Lecture 26

Paul J Flory
1910-1985

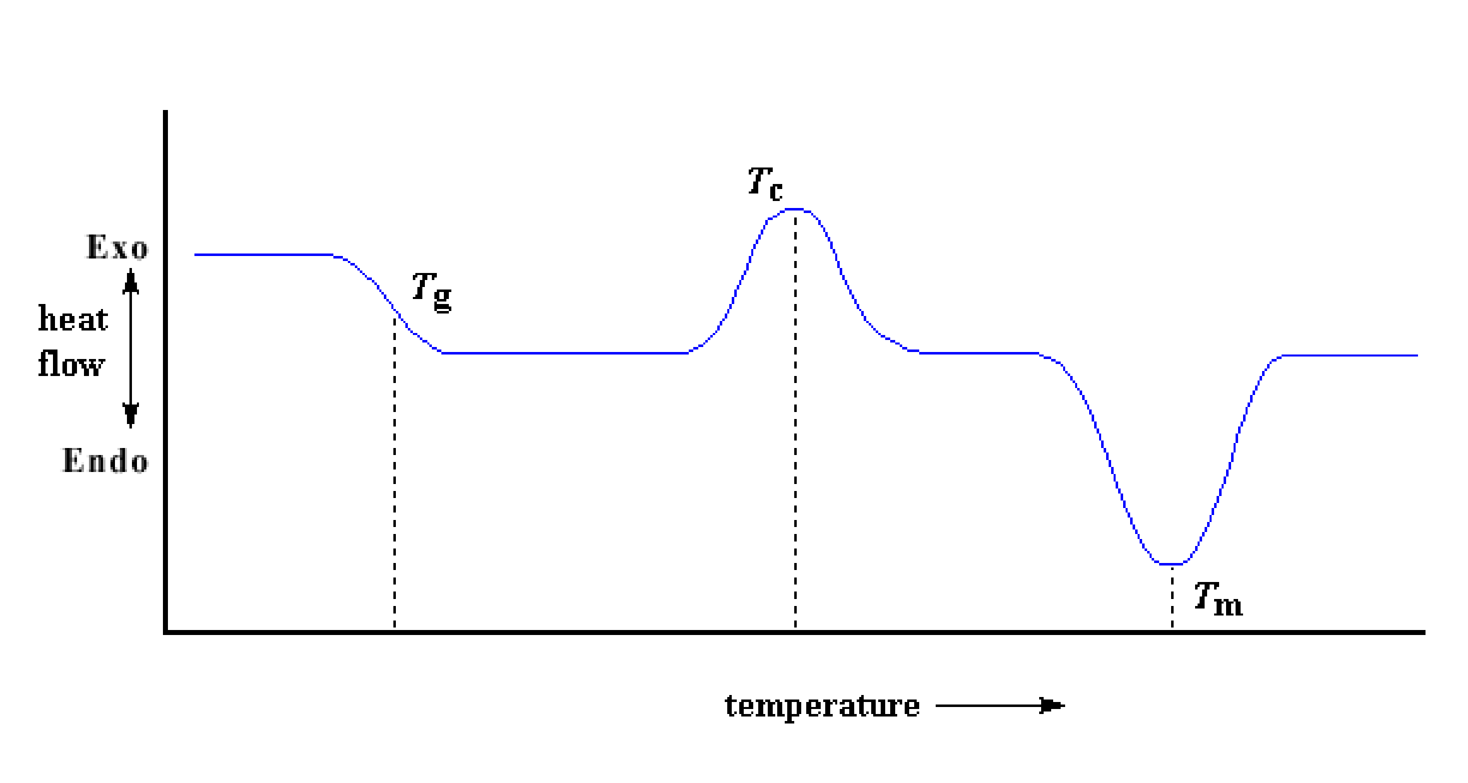
The Nobel Prize in Chemistry 1974

"for his fundamental achievements, both theoretical and experimental, in the physical chemistry of the macromolecules"

Morphology

- Amorphous polymers are referred to as glassy polymers
  - they lack crystalline domains that scatter light and are transparent….Poly(methyl methacrylate)
  - they are weaker polymers and generally more flexibility
  - on heating, amorphous polymers are transformed from a hard glass to a soft, flexible, rubbery state
- Glass transition temperature, T_g: the temperature at which a polymer undergoes a transition from a hard glass to a rubbery solid (ca. 100 degrees for polystyrene)

A DSC Plot for PET



Morphology

- Amorphous PET is formed by cooling the melt quickly
  - plastic beverage bottles are PET with a low degree of crystallinity
- By cooling slowly, more molecular diffusion occurs, chains become more ordered and crystalline domains form
  - PET with a high degree of crystallinity can be drawn into textile fibers and tire cords (dacron)

Classification

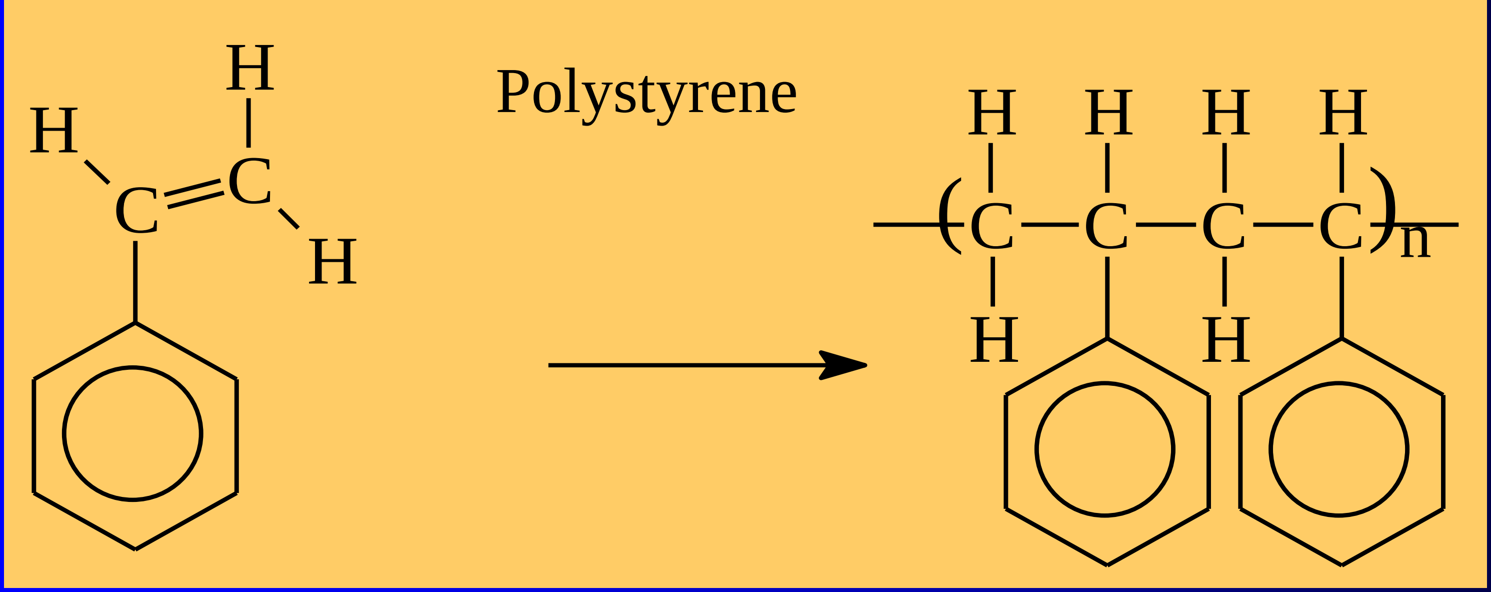
Order out of chaos

- Condensation Polymers
- Addition Polymers

Carothers, W.H., J. Am. Chem. Soc. 1929, *51*, 2548-58

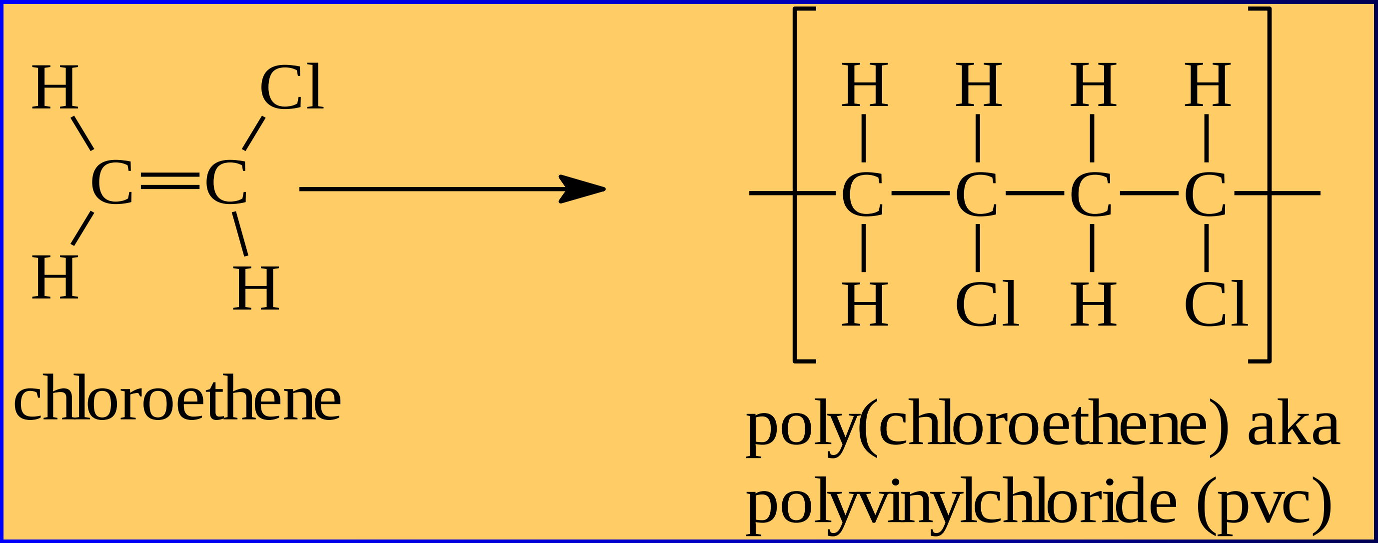
Addition polymer

- Empirical formula is unchanged



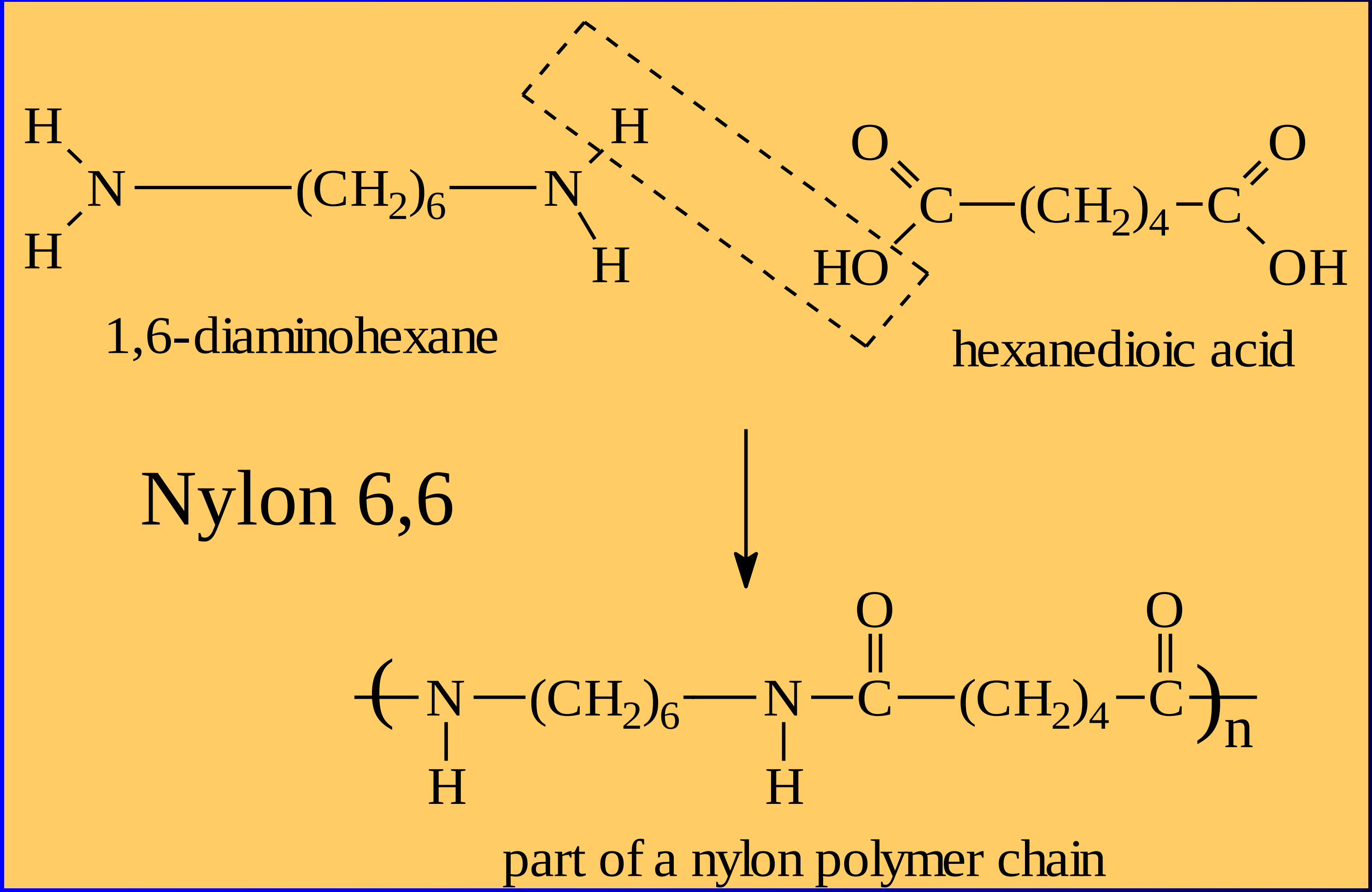
Addition Polymer

- This is easy, basically open out the double bond.

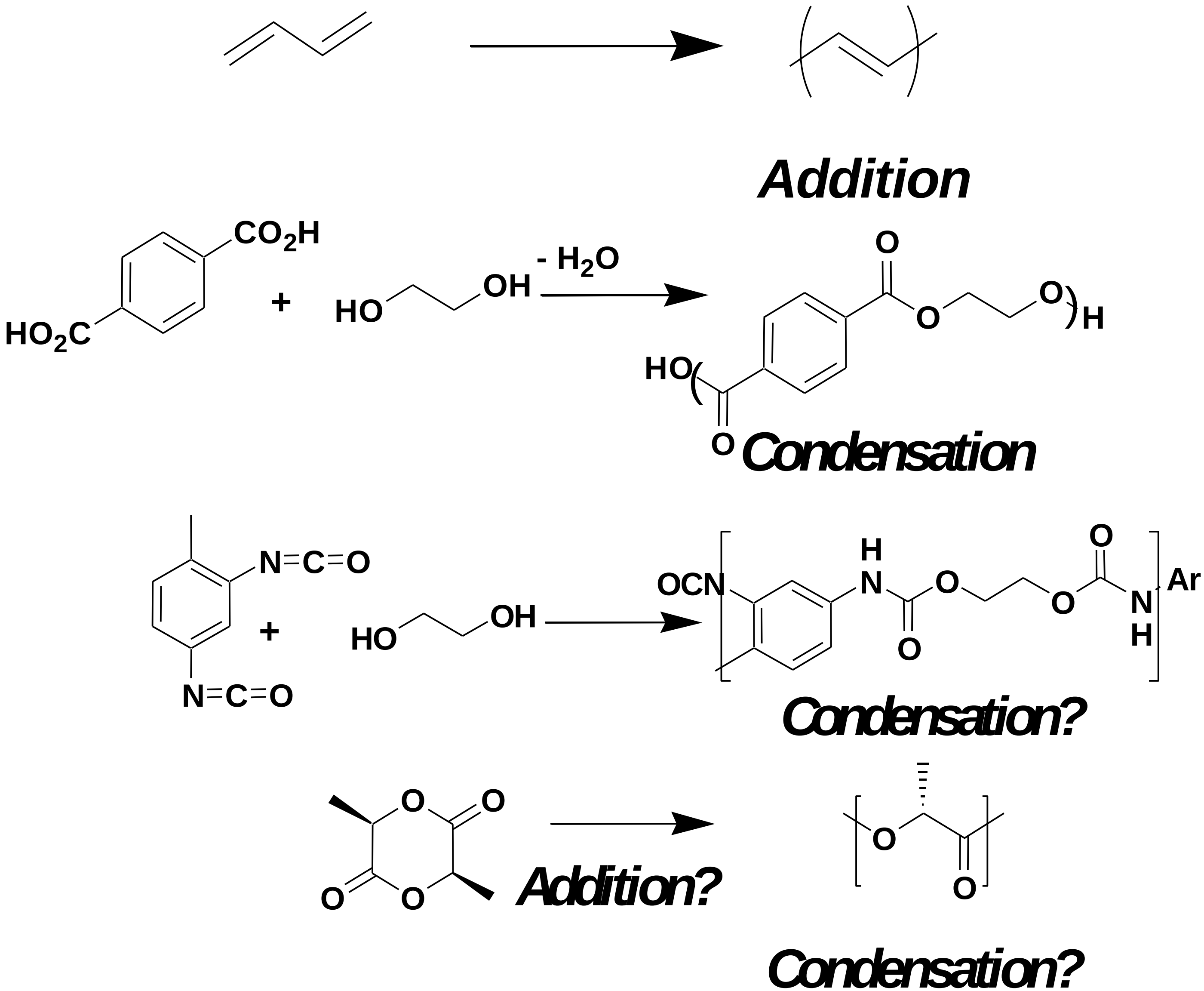


Condensation Polymer

- Empirical formula is changed…stuff is lost!



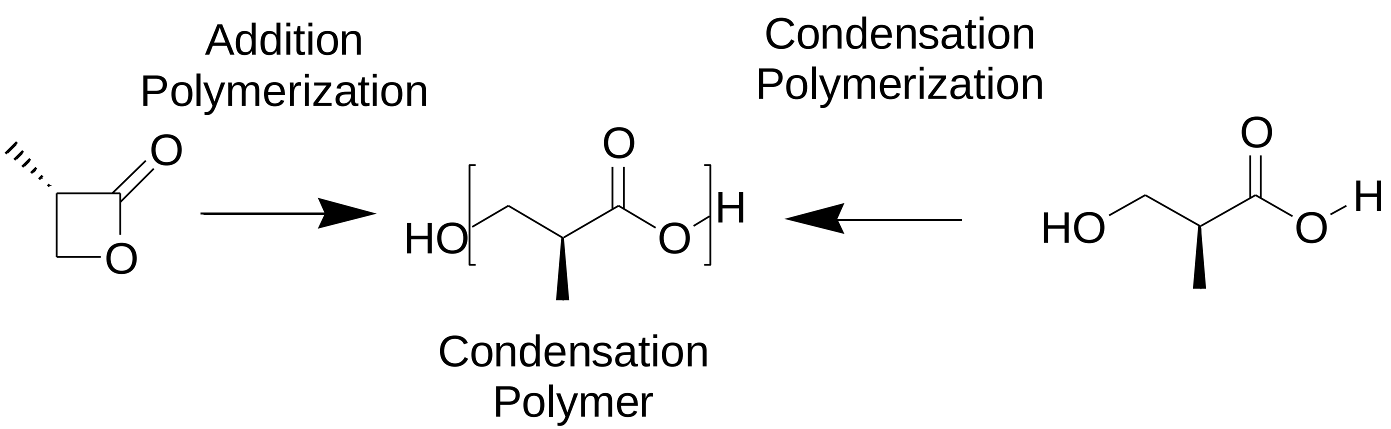
Problems with Carothers Definition



Paul J Flory 1910-1985

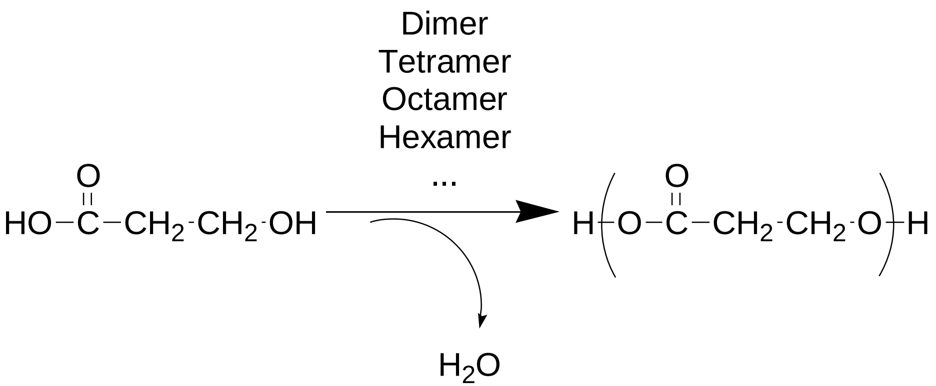
Flory Clears Things Up

We need to classify based on the mechanism, the process rather than the product.

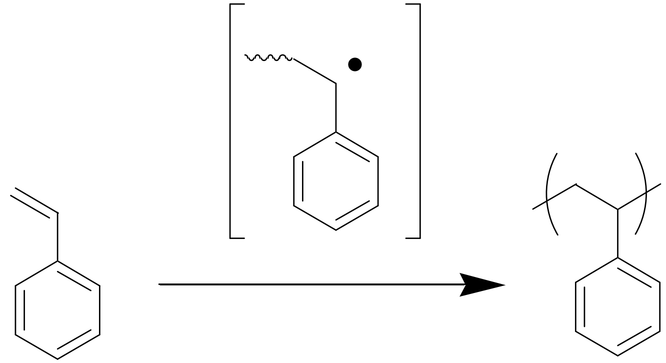


Basic Types of Polymerization Mechanisms

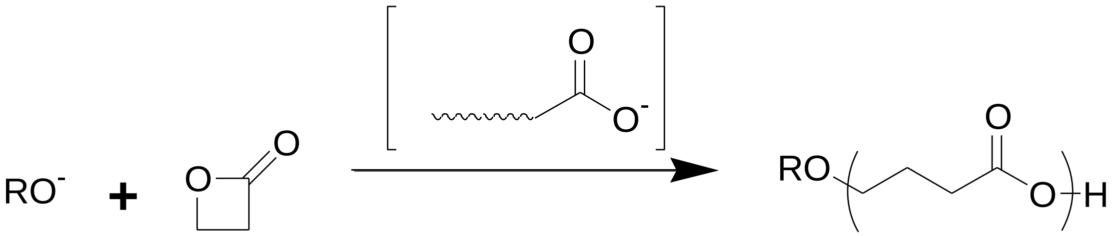
Step-growth



Chain-growth



Ring-opening



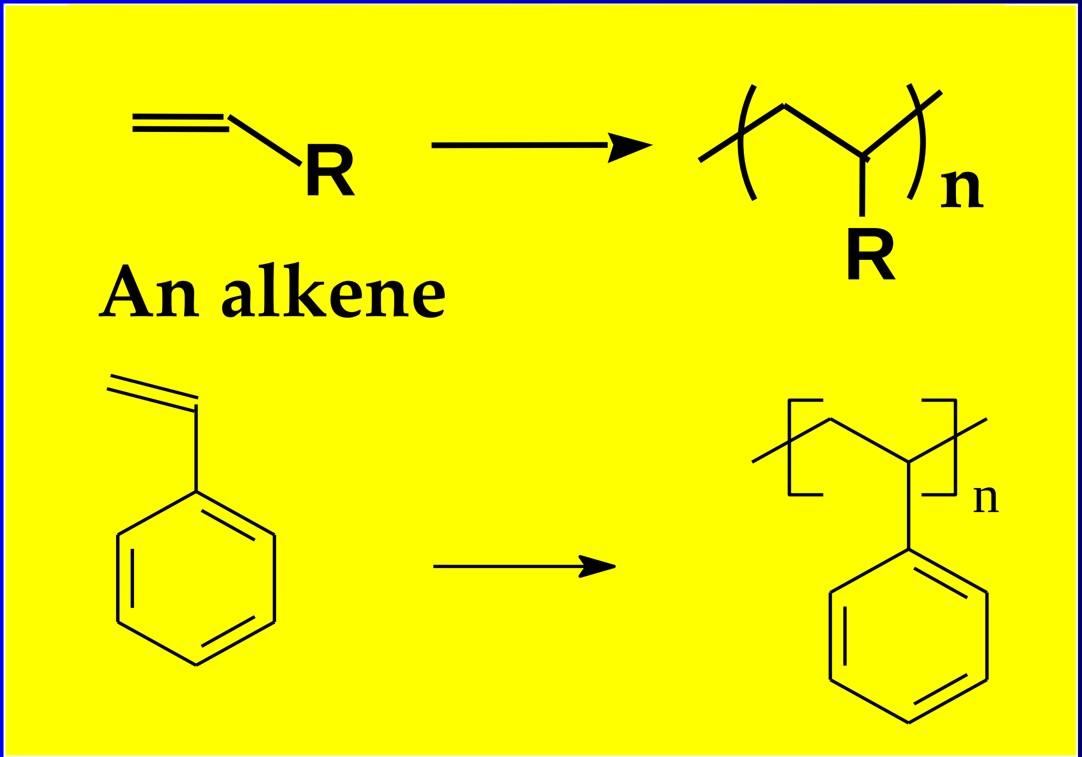
Chain-Growth Polymers

- **Chain-growth polymerization:** a polymerization that involves sequential addition reactions, either to unsaturated monomers or to monomers possessing other reactive functional groups

- Reactive intermediates in chain-growth polymerizations include radicals, carbanions, carbocations, and organometallic complexes

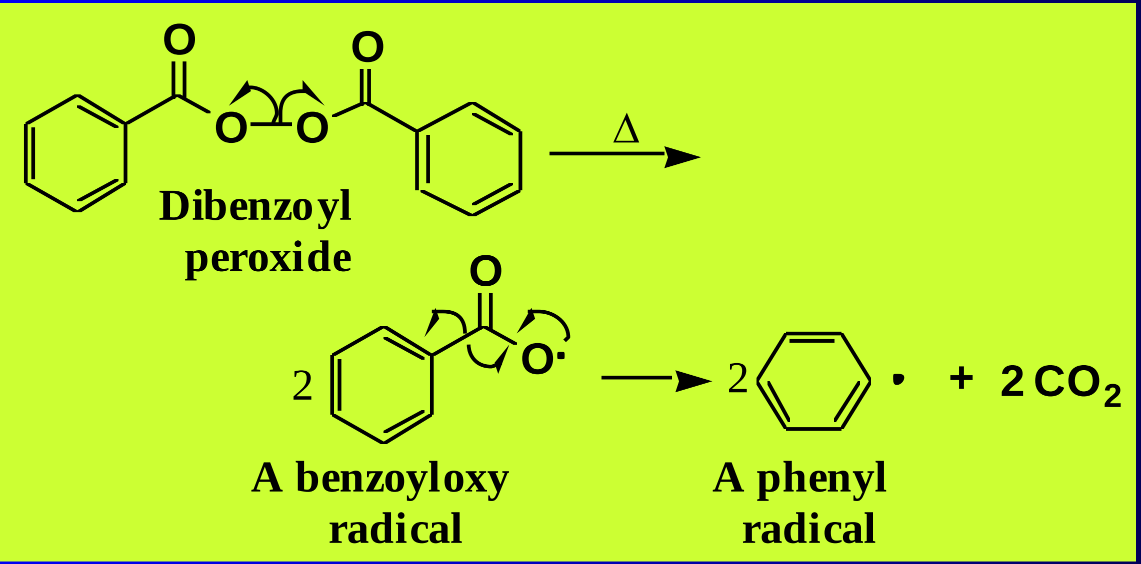
Chain-Growth Polymers

- We will concentrate on chain-growth polymerizations of ethylene and substituted ethylenes



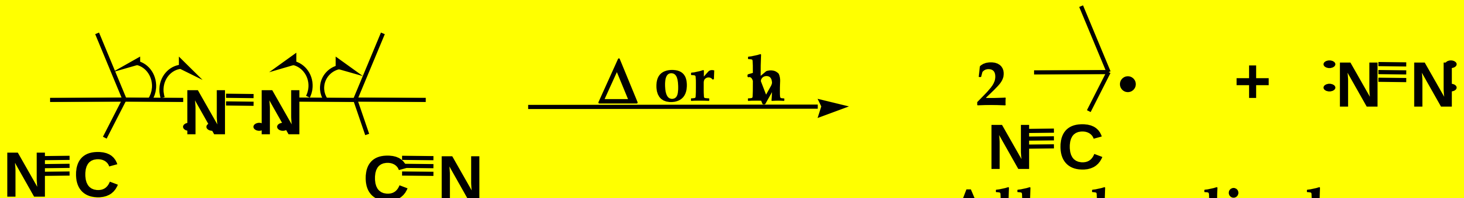
Radical Chain Growth Polymerization

- Among the initiators used for radical chain-growth polymerization are diacyl peroxides, which decompose as shown on mild heating



Radical Chain Growth Polymerization

- Another common class of initiators are azo compounds, which also decompose on mild heating or with absorption of UV light

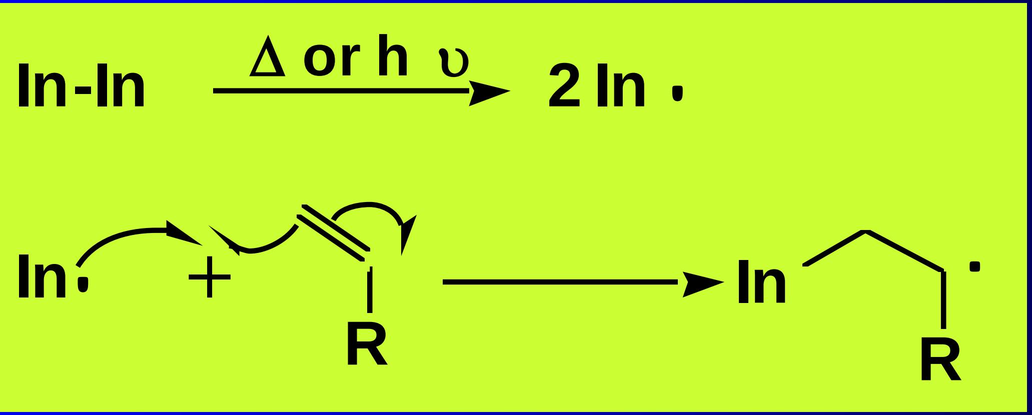


Azoisobutyronitrile (AIBN)

Alkyl radicals

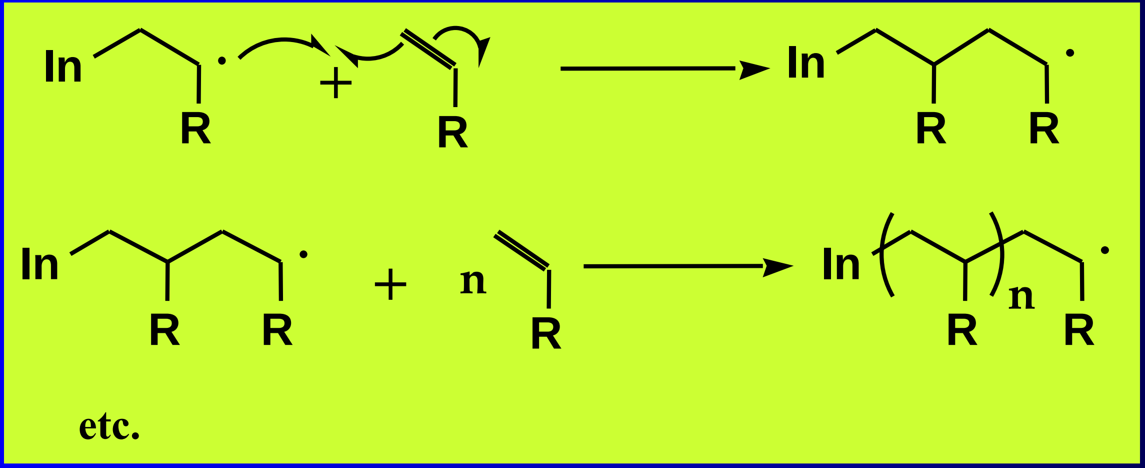
Radical Chain Growth Polymerization

- Chain initiation, chain propagation, and chain termination steps for radical polymerization of a substituted ethylene are shown for the monomer $RCH=CH_2$
  - chain initiation



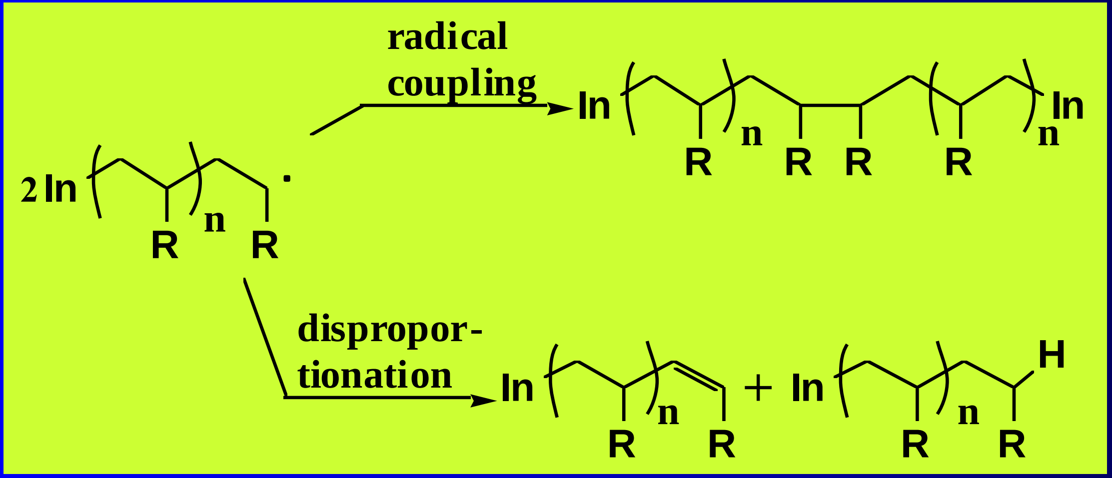
Radical Chain Growth Polymerization

– chain propagation



Radical Chain Growth Polymerization

– Chain termination



Radical Chain-Growth

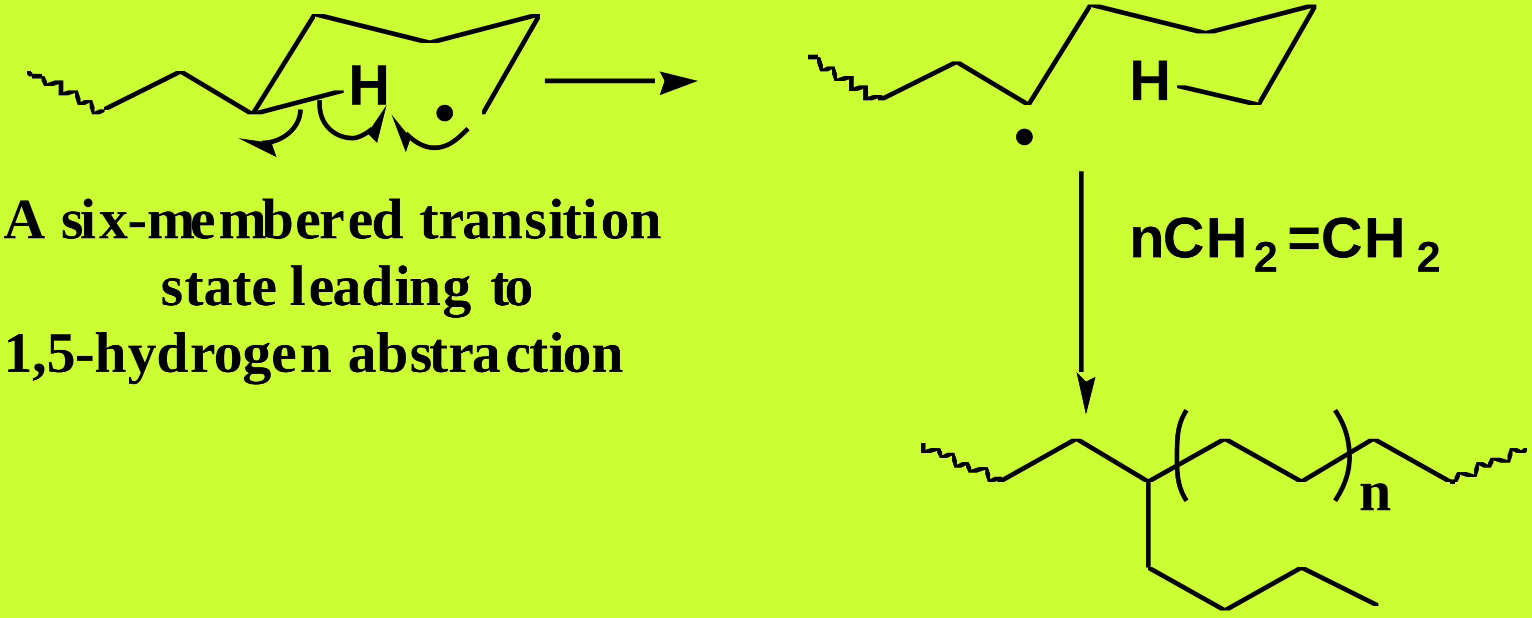
- Chain-transfer reaction: the reactivity of an end group is transferred from one chain to another, or from one position on a chain to another position on the same chain
  - polyethylene formed by radical polymerization exhibits a number of butyl branches on the polymer main chain
  - these butyl branches are generated by a "back-biting" chain transfer reaction in which a 1° radical end group abstracts a hydrogen from the fourth carbon back
  - polymerization then continues from the 2° radical

Polyethylene

- polyethylene played a key role during World War II. It was first used as an underwater cable coating and then as a critical insulating material for radar insulation. It was so light and thin that it made placing radar onto airplanes possible. The substance was a highly guarded secret.
- It was the first plastic in the US to sell more than a billion pounds a year. It is currently the largest volume plastic in the world.

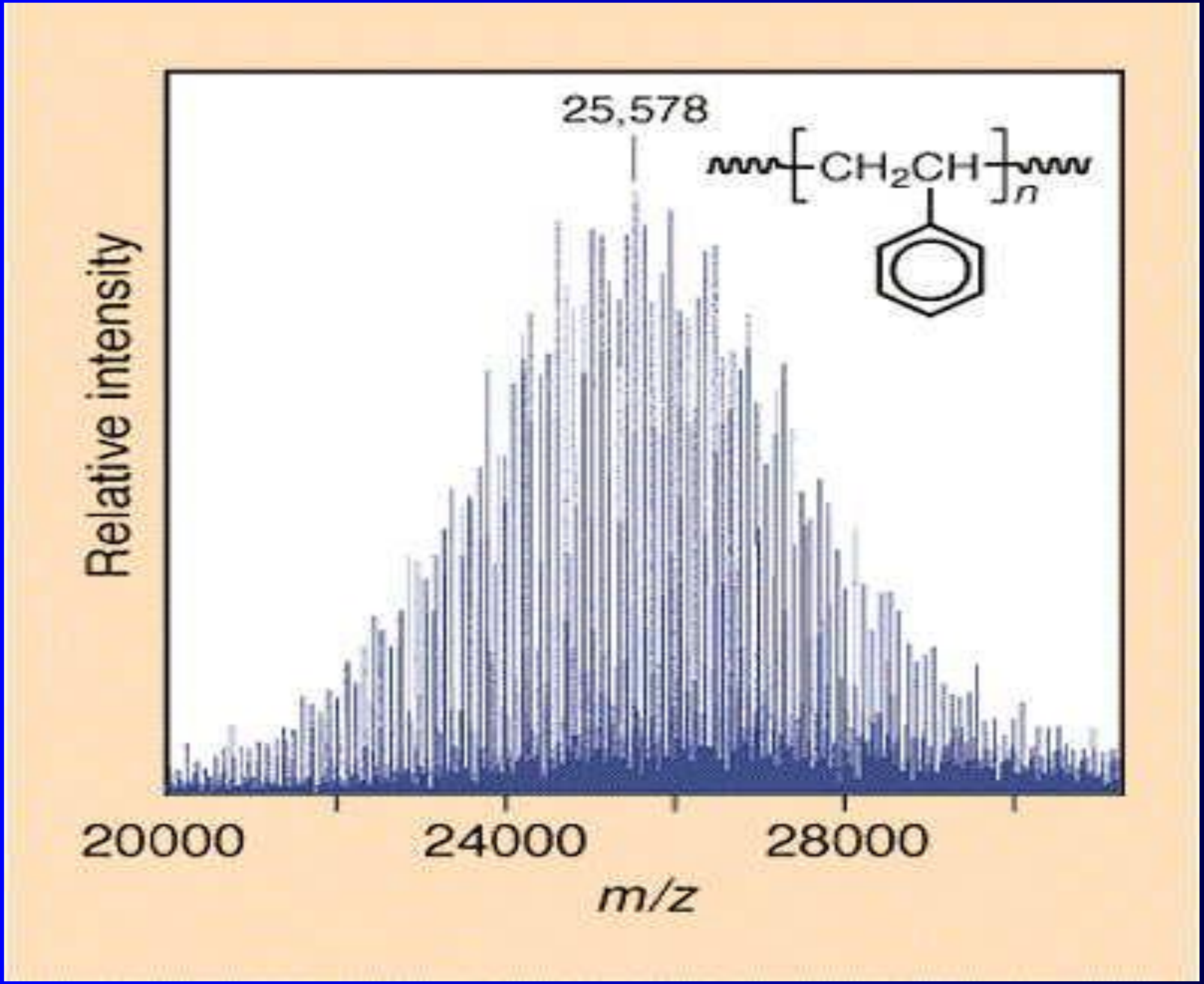
Radical Chain-Growth

Back biting



A six-membered transition state leading to 1,5-hydrogen abstraction

MALDI Mass Spectrum of Polystyrene



Molecular Weight

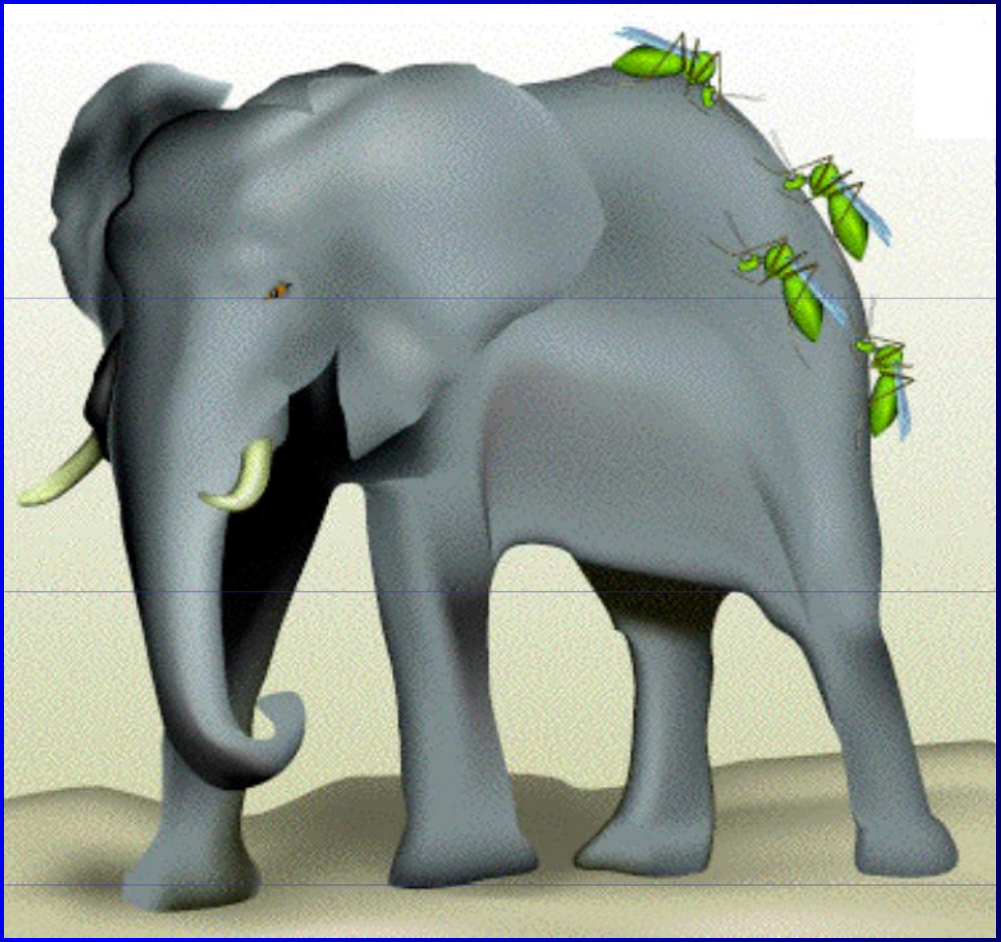
- All polymers are mixtures of individual polymer molecules of variable MWs
  - Number average Mn: count the number of chains of a particular MW, multiply each number by the MW, sum these values, and divide by the total number of polymer chains

$$Mn = \frac{\sum MiNi}{\sum Ni}$$

  - weight average Mw: record the weight of each chain of a particular length, sum these weights, and divide by the total weight of the sample

$$Mw = \frac{\sum WiMi}{\sum Wi} = \frac{\sum NiMi^2}{\sum NiMi}$$

Another silly example



Flies weigh 1.0lb and elephants weigh 2000lbs

Population Weight Calculations

$$Mn = \frac{\sum MiNi}{\sum Ni}$$

$$Mw = \frac{\sum WiMi}{\sum Wi} = \frac{\sum NiMi^2}{\sum NiMi}$$

$$= \frac{4(1) + 1(2000)}{5}$$

$$Mn = 400 \text{ lbs}$$

$$= \frac{4(1)^2 + 1(2000)^2}{2005}$$

$$Mw = 2000\text{lbs}$$

If this population steps on your foot, which is the more "pertinent" average???

Average calculation

Memphis	700,000
Montrose, Co	10,000
Effington, Ill	12,000
Freeman, SD	1,500

$$\Sigma = 723{,}500 / 4 = 180{,}875$$

The average population is 180,875

Weight average calculation

- Fraction of population in Memphis is
  700,000/723,500 = 0.9675
- That is….96.75% of this population lives in Memphis

Weight average calculation

700,000 x (700,000/723,500) = 700,000 x 0.9675 = 677,263

10,000 x (10,000/723,500) = 10,000 x 0.0138 = 138

12,000 x (12,000/723,500) = 12,000 x 0.0166 = 199

1,500 x (1,500/ 723.500) = 1,500 x 0.00207 = 3.2

Σ = 677,603.2

Average person lives in a city of about 677,600

What the Weights Mean

M_n: This gives you the true average molecular 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/mole

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.

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

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

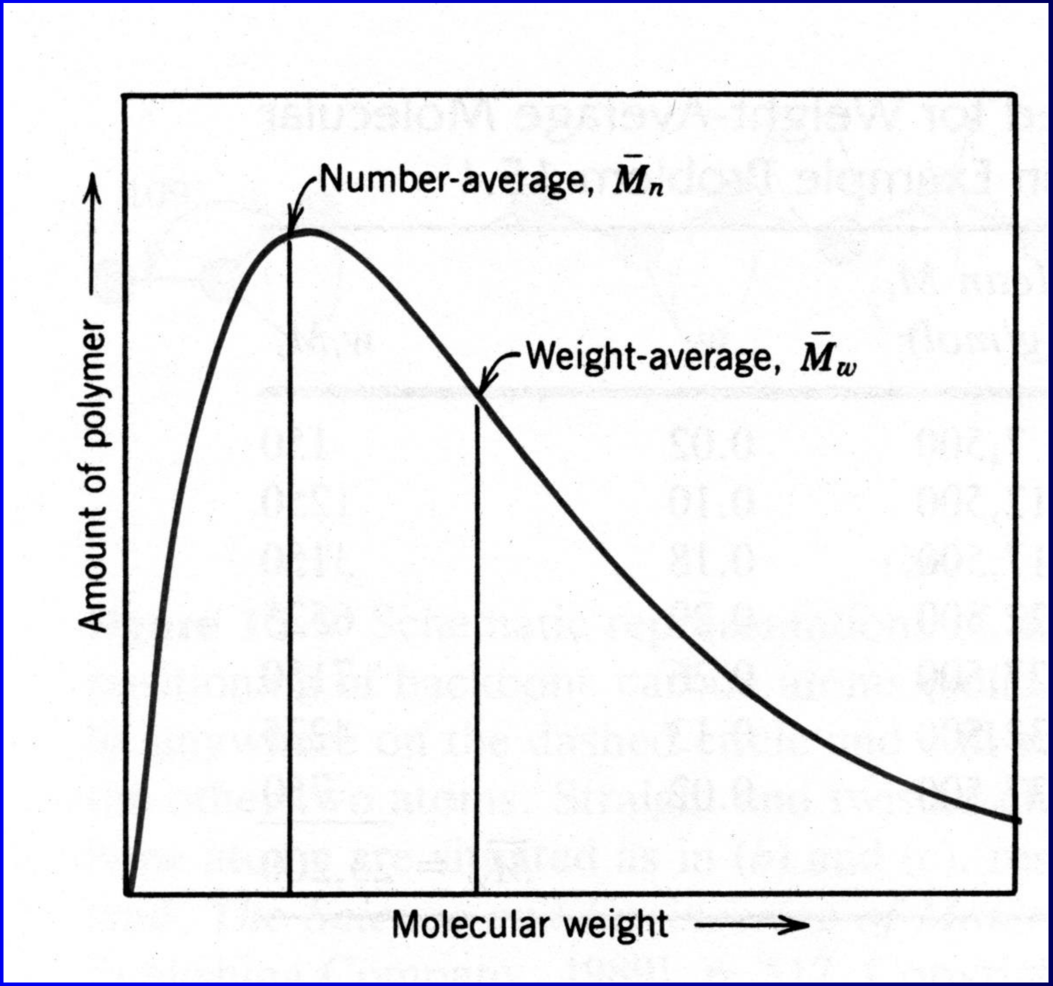
$$\frac{4,000,000}{10,000,000} = 0.40 \times 400,000 = 160,000$$

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

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

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

Distribution of Molecular Weights

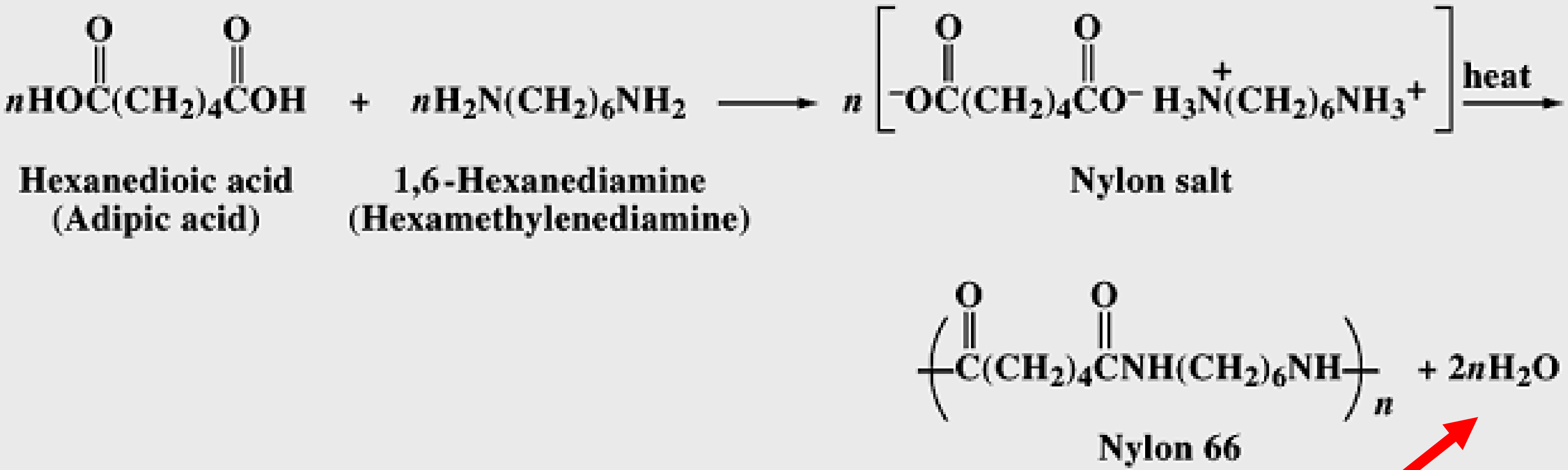


Polymers: Molecular Weight

- Ratio of M_w to M_n is known as the polydispersity index (PDI) Đ
  - a measure of the breadth of the molecular weight distribution
  - Đ = 1 indicates $M_w = M_n$, i.e. all molecules have equal length (monodisperse)
  - Đ = 1 is possible for natural proteins whereas synthetic polymers have 1.1 < PI < 5
  - At best Đ < 1.1 can be attained with special techniques

Step Growth: The Carothers Legacy

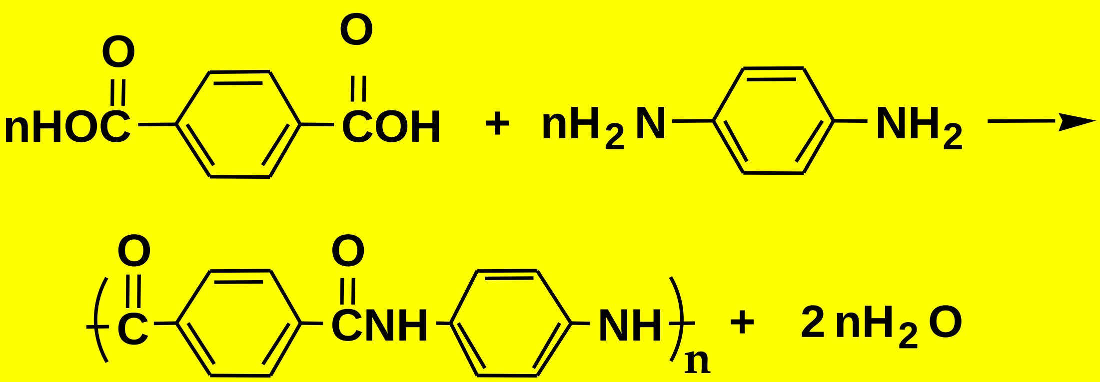
Synthesis of nylon 66



Stuff is lost in this reaction

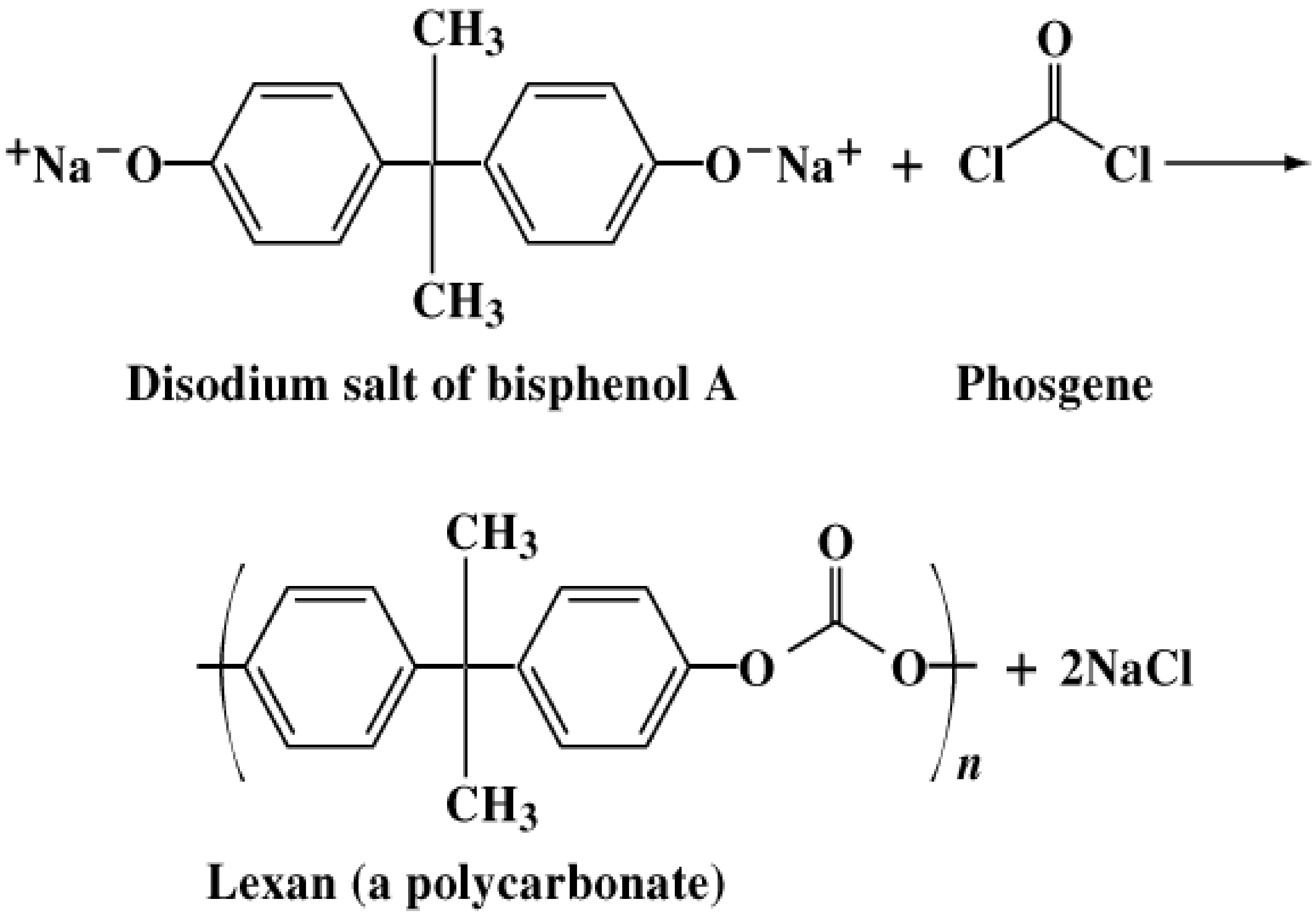
Polyamides

- Kevlar is a polyaromatic amide (an aramid) used in tire cords and bullet proof vests



  – cables of Kevlar are as strong as cables of steel, but only about 20% the weight. Kevlar fabric is used for bulletproof vests, jackets, and raincoats

Synthesis of lexan (a polycarbonate)



Step Growth Polymerization

- The forgoing were all examples of *step growth* polymerizations
  - What Carothers called condensation polymerizations
- A-A, B-B vs A-B advantages
- Problems with achieving high Mol. Wt.
- But….there are tricks to be played
  - Interfacial polymerization, etc.

Comparison of Step and Chain

Step Growth

- Growth throughout the matrix between monomers, oligomers and polymers
- DP is low to moderate
- Monomer is consumed rapidly but Mw increases slowly
- No initiator needed and reaction same throughout process
- No termination step…chain ends still reactive
- Rate decreases steadily as funcional groups are consumed

Chain Growth

- Successive addition of monomer to a limited number of growing chain ends
- DP can be very high
- Initiation and propagation reactions are different
- Generally a chain termination step
- Polymerization rate increases initially remains relatively constant until monomer depleted