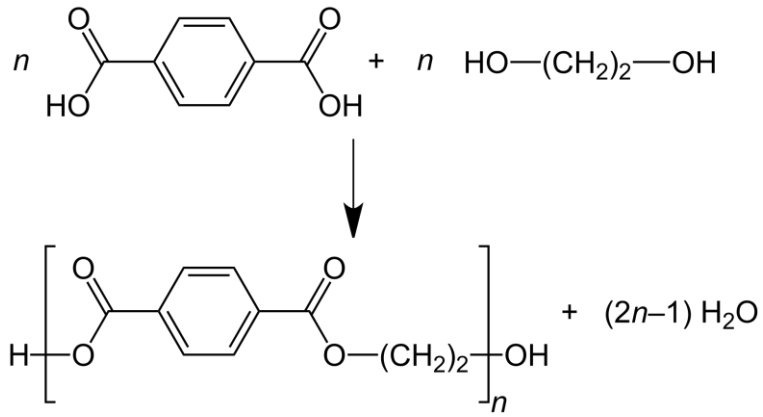
Polyesters



The most common type of polyester is polyethylene terephthalate (PET)

- Typically semi-crystalline (T_g ~ 70°C, T_m ~ 270°C)
- Strong and impact-resistant
- Good barrier properties to water and oxygen

What are potential problems with the following process?

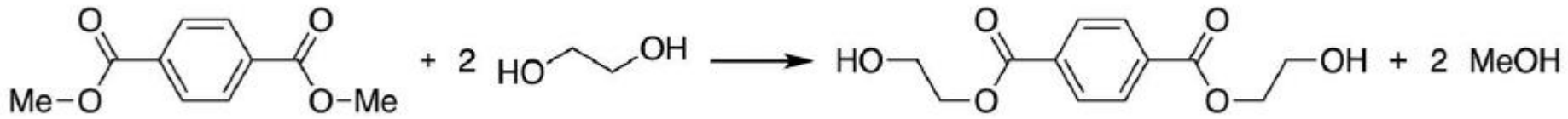


- Precise stoichiometric control is needed to achieve a high molecular weight.
- Terephthalic acid, the starting material, has been difficult to obtain in sufficient purity until recently.
- Since K_{eq} is small, constant removal of water is necessary.
- The esterification reaction proceeds slowly, requiring high temperatures.

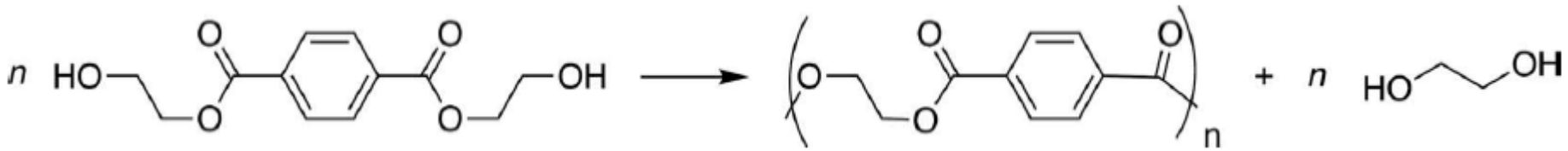
Process Conditions for PET

Industrial product of PET uses transesterification reaction

Stage 1: In solution below 200°C



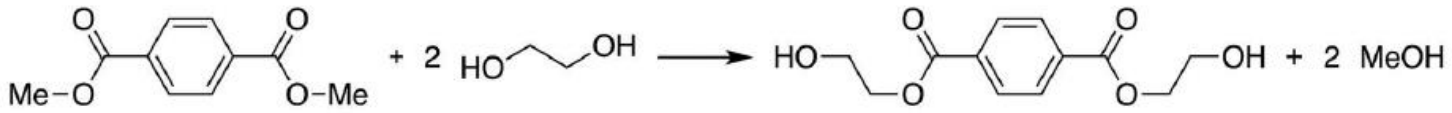
Stage 2: *Bulk polymerization* around 280 °C under partial vacuum with some acid catalyst



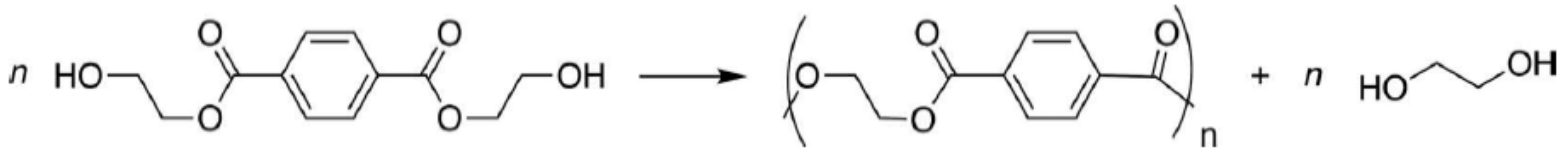
- No external stoichiometric control is needed.
- Transesterification is faster than esterification.
- High-purity dimethyl terephthalate is readily available.
- Ethylene glycol needs to be removed under vacuum to shift the equilibrium.

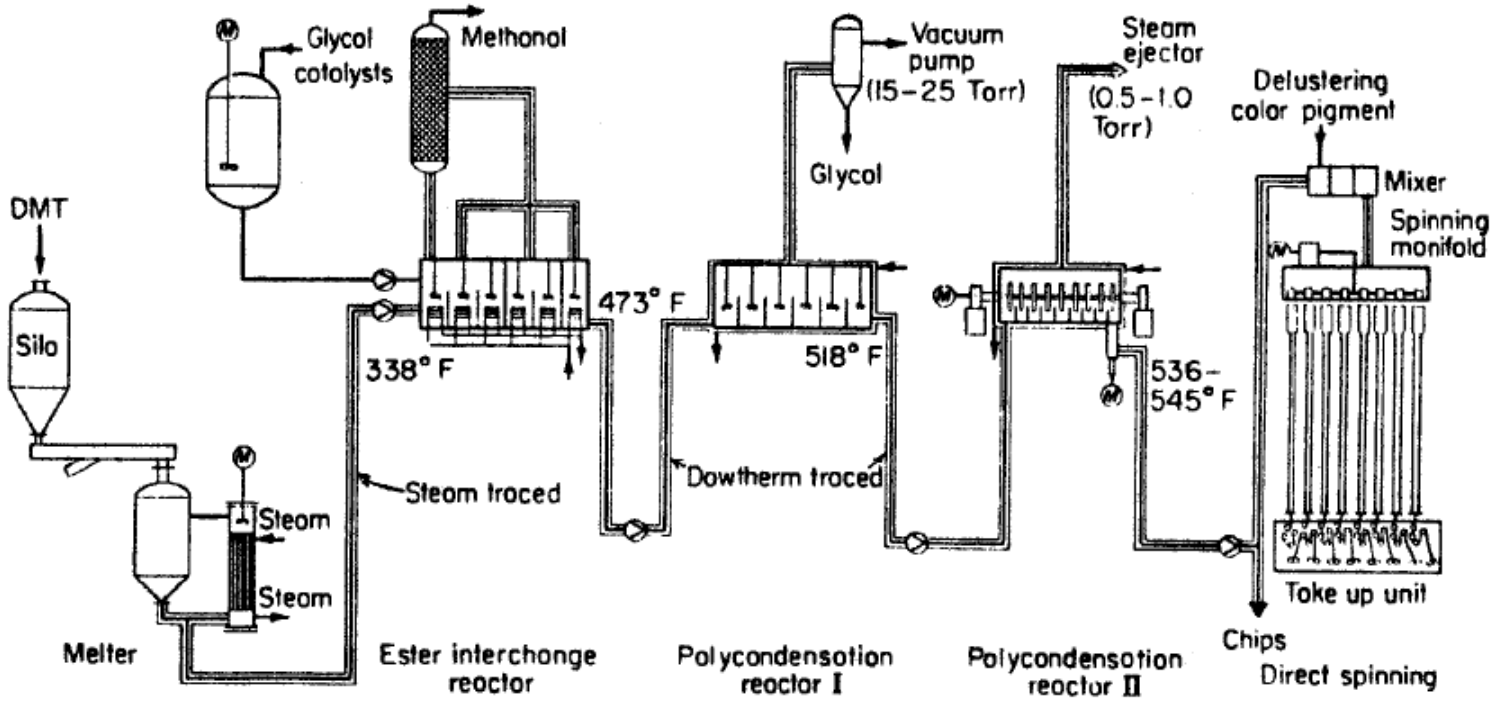
Process Conditions for PET

Stage 1:

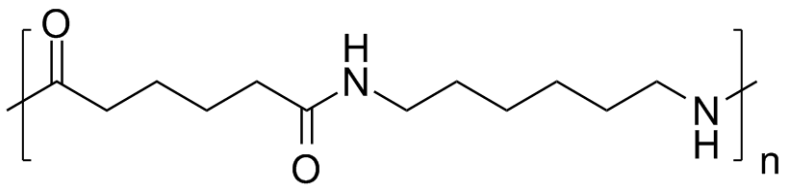


Stage 2:

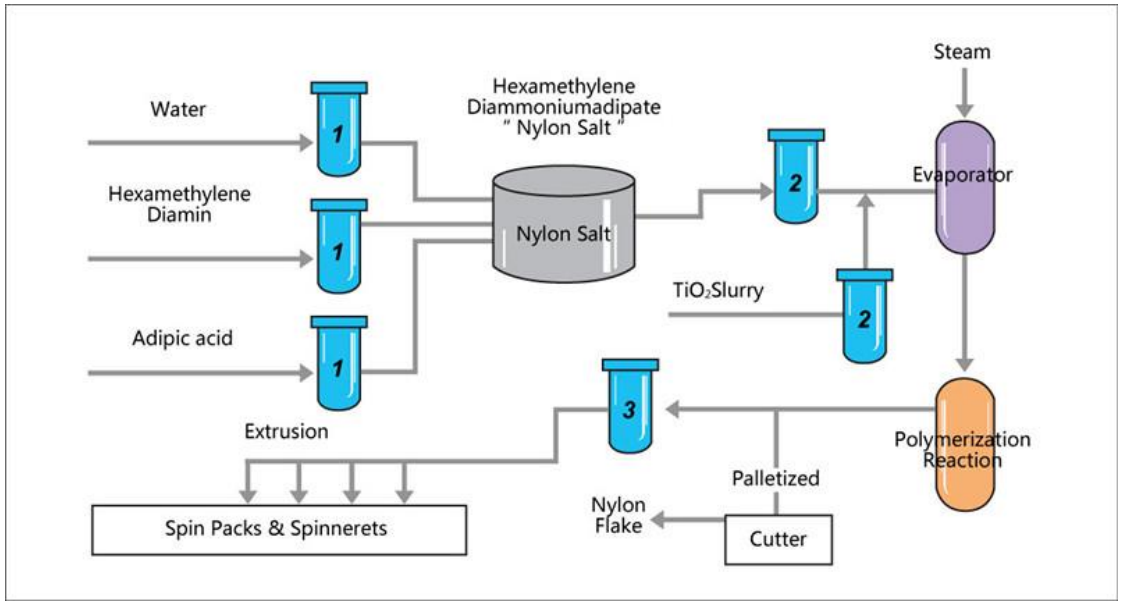




Polyamides



Nylon 6,6



Stage 1: Formation of "nylon salt" in aqueous solution at a concentration of 50%

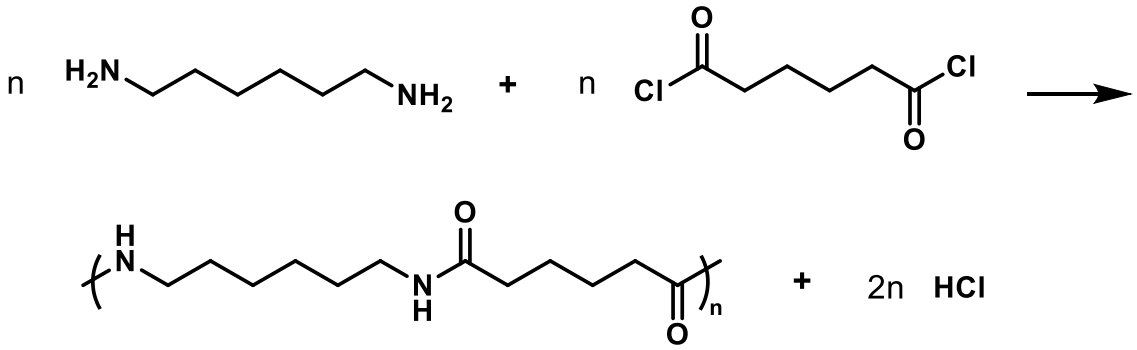
$$n H_2N(CH_2)_6NH_2 \quad + \quad n HO_2C(CH_2)_4CO_2H \longrightarrow n\left[\begin{matrix} {}^{-}O_2C(CH_2)_4CO_2^{-} \\ {}^{+}H_3N(CH_2)_6NH_3^{+} \end{matrix}\right]$$

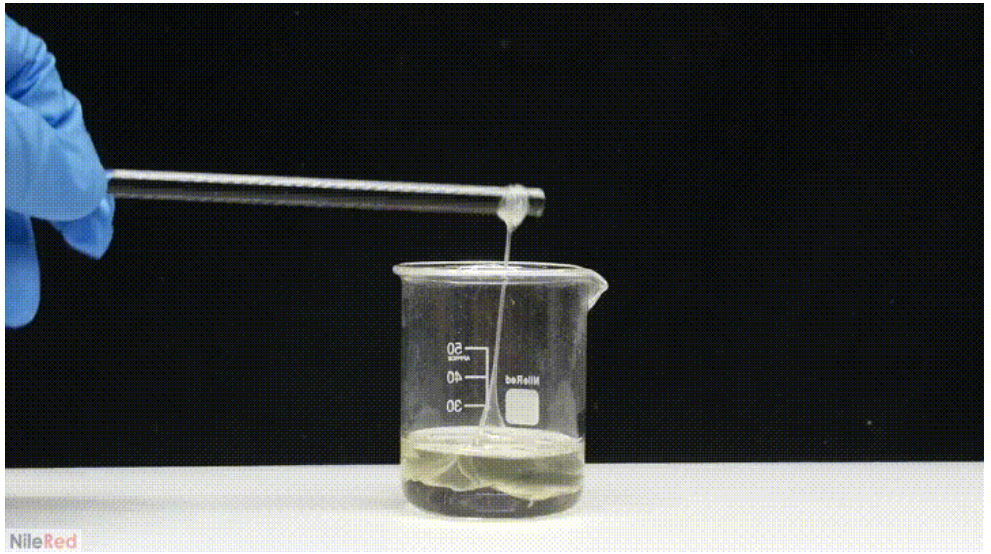
Stage 2: Polymerization starts at about 200°C and rises to 275°C to drive off water and attain a high molecular weight polymer (*bulk polymerization*).

$$n\left[\begin{matrix} {}^{-}O_2C(CH_2)_4CO_2^{-} \\ {}^{+}H_3N(CH_2)_6NH_3^{+} \end{matrix}\right] \longrightarrow H\left[NH-(CH_2)_6-NHCO-(CH_2)_4-CO\right]_n OH \quad + \quad (2n-1)H_2O$$

Polyamides Made from Acyl Chlorides

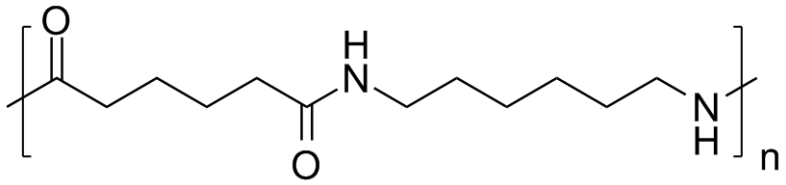
The kinetic constant *k* for typical step-growth polymerization is on the order of 10^{-3} L mol^{-1} s^{-1}, but for reactions between acyl chloride and amine, *k* is close to 10^{5} L mol^{-1} s^{-1}.



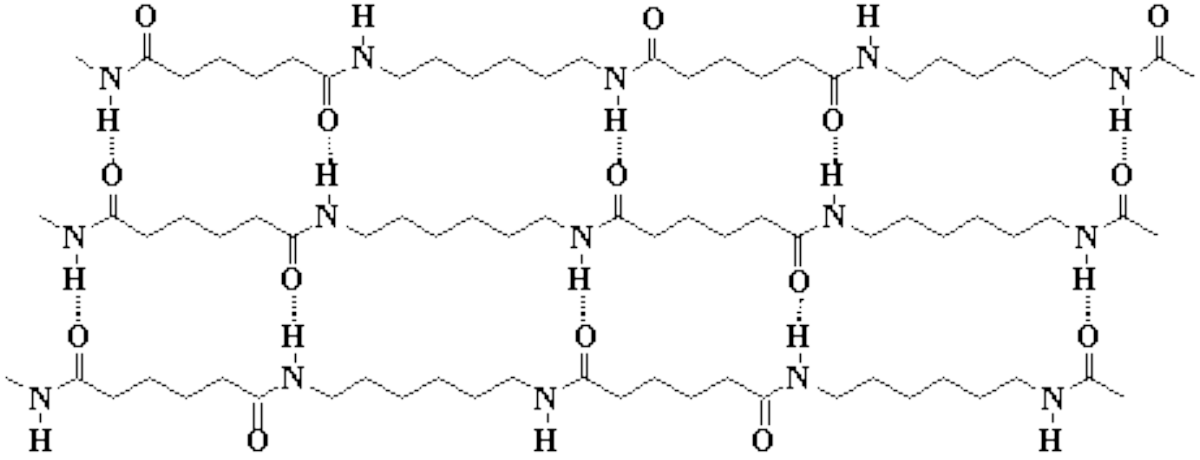


- Acyl chloride is much more reactive than acid, making polymerization faster.
- Bulk polymerization is unsuitable due to this highly exothermic reaction. Interfacial polymerization is well-suited.
- The diamine monomer is in the aqueous phase, and the diacyl chloride monomer is in the organic phase.
- Monomers diffuse to the interface to form polymers, with an inorganic base in the aqueous phase neutralizing the HCl byproduct.
- Although this method is a convenient demonstration and allows for the synthesis of high molecular weight Nylon under mild conditions, it is not used industrially due to the cost and instability of acyl chlorides.

Nylon Is Highly Crystalline



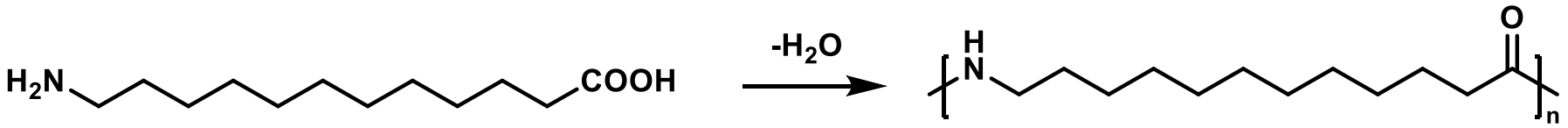
Nylon 6,6



In nylon 6,6, the carbonyl oxygens and amide hydrogens can hydrogen bond with each other. This allows the chains to line up in an orderly fashion to form fibers.

- Semi-crystalline (T_g ~ 70°C, T_m ~ 265°C)
- High mechanical strength
- Good stability under heat and/or chemical resistance

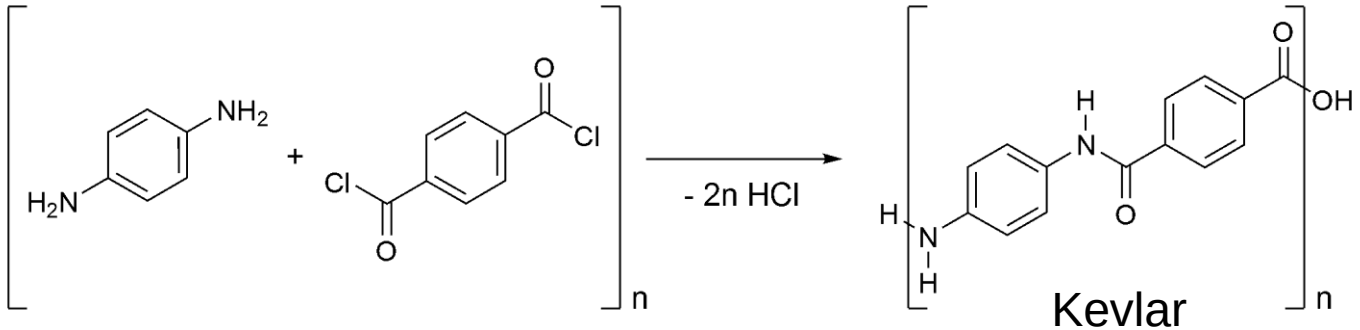
Changing the Spacer Length Tunes the Properties of Polyamides



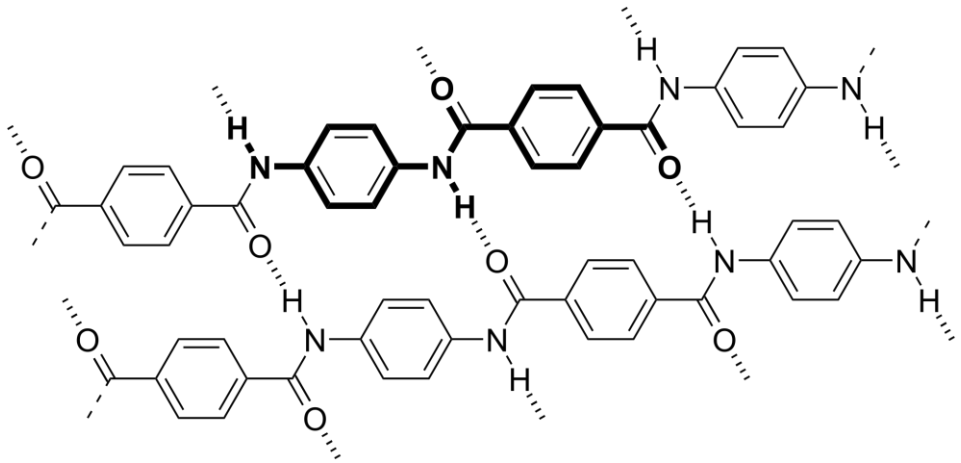
Nylon 12

The melting point of Nylon 12 is 178 °C, much lower than that of Nylon 6,6. This is because the longer aliphatic chain in Nylon 12 makes chain packing less efficient. Nylon 12 has properties similar to Nylon 6,6, but it is easier to process and more flexible due to the longer aliphatic chain.

Aromatic Polyamides



Kevlar



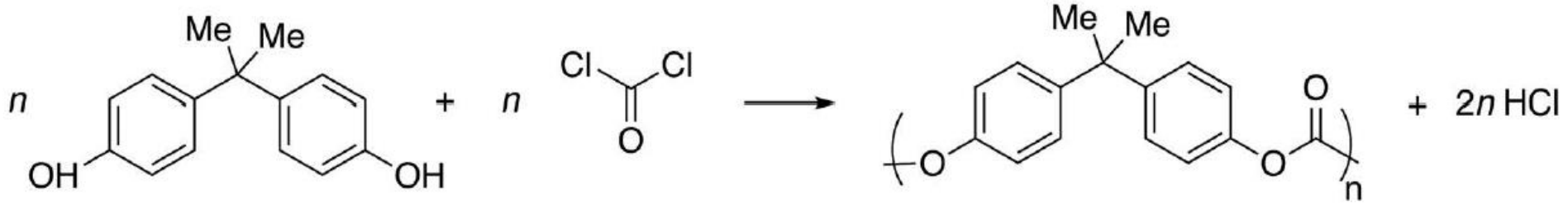
“Engineering plastic”

Bulletproof

Flame resistant

- Aromatic amines are less nucleophilic than aliphatic amines, so acyl chlorides need to be used for polymerization.
- *Solution polymerization* is used (under 100°C in highly polar organic solvents such as NMP).
- The resulting polymer solutions are often used directly to spin fibers.

Polycarbonate (PC)

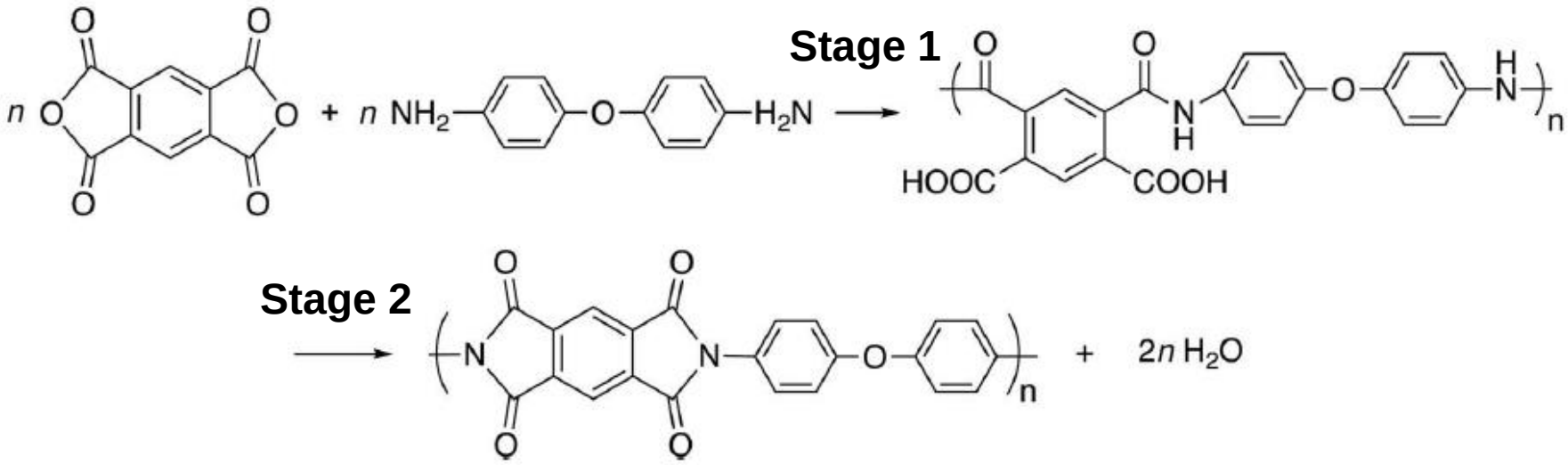


bisphenol A (BPA) phosgene

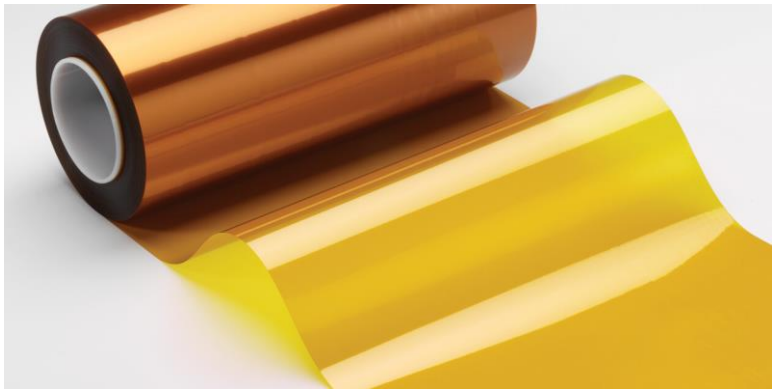
The reaction is often performed as a *stirred interfacial polymerization*, where the BPA is dissolved in an aqueous base to yield the phenolate salt (and neutralize the produced HCl), and the organic solvent is added (along with phosgene) to maintain polymer solubility.

- Amorphous (T_g ~ 150°C)
- Exceptional transparency
- High impact-resistance

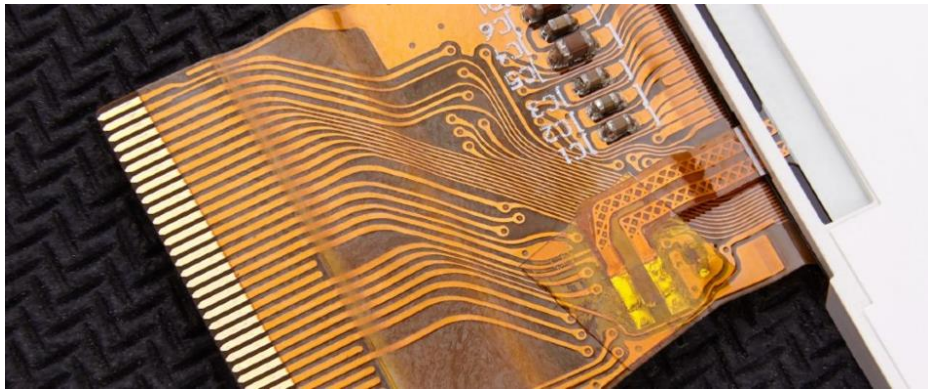
Polyimide (PI)



In the first stage, conducted in a polar solvent, a high molar mass polyamic acid is produced. In the second, high temperature is used to facilitate removal of the water and any residual solvent from the earlier reaction.

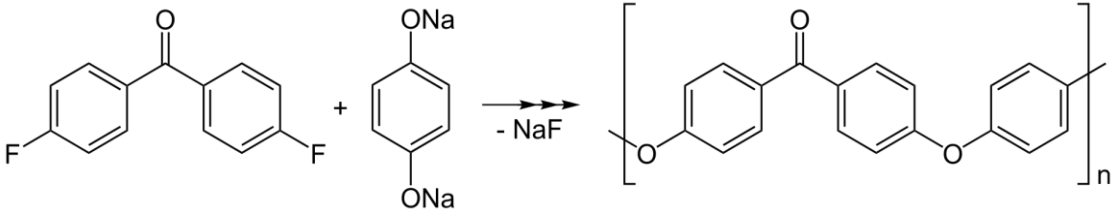


Kapton

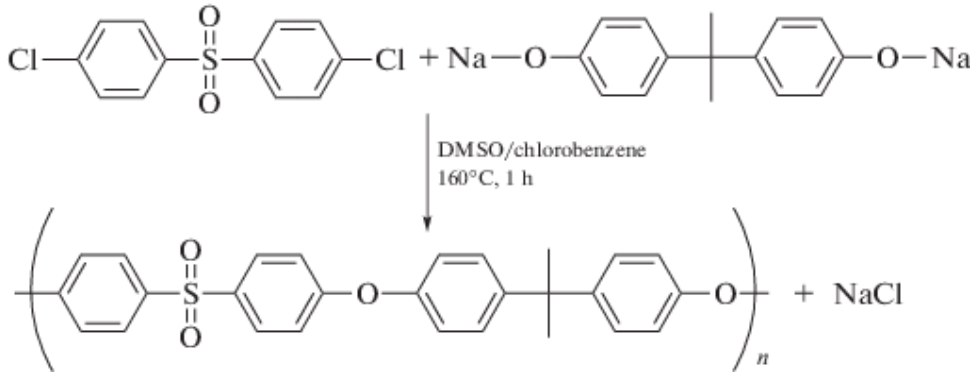


High heat-resistance (T_g > 300°C)

Aromatic Polyethers



Polyether ether ketone (PEEK)



Polysulfone (PSU)

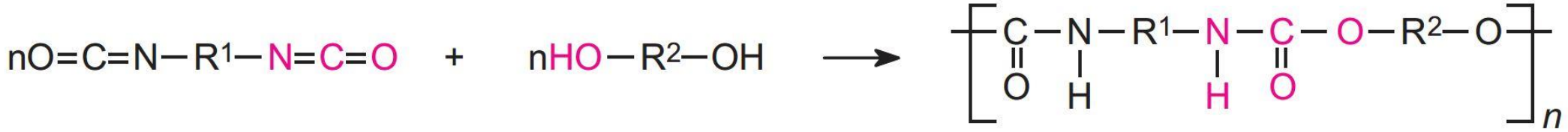
Polymerization is typically conducted in polar aprotic solvent (e.g., DMSO) at high temperature

PEEK parts

Polysulfone membrane filters

- Amorphous (T_g ~ 230°C)
- Good mechanical properties
- Acid/base/oxidant resistance

Polyurethane (PU)

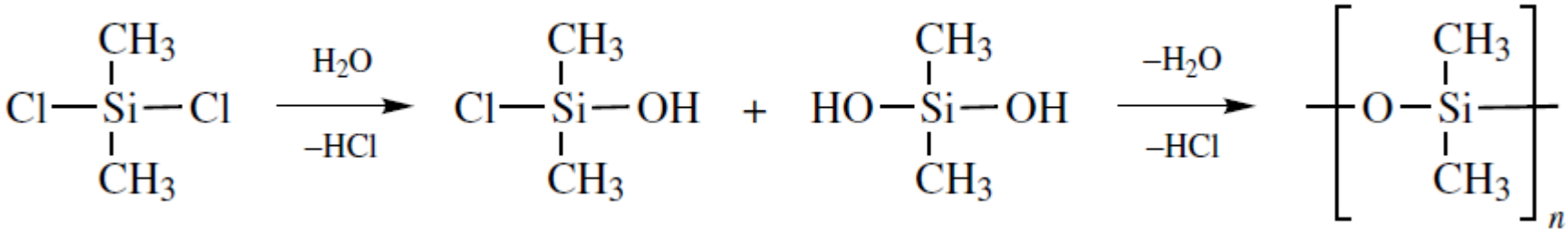


isocyanate carbamate

Solution polymerization is used since the reaction is highly exothermic.

The rich choice of R^1 and R^2 produces polyurethanes with various chemical structures, leading to many different applications.

Polysiloxanes ("Silicones")



Polydimethylsiloxane (PDMS)

The reaction can be carried out in acidic or basic conditions depending on the desired product molecular weight.

Lubricant

Oil bath

- Have very good low-temperature flexibility because of the low T_g value (-127 °C)
- Very stable to high temperature, oxidation, chemical and biological environments