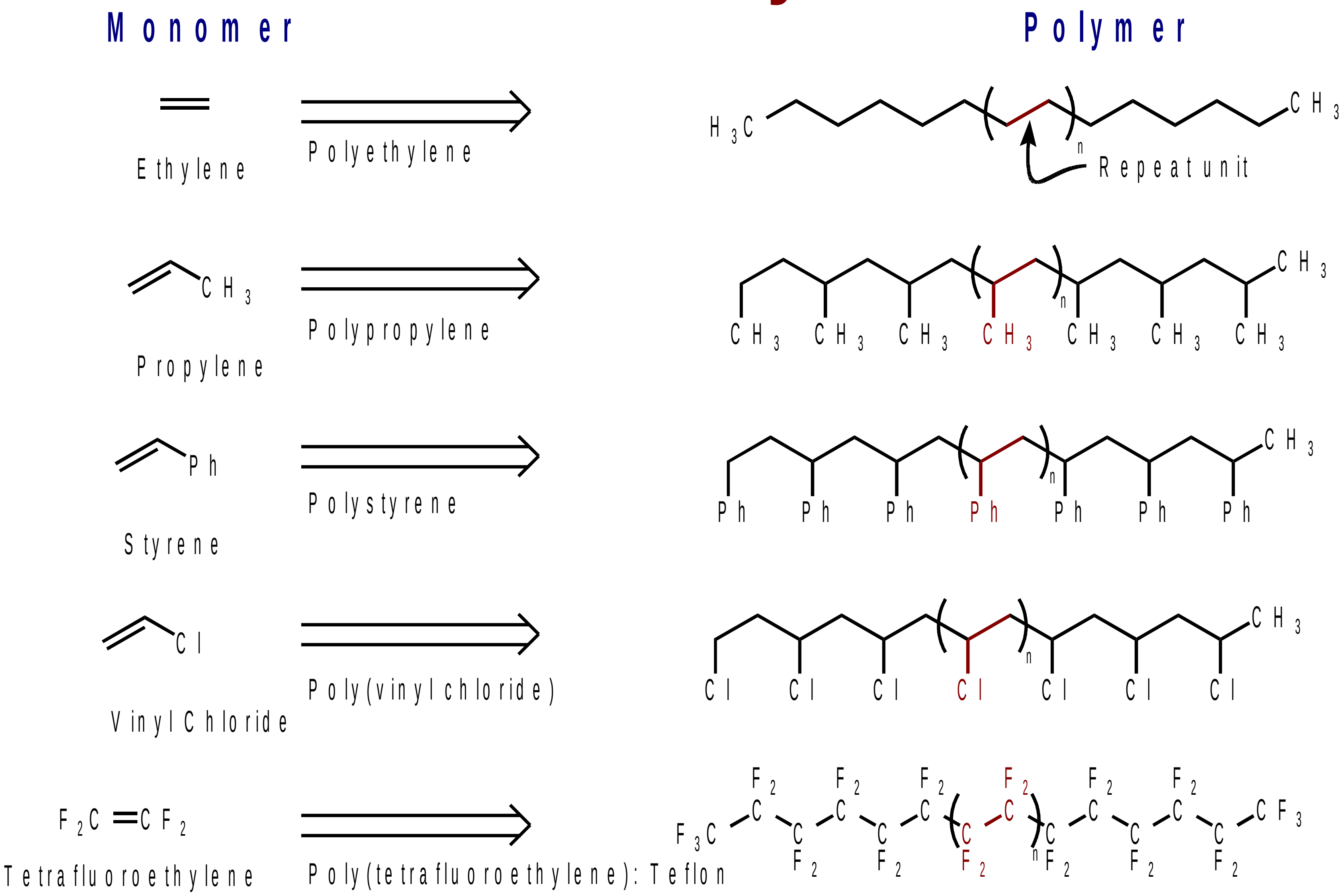
Polymers: Introduction

- Polymer: High molecular weight molecule made up of a small repeat unit (monomer).
  - A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A
- Monomer: Low molecular weight compound that can be connected together to give a poymer
- Oligomer: Short polymer chain
- Copolymer: polymer made up of 2 or more monomers
  - Random copolymer: A-B-B-A-A-B-A-B-A-B-B-B-A-A-B
  - Alternating copolymer: A-B-A-B-A-B-A-B-A-B-A-B-A-B
  - Block copolymer: A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B

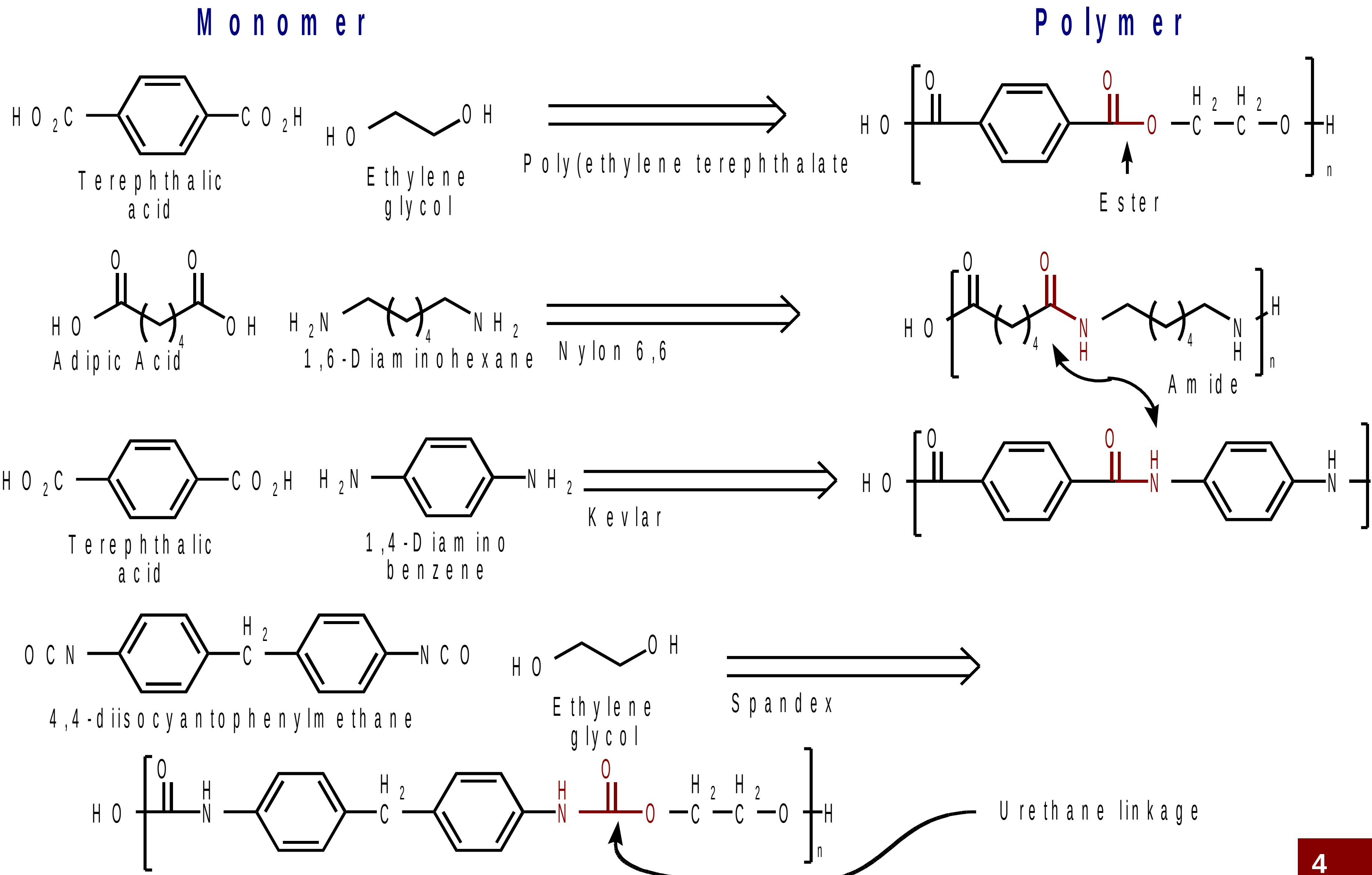
Types of Polymers

- Polymer Classifications
  - Thermoset: cross-linked polymer that cannot be melted (tires, rubber bands)
  - Thermoplastic: Meltable plastic
  - Elastomers: Polymers that stretch and then return to their original form: often thermoset polymers
  - Thermoplastic elastomers: Elastic polymers that can be melted (soles of tennis shoes)
- Polymer Families
  - Polyolefins: made from olefin (alkene) monomers
  - Polyesters, Amides, Urethanes, etc.: monomers linked by ester, amide, urethane or other functional groups
  - Natural Polymers: Polysaccharides, DNA, proteins

Common Polyolefins

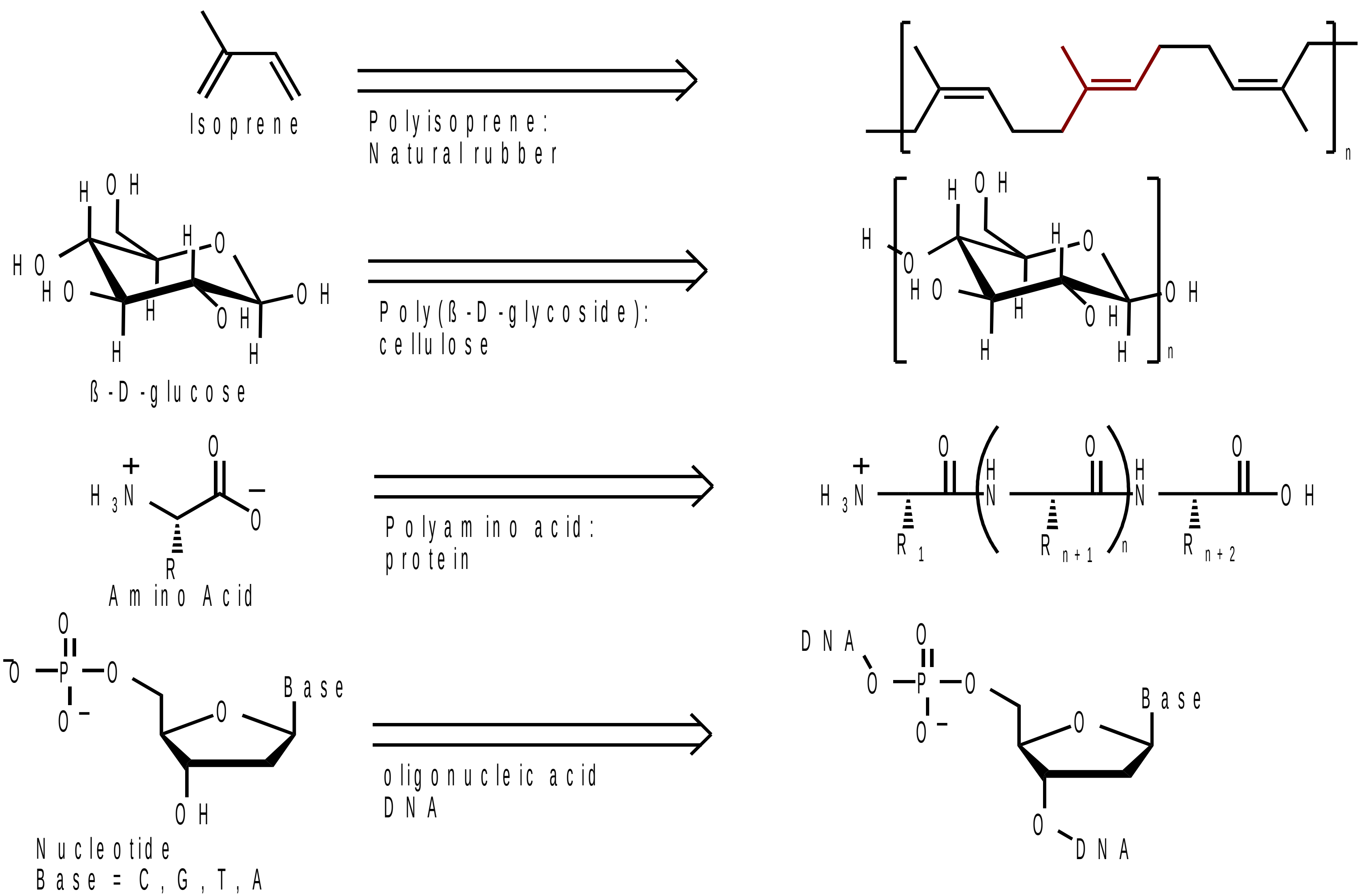


Polyesters, Amides, and Urethanes



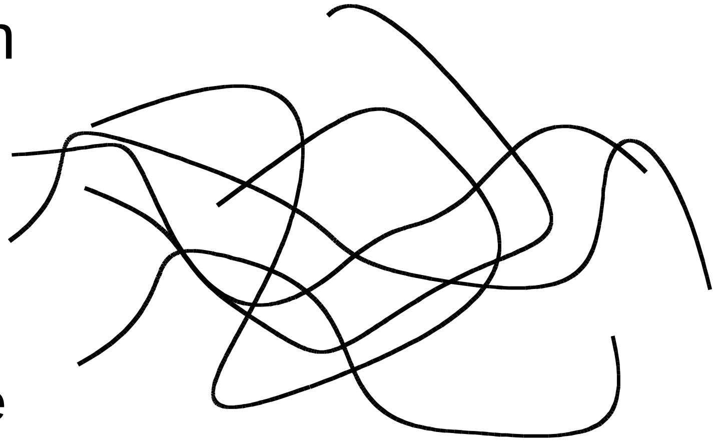
Natural Polymers

Monomer | **Polymer**



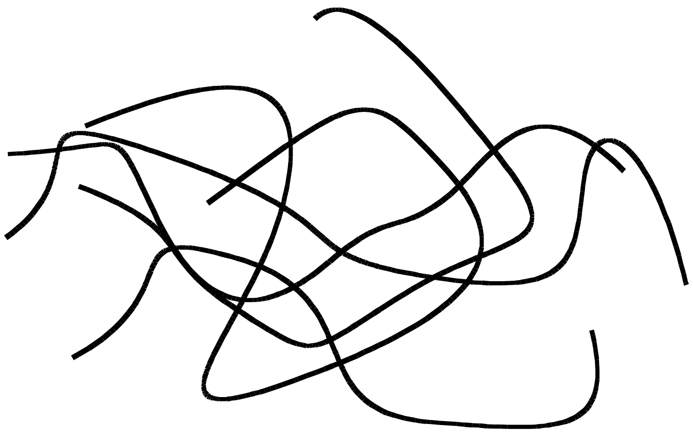
What Makes Polymers Unique?

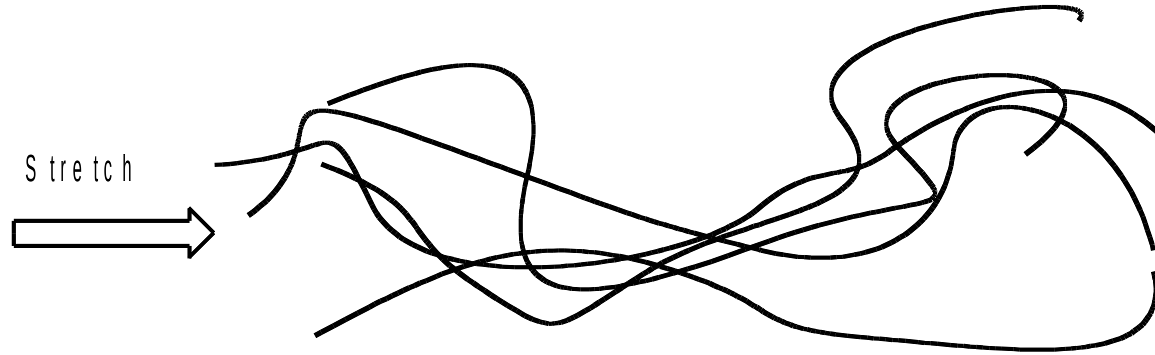
- Really big molecules (macromolecules) like polymers have very different properties than small molecules
  - Chain entanglement: Long polymer chains get entangled with each other.
    - When the polymer is melted, the chains can flow past each other.
    - Below the melting point, the chains can move, but only slowly. Thus the plastic is flexible, but cannot be easily stretched.
    - Below the glass transition point, the chains become locked and the polymer is rigid



Physical Properties

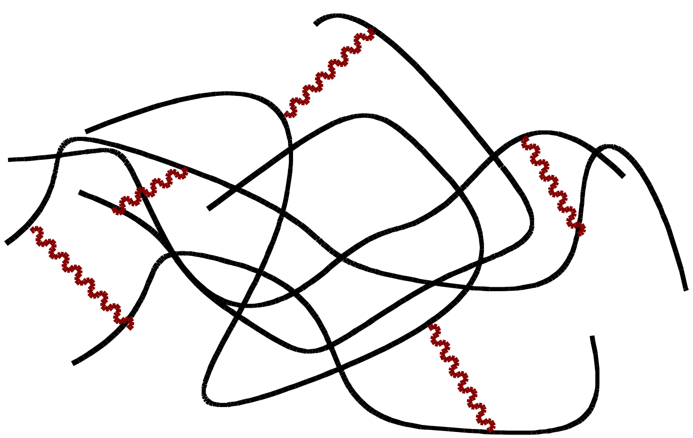
Linear Polymer

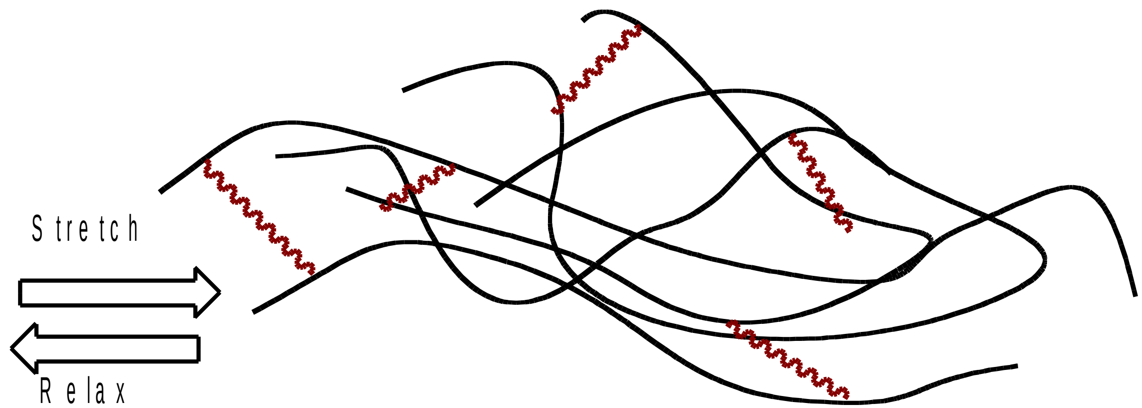




The chains can be stretched, which causes them to flow past each other. When released, the polymer will not return to its original form.

Cross-Linked Polymer



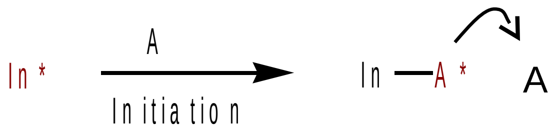


The cross-links hold the chains together. When released, the polymer will return to it's original form.

Polymer Synthesis

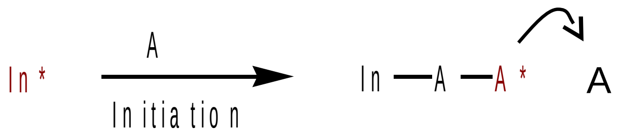
- There are two major classes of polymer formation mechanisms
  - Addition polymerization: The polymer grows by sequential addition of monomers to a reactive site
    - Chain growth is linear
    - Maximum molecular weight is obtained early in the reaction
  - Step-Growth polymerization: Monomers react together to make small oligomers. Small oligomers make bigger ones, and big oligomers react to give polymers.
    - Chain growth is exponential
    - Maximum molecular weight is obtained late in the reaction

Addition Polymerization



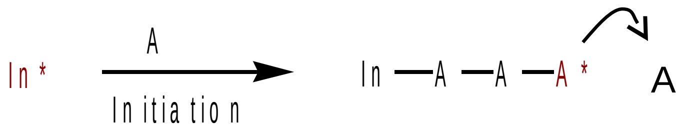
Addition Polymerization

Propagation

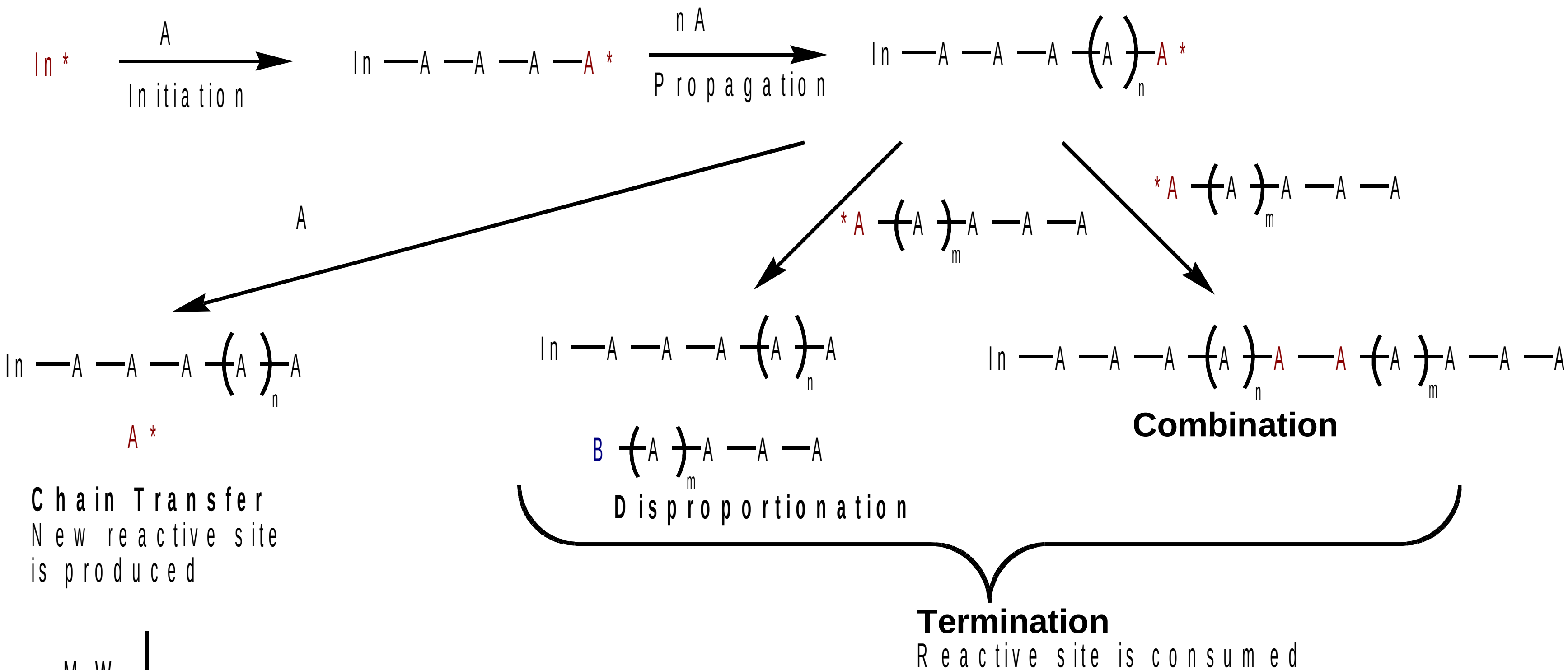


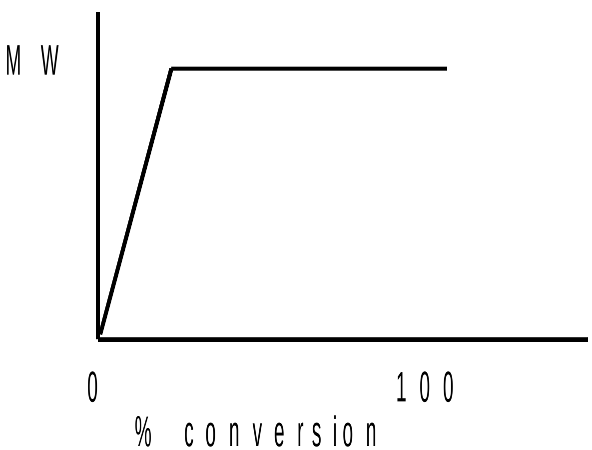
Addition Polymerization

Propagation



Addition Polymerization

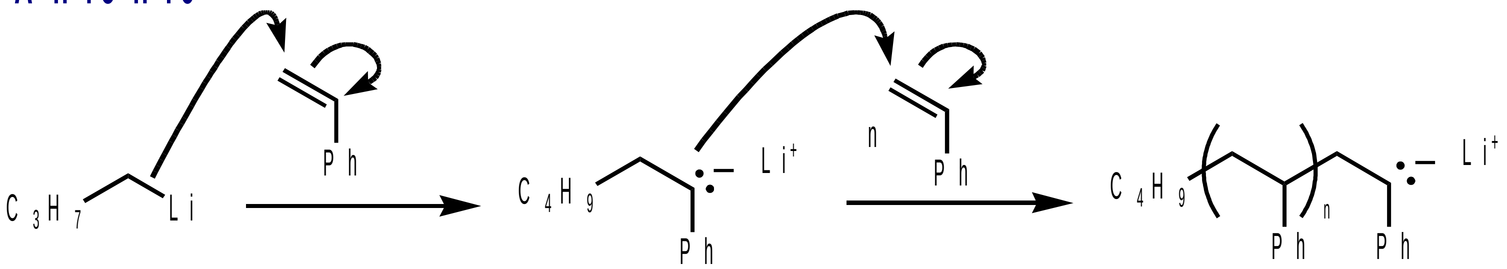




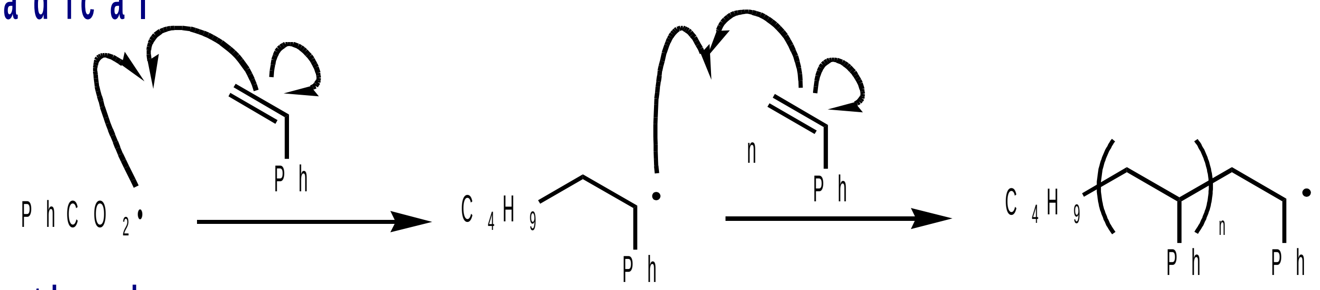
$$MW \propto \frac{k_{propagation}}{k_{termination}}$$

Types of Addition Polymerizations

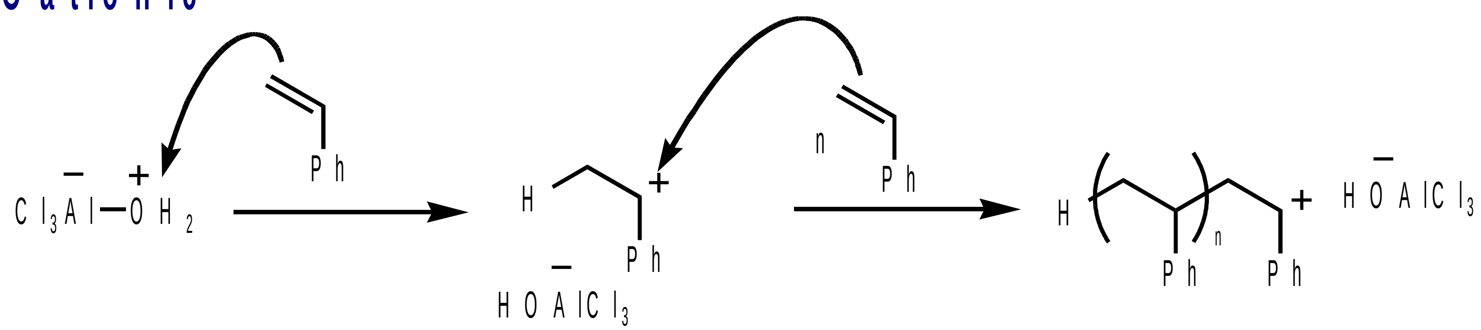
Anionic



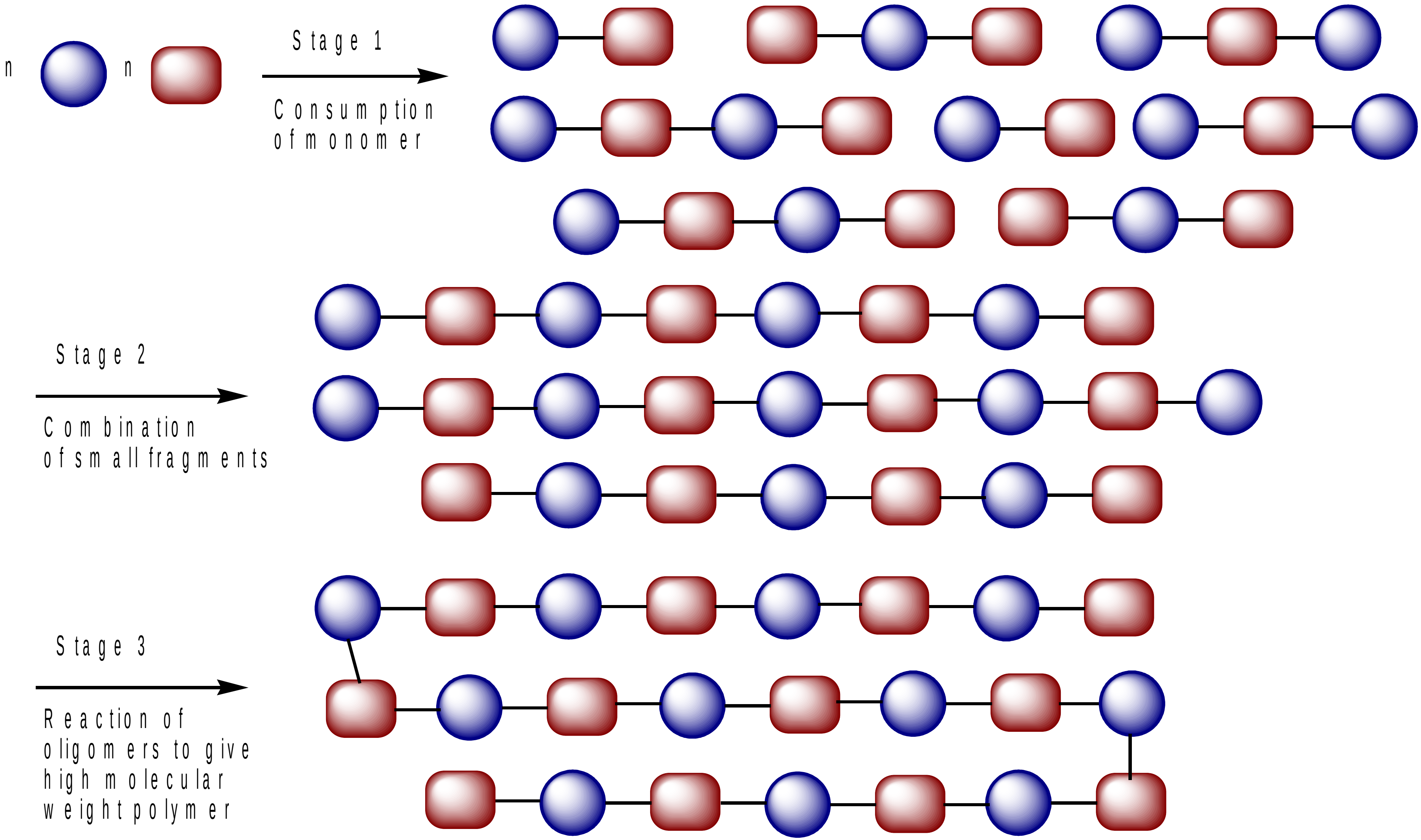
Radical



Cationic

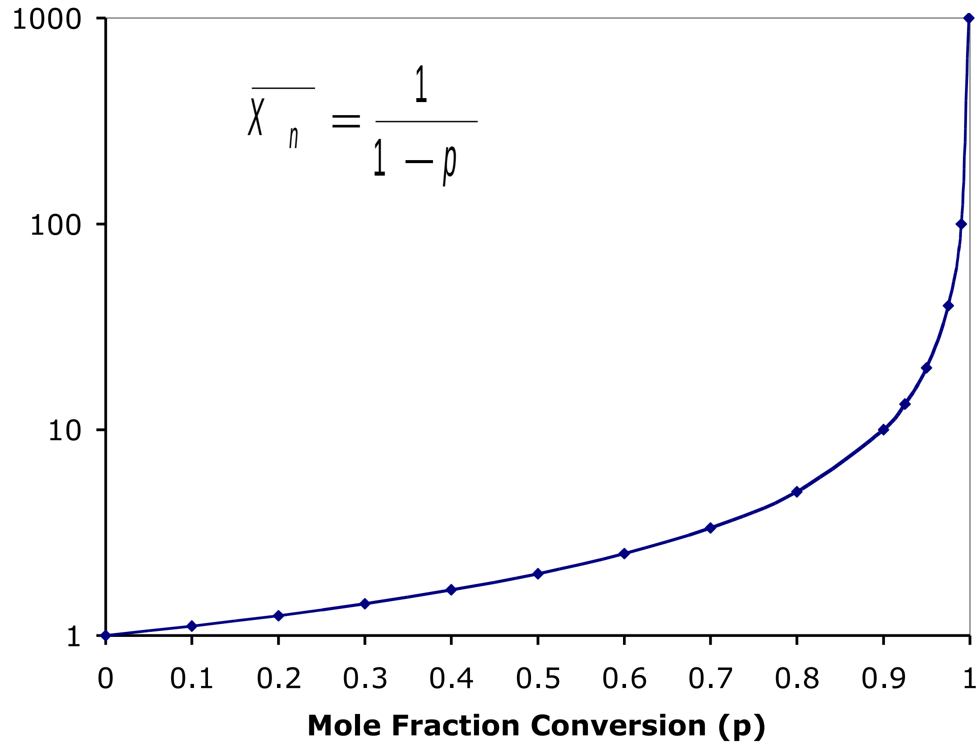


Step-Growth Polymerization



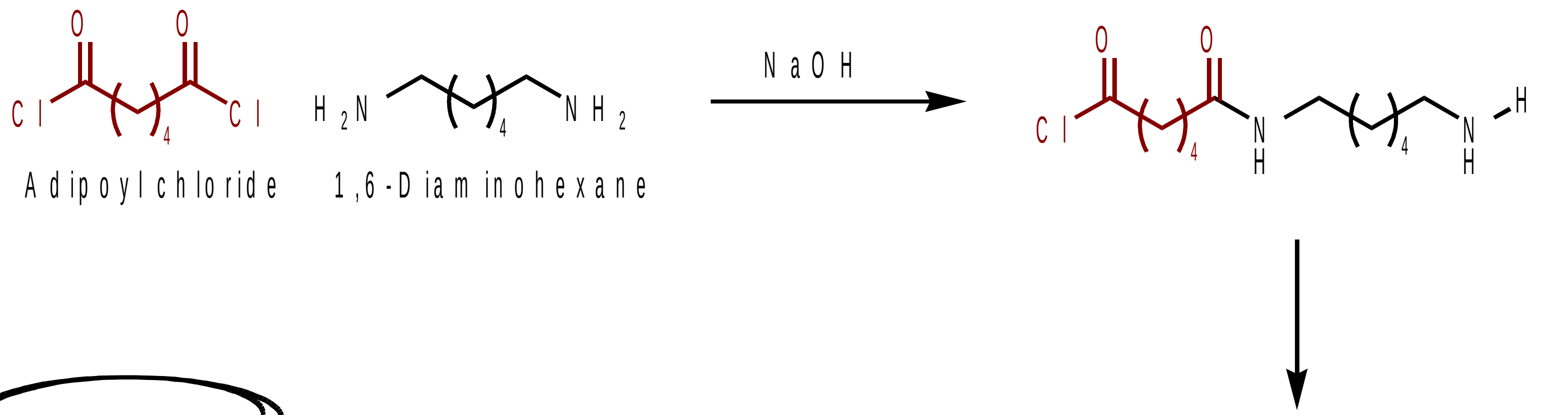
Step-Growth Polymerization

- Because high polymer does not form until the end of the reaction, high molecular weight polymer is not obtained unless high conversion of monomer is achieved.

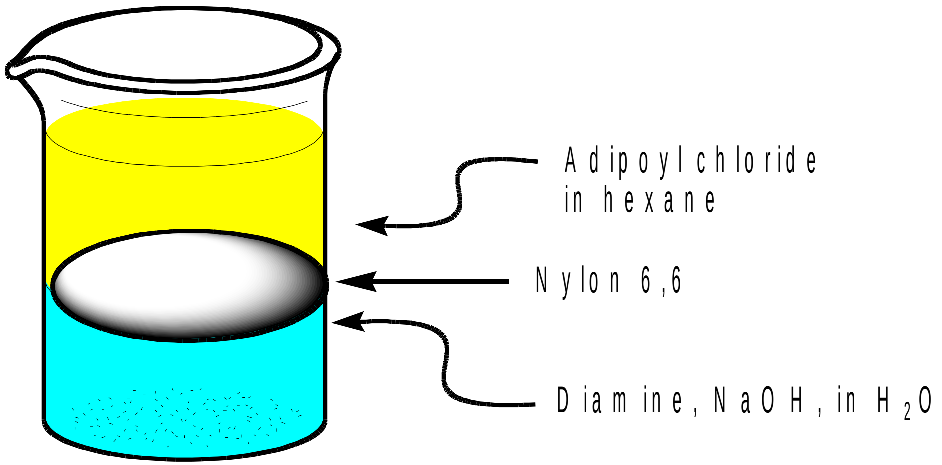


$\overline{X}_n$ = Degree of polymerization
p = mole fraction monomer conversion

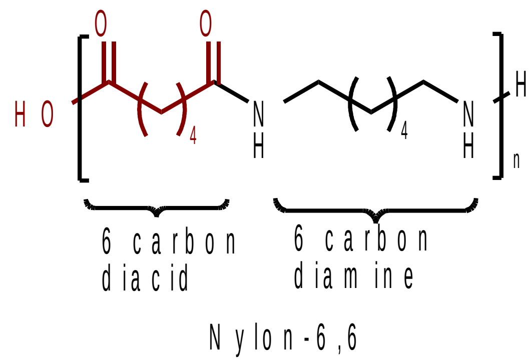
Nylon-6,6



O O
Cl Cl
4
H2N NH2
Adipoyl chloride
1,6-Diaminohexane
NaOH
N H
H



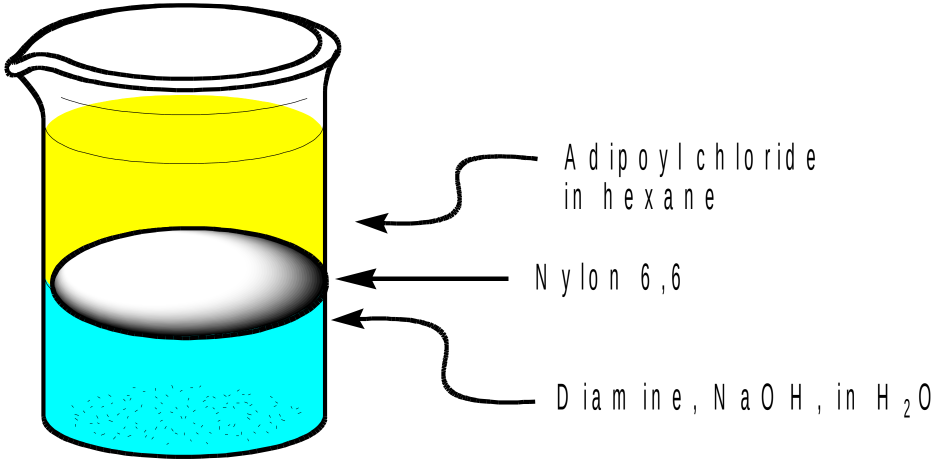
Adipoyl chloride in hexane
Nylon 6,6
Diamine, NaOH, in H2O

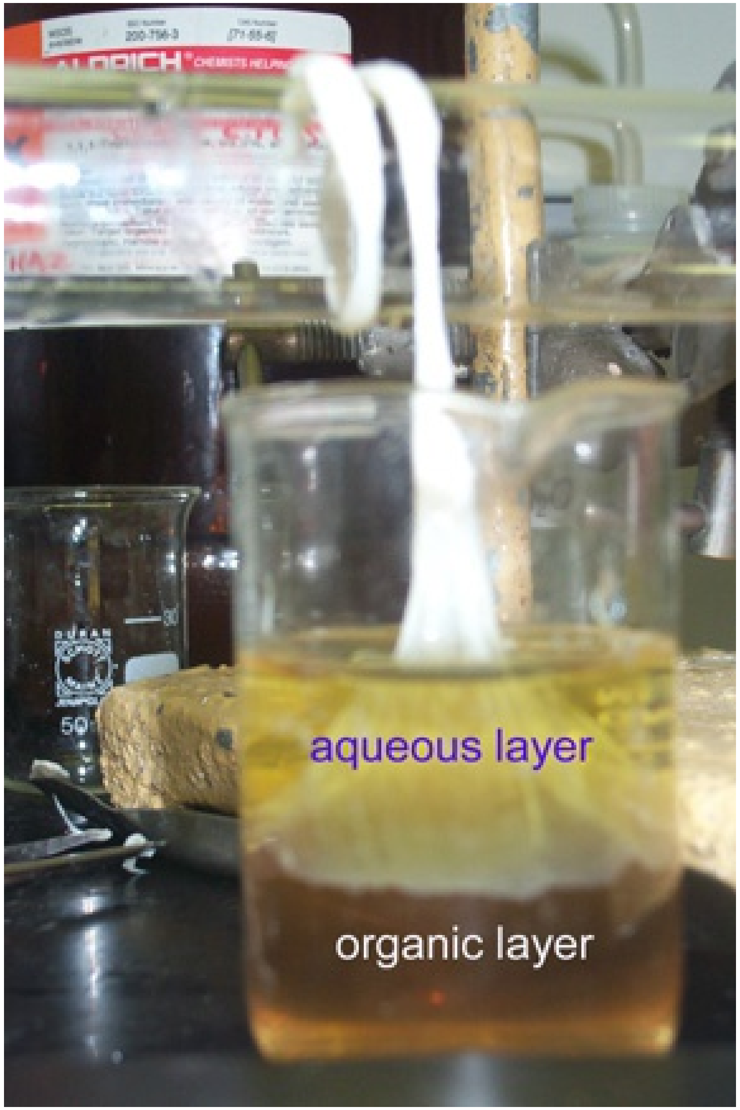


HO
O O
N H
H
n
6 carbon diacid
6 carbon diamine
Nylon-6,6

Nylon-6,6

Since the reactants are in different phases, they can only react at the phase boundary. Once a layer of polymer forms, no more reaction occurs. Removing the polymer allows more reaction to occur.

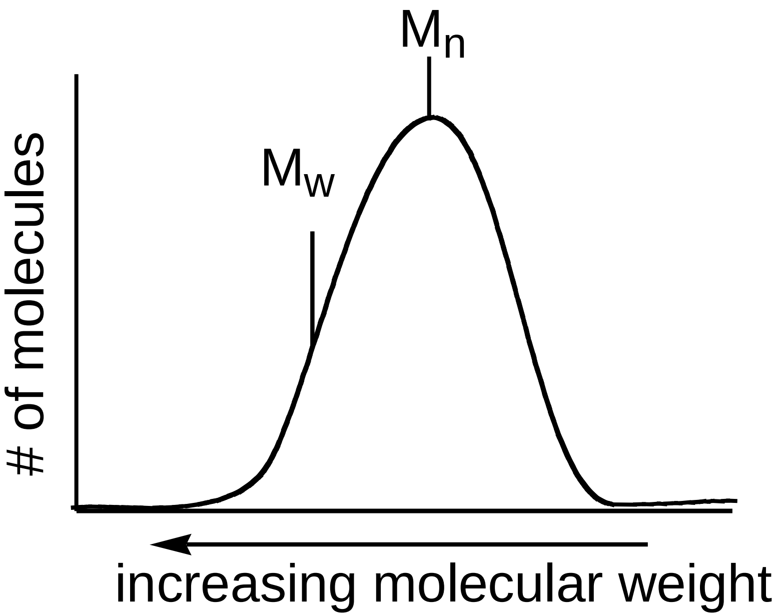




Molecular Weight of Polymers

Unlike small molecules, polymers are typically a mixture of differently sized molecules. Only an average molecular weight can be defined.

- Measuring molecular weight
  - Size exclusion chromatography
  - Viscosity
- Measurements of average molecular weight (M.W.)
  - Number average M.W. (M_n): Total weight of all chains divided by # of chains
  - Weight average M.W. (M_w): Weighted average. Always larger than M_n



What the Weights Mean

M_n: This gives you the true average weight

Let's say you had the following polymer sample:

2 chains:	1,000,000 Dalton	2,000,000
5 chains:	700,000 Dalton	3,500,000
10 chains:	400,000 Dalton	4,000,000
4 chains:	100,000 Dalton	400,000
2 chains:	50,000 Dalton	100,000
		10,000,000

10,000,000/23 = 435,000 Dalton

1 Dalton = 1 g/Na

Weight Average Molecular Weight

M_w: Since most of the polymer mass is in the heavier fractions, this gives the average molecular weight of the most abundant polymer fraction by mass.

$$\frac{2,000,000}{10,000,000} = 0.20 \times 1,000,000 = 200,000$$

$$\frac{3,500,000}{10,000,000} = 0.35 \times 700,000 = 245,000$$

$$\frac{4,000,000}{10,000,000} = 0.40 \times 400,000 = 160,000$$

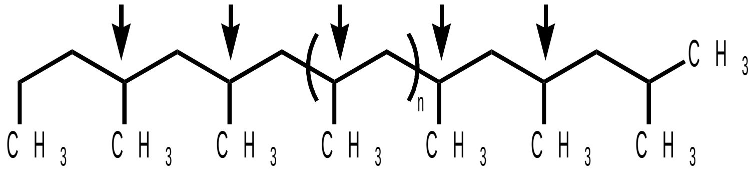
$$\frac{400,000}{10,000,000} = 0.04 \times 100,000 = 4,000$$

$$\frac{100,000}{10,000,000} = 0.01 \times 50,000 = 500$$

$$\text{Total} = 609,500$$

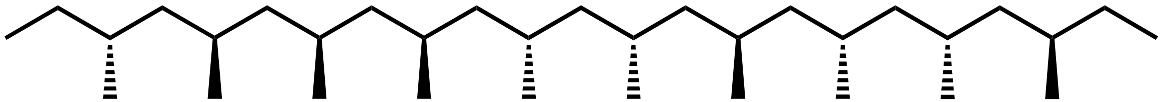
Polymer Microstructure

Polyolefins with side chains have stereocenters on every other carbon

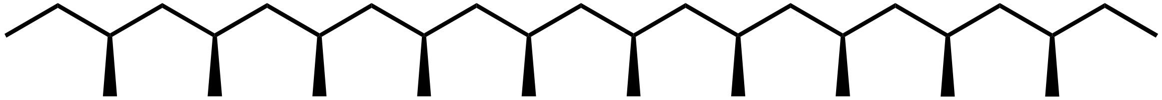


With so many stereocenters, the stereochemistry can be complex. There are three main stereochemical classifications for polymers.

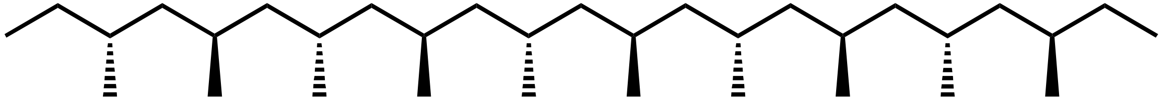
Atactic: random orientation



Isotactic: All stereocenters have same orientation



Syndiotactic: Alternating stereochemistry



Why is this important?

- Tacticity affects the physical properties
  - Atactic polymers will generally be amorphous, soft, flexible materials
  - Isotactic and syndiotactic polymers will be more crystalline, thus harder and less flexible
- Polypropylene (PP) is a good example
  - Atactic PP is a low melting, gummy material
  - Isoatactic PP is high melting (176º), crystalline, tough material that is industrially useful
  - Syndiotactic PP has similar properties, but is harder to synthesize