#### **Topics to be Covered**

•Elements of Step-Growth Polymerization

•Branching Network Formation

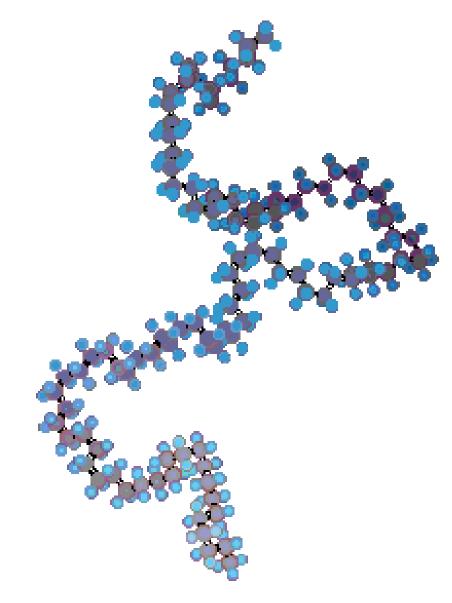
Chapters 1 & 2 in CD (Polymer Science and Engineering)

# **Dawn of Understanding**

"I am inclined to think that the development of polymerization is perhaps the biggest thing that chemistry has done, where it has had the biggest effect on everyday life"

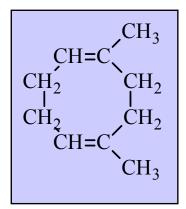
-Lord Todd,1980



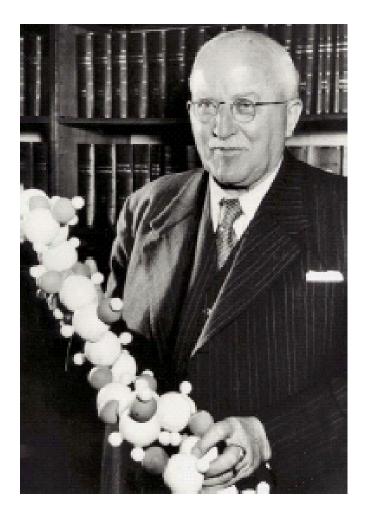


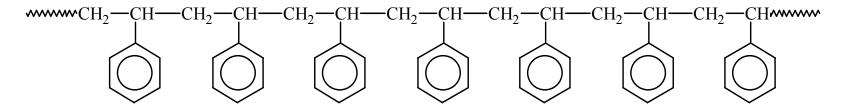
## Staudinger

"My dear chap, give up your ideas on big molecules. There are no organic molecules with a molecular weight of more than 5000. Just clean up your products and they will crystallize and reveal themselves as low-molecularweight compounds".



A cyclic isoprene dimer





# Timeline

#### 1920 – STAUDINGER; *The macromolecular hypothesis.*

1926 – CHARLES STINE; Initiates a program of fundamental research at du Pont.

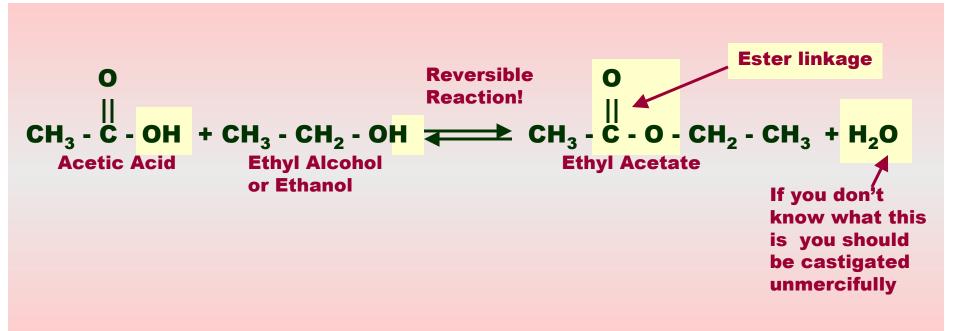
#### LATE 1920's – CAROTHERS;

Set out to prove the existence of macromolecules by systematically building them from small molecules using well known chemistry.

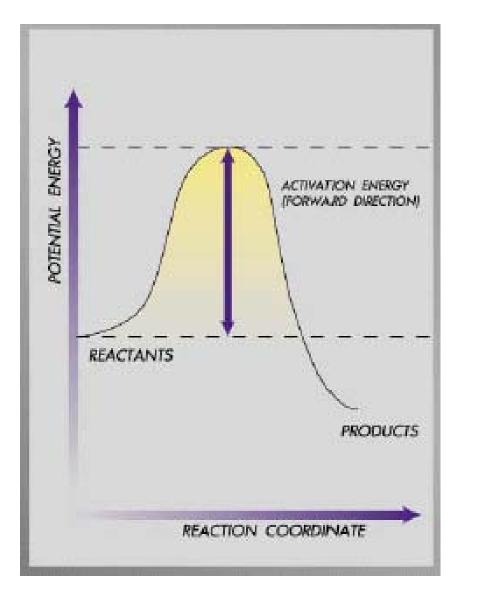


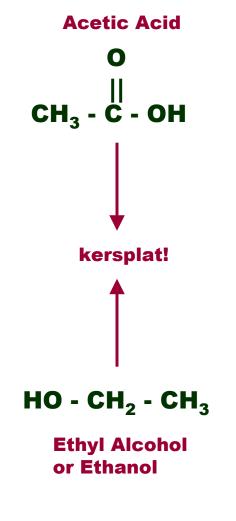


#### **Condensation Reactions**

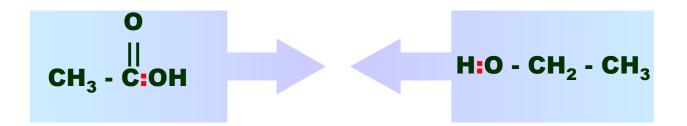


#### Why do Molecules React?





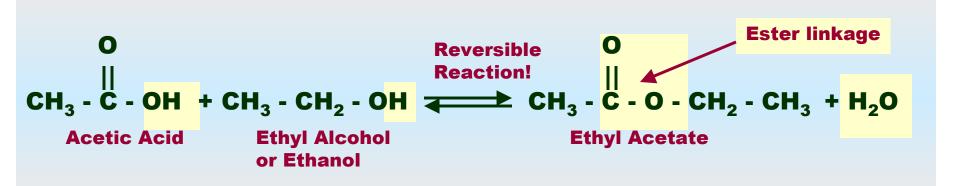
#### Why do Molecules React?



HO' + 'H  $\longrightarrow$  HO:H ~ H<sub>2</sub>O O O CH<sub>3</sub> - C' + O - CH<sub>2</sub> - CH<sub>3</sub>  $\longrightarrow$  CH<sub>3</sub> - CH<sub>2</sub> - CH<sub>2</sub> - CH<sub>3</sub>

This isn't what really happens, but shows you how the valency electrons get rearranged

## **Making a Polymer**



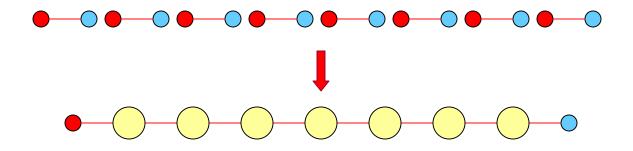
If we heat acetic acid and ethanol up to just over  $100^{\circ}C$ , to get the reaction going and drive off water, why don't we form polymer?

# **Making a Polymer**

The molecules are monofunctional;

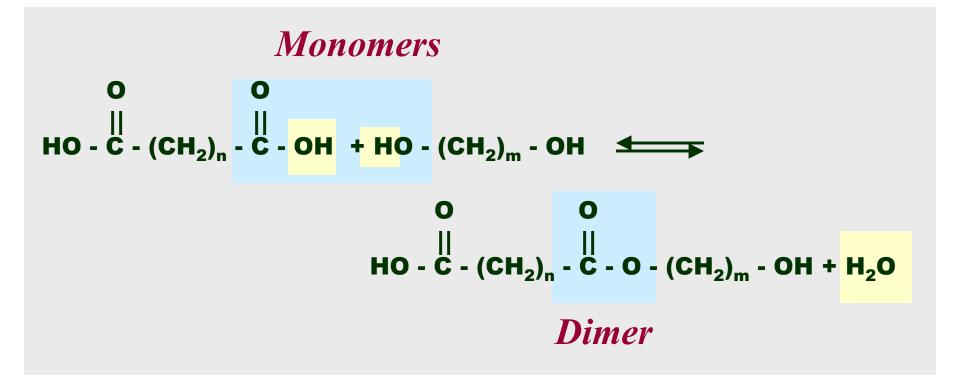


To make linear chains we need bifunctional molecules;

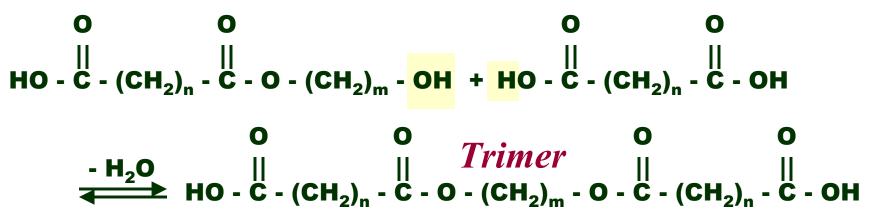


Except the reaction doesn't happen all in one go, like this, but in a step-growth fashion.

#### **Making a Polyester**



#### **Making a Polyester**



Note, reacting a diacid and a dialcohol will give you a polyester!

$M_1 + M_1 \longrightarrow M_2$
$M_2 + M_1 \longrightarrow M_3$
$M_2 + M_2 \longrightarrow M_4$
$M_3 + M_1 \longrightarrow M_4$
$M_4 + M_1 \longrightarrow M_5$
$M_3 + M_2 \longrightarrow M_5$
$M_5 + M_1 \longrightarrow M_6$
Etc.

# **The Invention of Nylon**

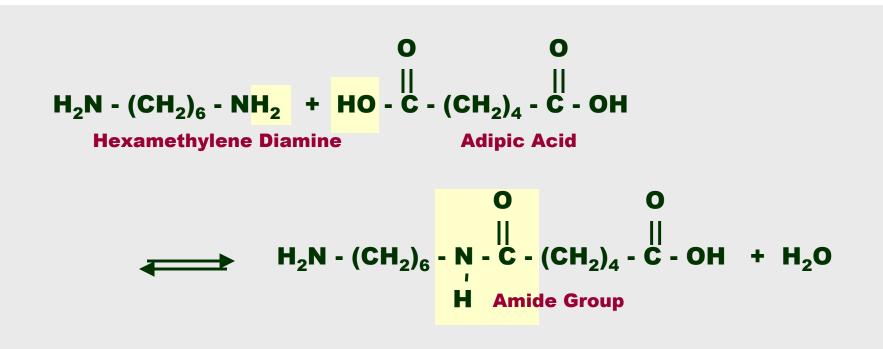
1927 - Stine offers Carothers a job. 1929 - Carothers and his group succeed in making low molecular weight aliphatic polyesters



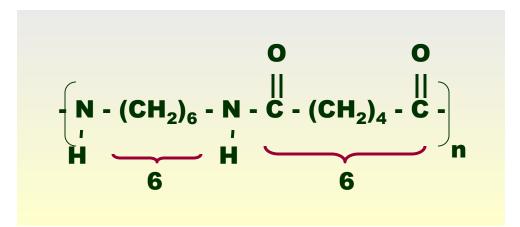
# The molecular still and the shift to polyamides



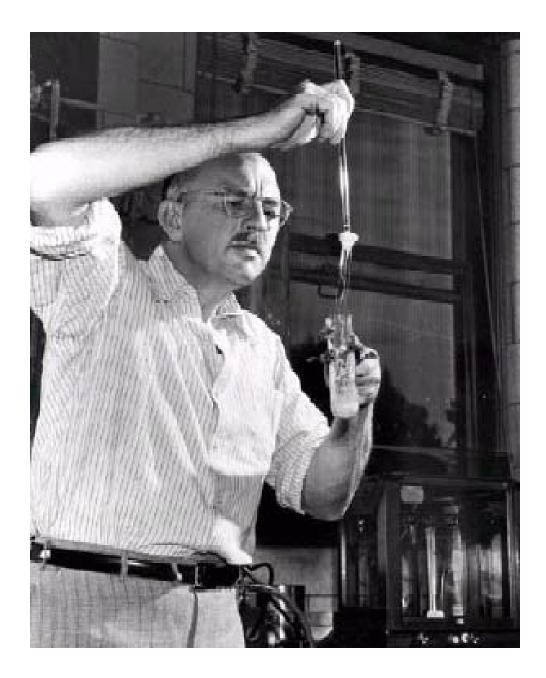
#### Nylons



# Nylon 6,6



Julian Hill reenacting the discovery of Nylon



Ad. from N.Y. Herald Tribune, Oct. 30 1938

#### *1938*

"I am making the announcement of a brand new chemical textile fiber ---derivable from coal, air and water -- and characterized by extreme toughness and strength --" Charles Stine V.P. for research, Du Pont, 1938

#### Du Pont Announces for the World of Tomorrow...

a new word and a new material

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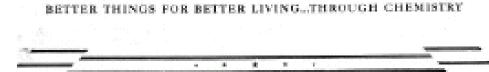
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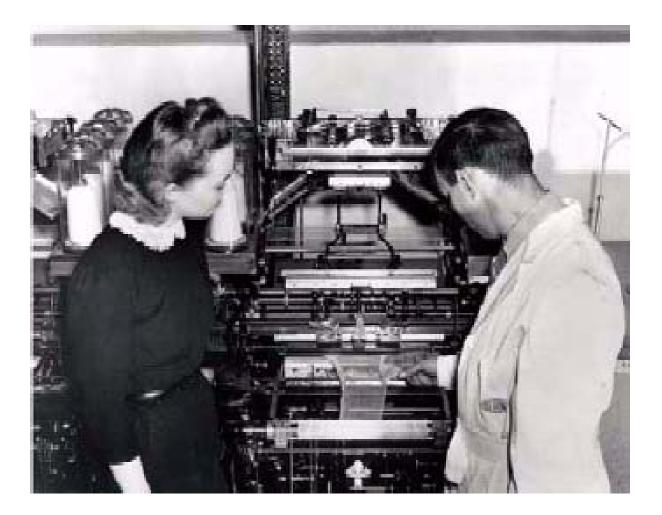
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# **Stockings!**



**Demonstration of knitting nylon stockings at the N.Y.** World's Fair, 1939



#### Marie Wilson's Leg, 2 ton 35 ft cast, N.Y. World's Fair1939

DuPont did a masterly job in two areas; – Advertising – Technical Service

# **Why Stockings?**

As skirts got shorter after the end of WWI, shocking expanses of leg were being revealed and the appearance and "feel" of stockings became a pressing fashion concern. And, there was money to be made! At that time nothing could compare with silk for sheerness. Wool was thick and scratchy; cotton was, well, cotton, not very exciting; rayon also was not sheer enough and tended to droop and bag at the ankles. But, silk was expensive and not very durable (silk stockings would "run" at the slightest provocation). Nevertheless, about 1.6 million pairs of silk stockings were being *a day* in the U.S. alone!

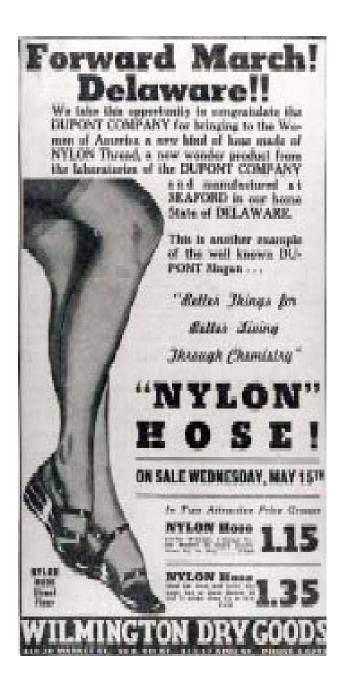


Golden Gate Exposition, 1939

#### Wilmington gets the first nylon stockings, 1939



May 15 1940 - "Nylon Day". Four Million pairs go on sale throughout the U.S. Supply exhausted in 4 days.



#### Nylon Parachute WWII



Betty Grable auctions her stockings for the war effort.



Post WWII stocking sale, NYC.





#### She couldn't wait!

#### Post WWII stocking sale, San Francisco.



# Sold Out!

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Carothers in happier times.

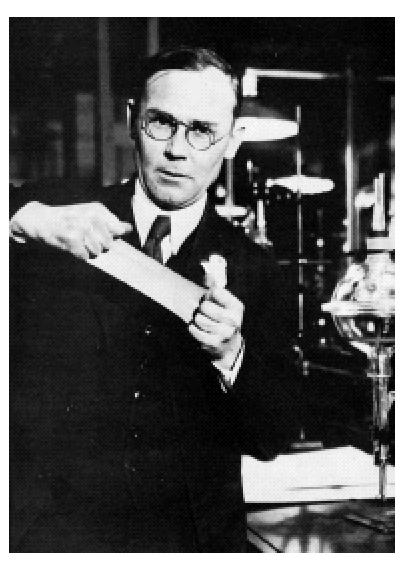
#### **Polymer Synthesis - Classification**

Carothers suggested that most polymers could be classified into two broad categories according to the mechanism of polymerization;

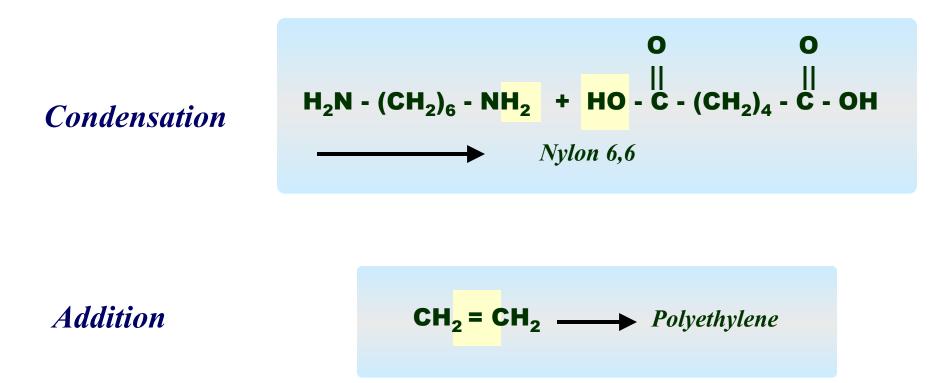
- Condensation
- Addition

As you will see, a better classification may be;

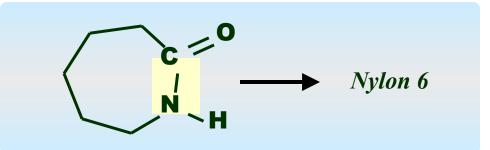
- Step-growth
- Chain



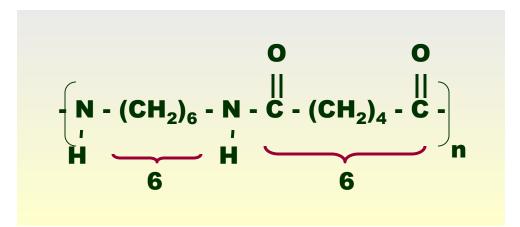
#### **Types of Reactions**



**Ring opening** 

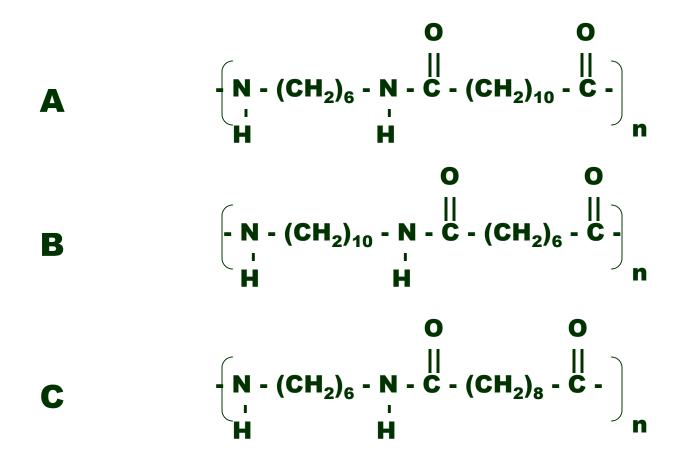


# Nylon 6,6



## Nylon 6,10

What would nylon 6,10 look like?



## **More on Nylons**



Applications Carpet Fibers Clothes Gear wheels Etc.

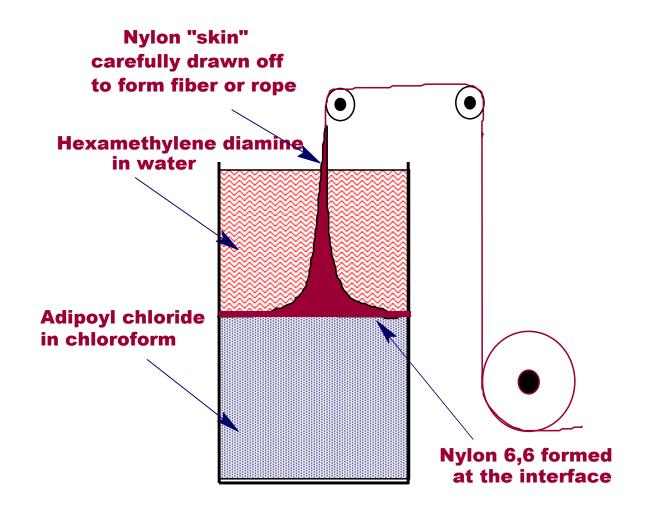
#### **Back to Condensation**

Is a molecule of water always split out?

$$H_{2}N - (CH_{2})_{6} - NH_{2} + CI - C - (CH_{2})_{4} - C - CI$$
Hexamethylene Diamine
$$H_{2}N - (CH_{2})_{6} - N - C - (CH_{2})_{4} - C - OH + HCI$$

$$H_{2}N - (CH_{2})_{6} - N - C - (CH_{2})_{4} - C - OH + HCI$$

## **The Nylon Rope Trick**



# The Nylon Rope Trick



#### **Polyurethanes**

A reaction that does not involve the splitting out of a small molecule;

$$O = C = N - (CH_2)_6 - N = C = O + HO - (CH_2)_2 - OH$$
  
Hexamethylene Diisocyanate Ethylene Glycol

$$O = C = N - (CH_2)_6 - N - C - O - (CH_2)_2 - OH$$

**Urethane Linkage** 

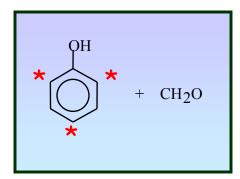
### **Network Formation**

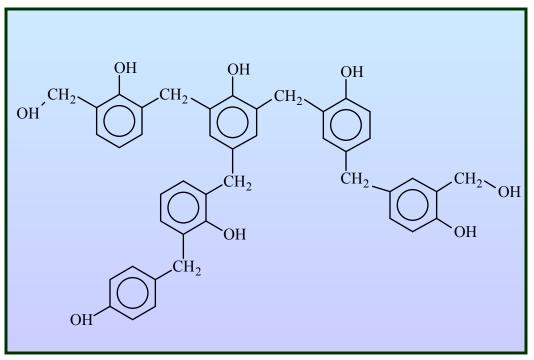
How would you make chains that branch and then perhaps interconnect to form networks?

- A. Use a mixture of bifunctional and monofunctional units
- B. Get a tube of Molecular Super Glue and stick a bunch of chains together
- C. Use multifunctional (f>2) monomers

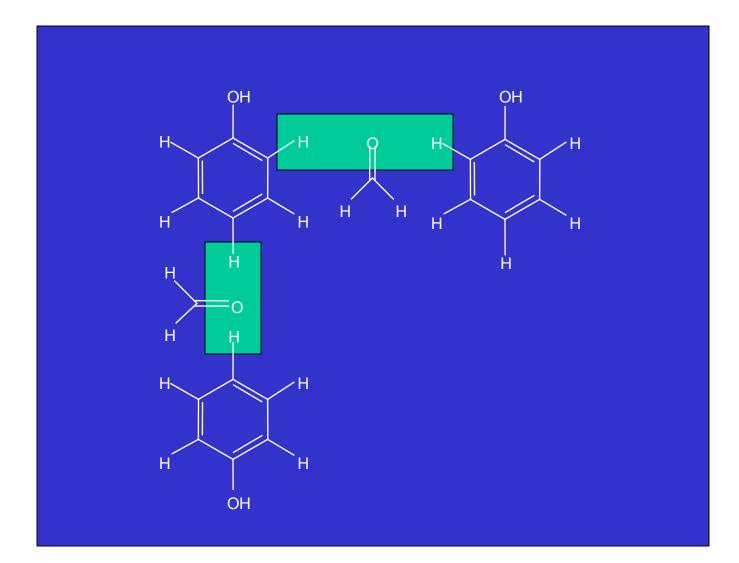
#### **Network Formation**

The hydrogens in the ortho and para positions to the OH group, which by convention are not usually shown but here are indicated by a \*, can react with fomaldehyde to form (initially) oligomers.

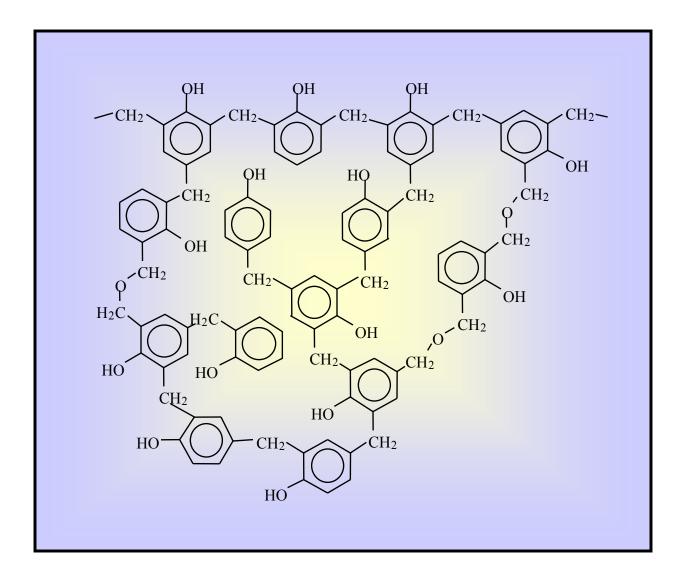




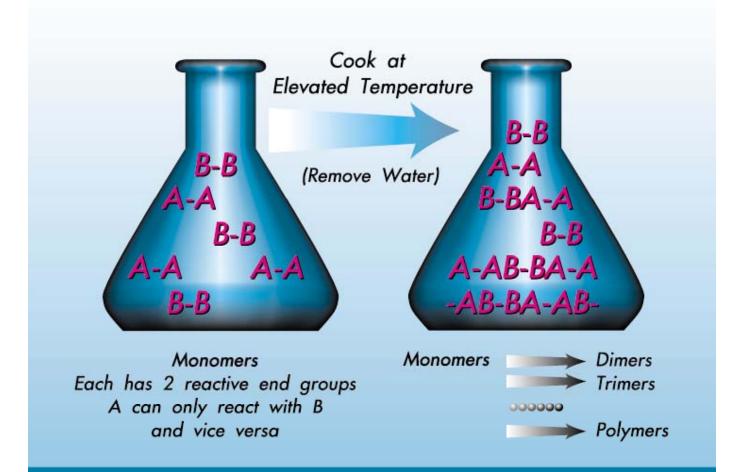
#### **Another Condensation Reaction**



## **Network Formation**



#### Step-Growth Polymerization ; Summary

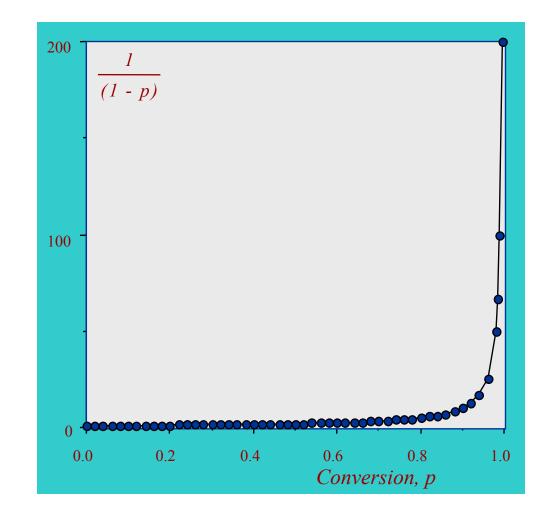


Schematic representation of step-growth polymerization

#### **Conversion and Molecular Weight in Step-Growth Polymerizations**

 $\bar{x}_n = \frac{1}{(1-p)}$ 

Note; you only get high molecular weight polymer at high degrees of conversion.



#### Some Important Step Growth Polymers

Nylons Polyesters Polyurethanes Polycarbonate Epoxies Phenolics