Topics to be Covered

- *Elements of Step-Growth Polymerization*
- *Branching Network Formation*

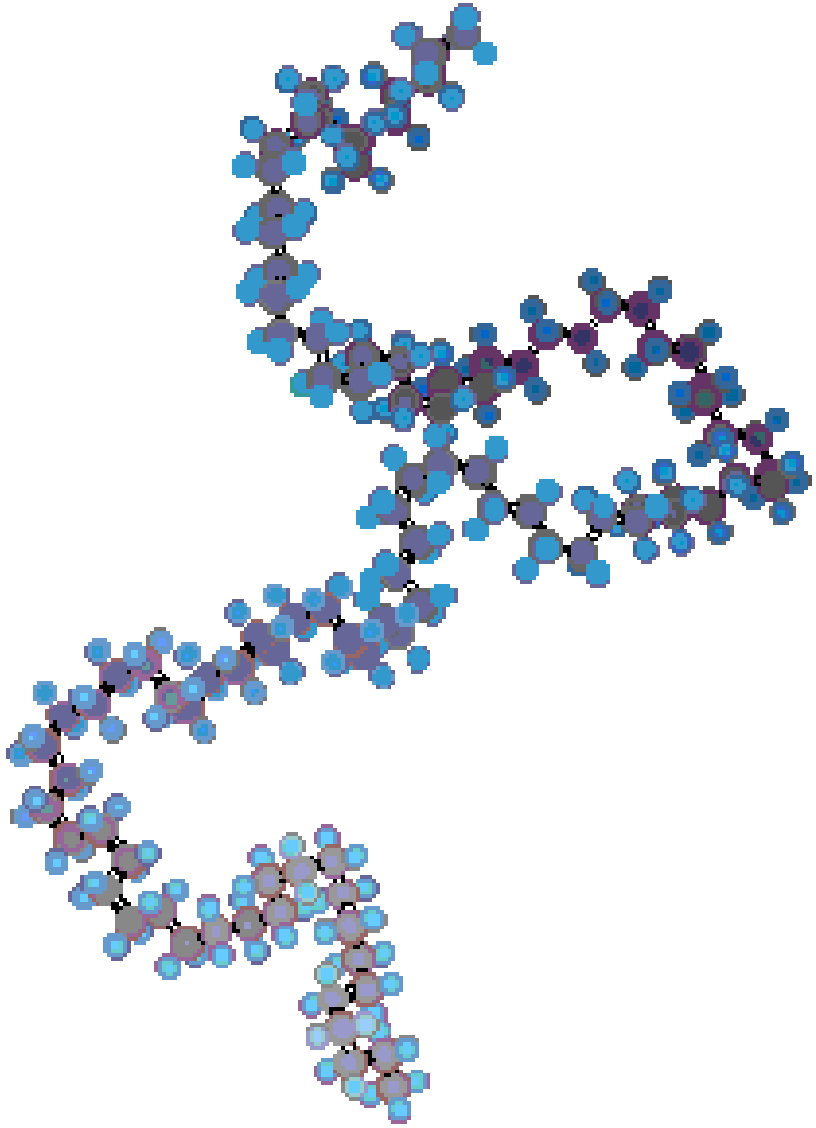
Chapters 1 & 2 in CD (Polymer Science and Engineering)

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"

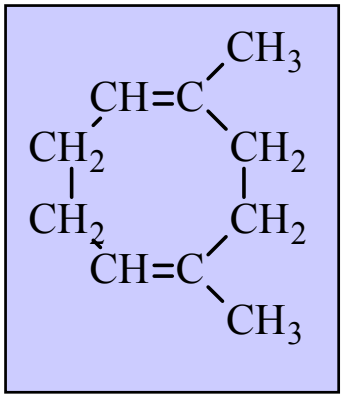
—Lord Todd,1980

Ethylene $CH_2=CH_2$ → (Magic ?) Polyethylene $[-CH_2-CH_2-]_n$

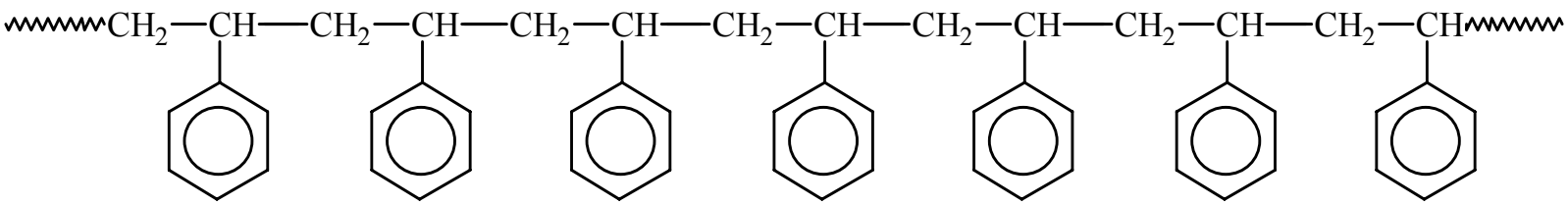


Staudinger

"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-molecular-weight compounds".



A cyclic isoprene dimer



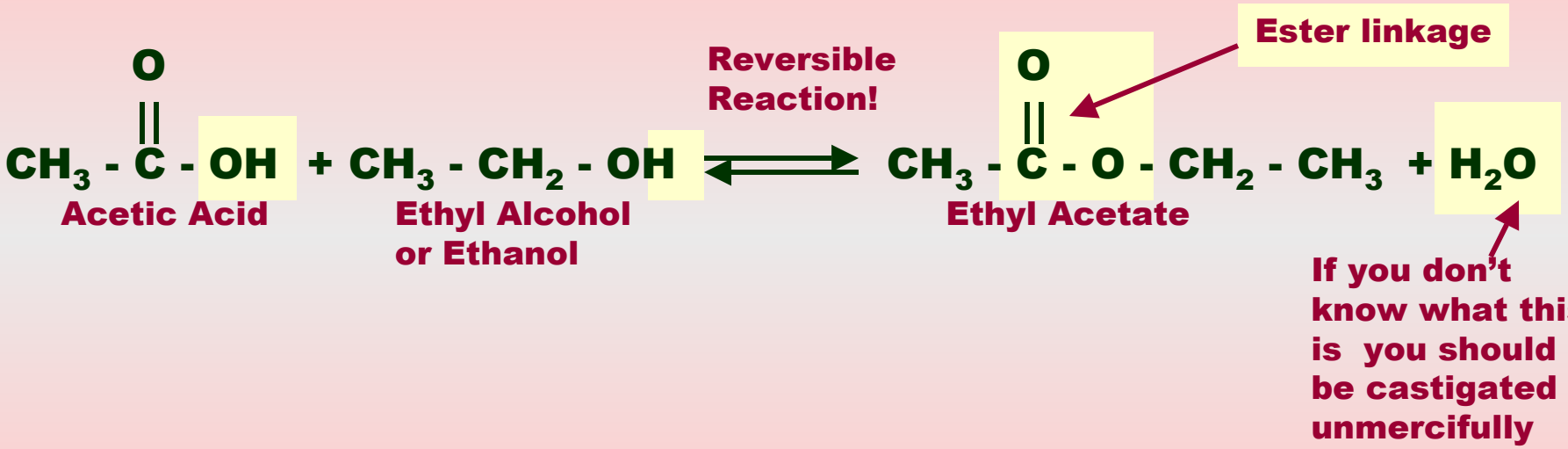
Timeline

1920 – STAUDINGER;
The macromolecular hypothesis.

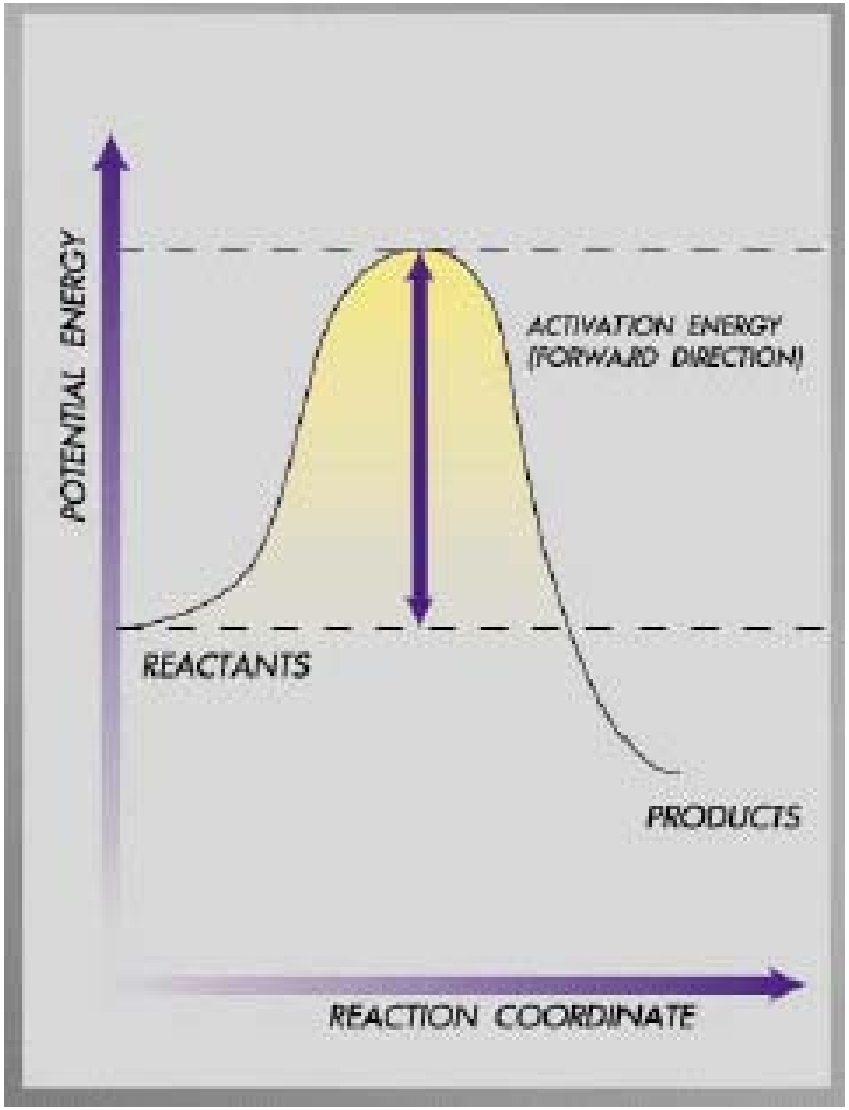
1926 – CHARLES STINE;
Initiates a program of fundamental research at du Pont.

LATE 1920's – CAROTHERS;
Set out to prove the existence of macromolecules by systematically building them from small molecules using well known chemistry.

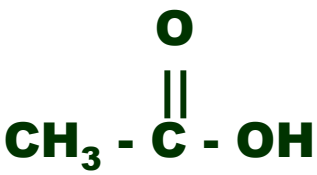
Condensation Reactions



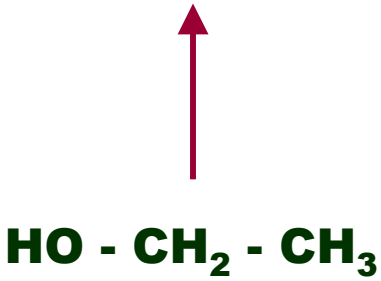
Why do Molecules React ?



Acetic Acid

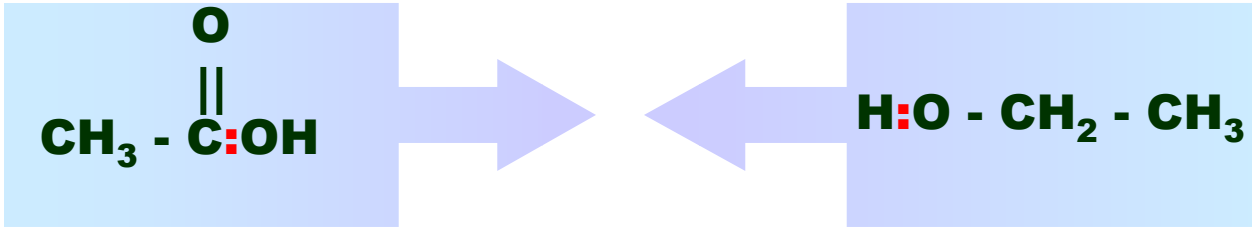


kersplat!



Ethyl Alcohol
or Ethanol

Why do Molecules React ?

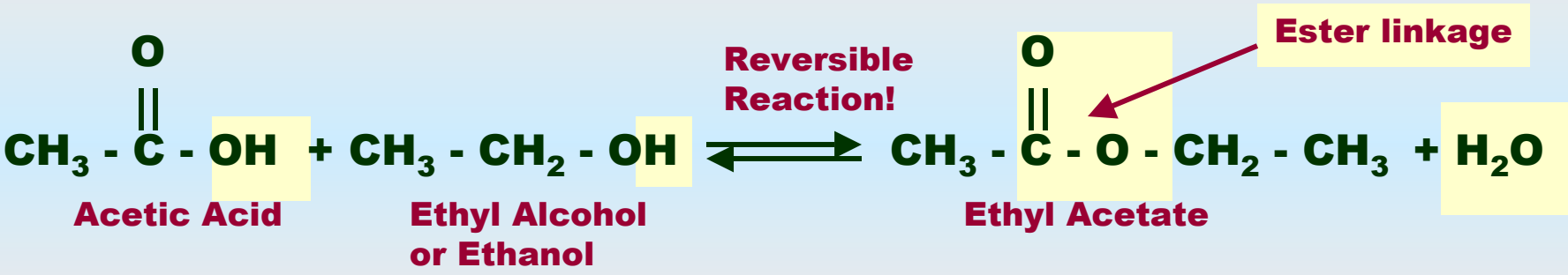


$$HO\cdot + \cdot H \rightarrow HO{:}H \sim H_2O$$

$$CH_3 - \overset{\overset{O}{\|}}{C}\cdot + \cdot O - CH_2 - CH_3 \rightarrow CH_3 - \overset{\overset{O}{\|}}{C}{:}O - CH_2 - CH_3$$

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

Making a Polymer

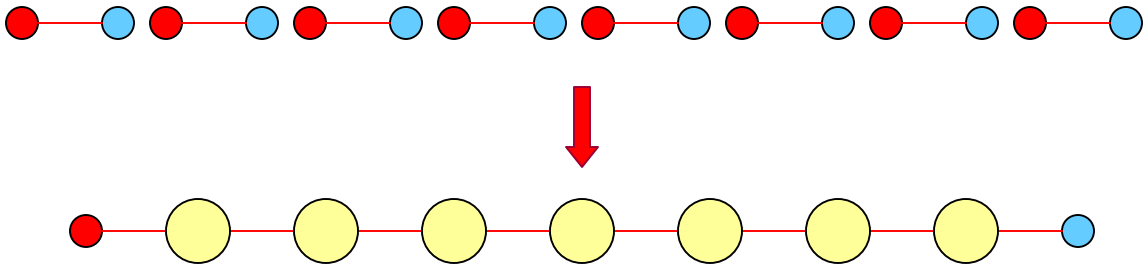


If we heat acetic acid and ethanol up to just over 100°C, to get the reaction going and drive off water, why don't we form polymer?

Making a Polymer

The molecules are monofunctional;

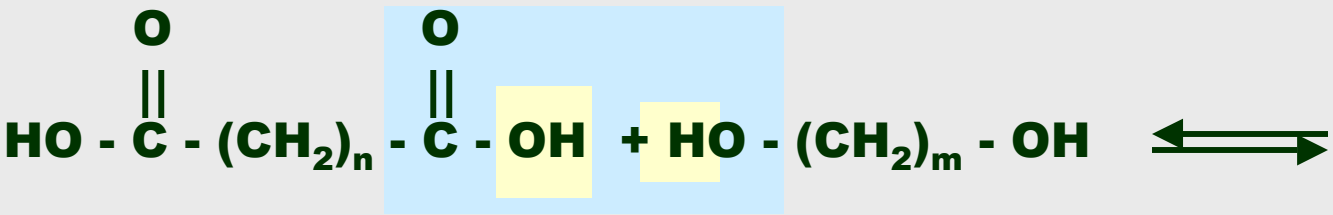
To make linear chains we need bifunctional molecules;

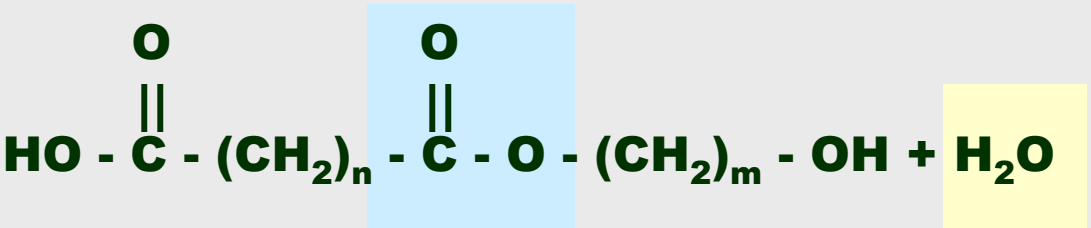


Except the reaction doesn't happen all in one go, like this, but in a step- growth fashion.

Making a Polyester

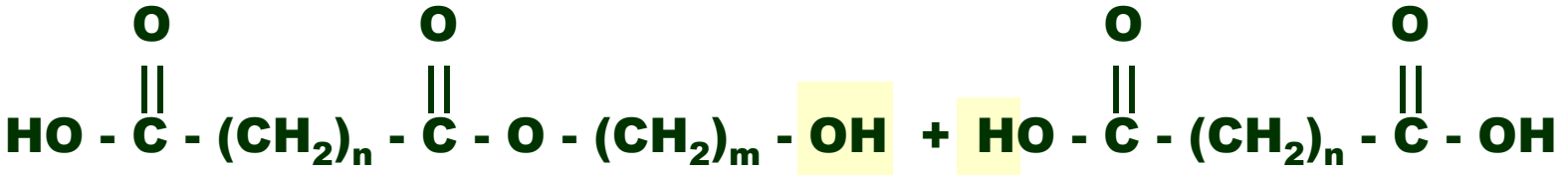
Monomers





Dimer

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.

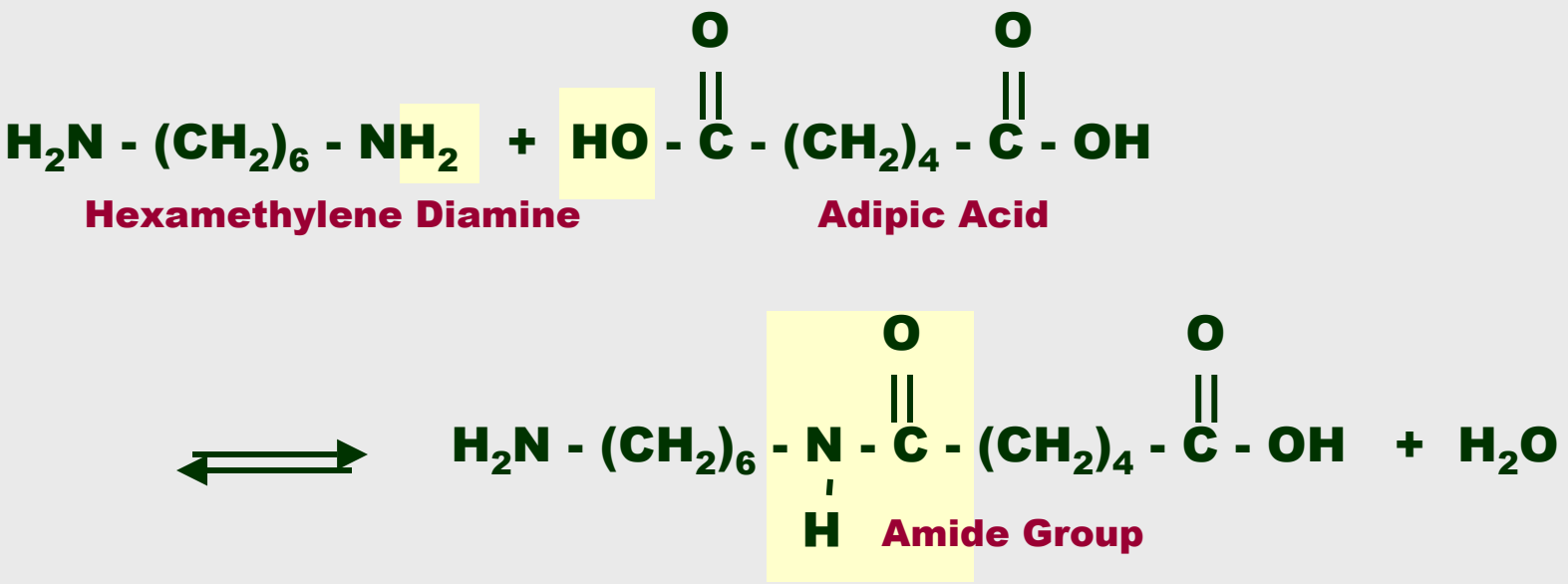
The Invention of Nylon

1927 - Stine offers Carothers a job.

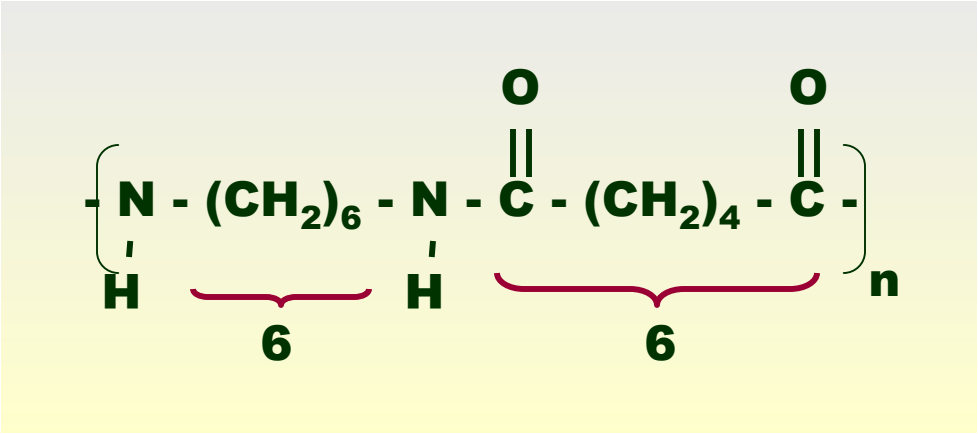
1929 - Carothers and his group succeed in making low molecular weight aliphatic polyesters

The molecular still and the shift to polyamides

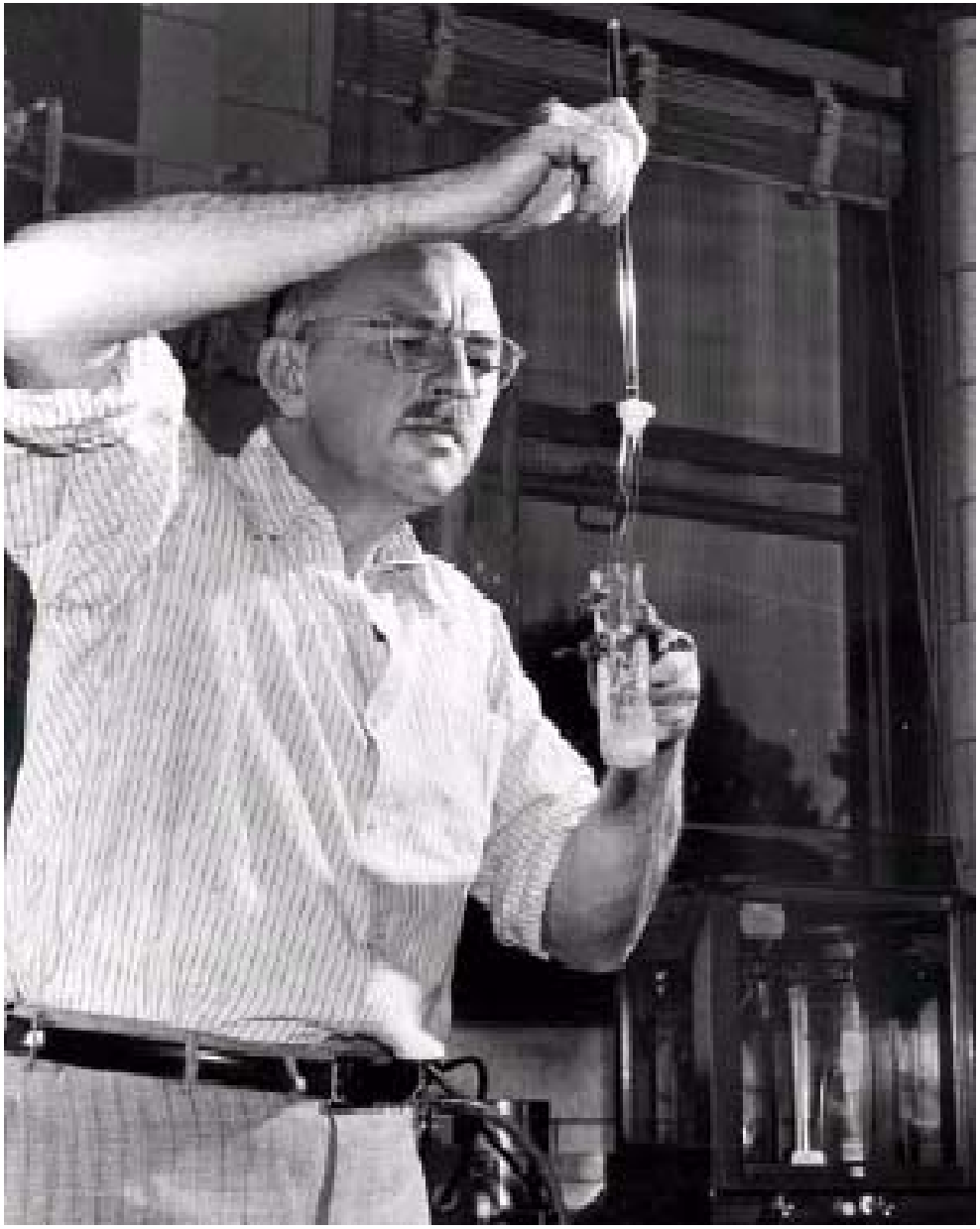
Nylons


O
O
H2N - (CH2)6 - NH2 + HO - C - (CH2)4 - C - OH
Hexamethylene Diamine
Adipic Acid
O
O
H2N - (CH2)6 - N - C - (CH2)4 - C - OH + H2O
H
Amide Group

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

NYLON

BETTER THINGS FOR BETTER LIVING...THROUGH CHEMISTRY

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*

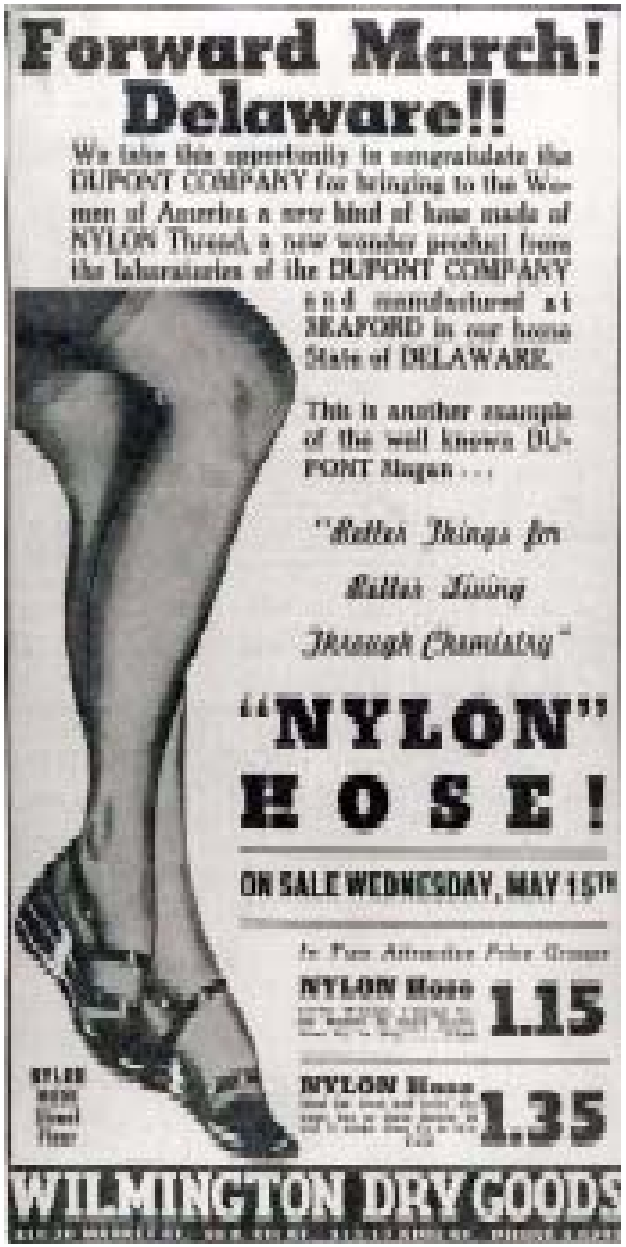
Why Stockings?

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

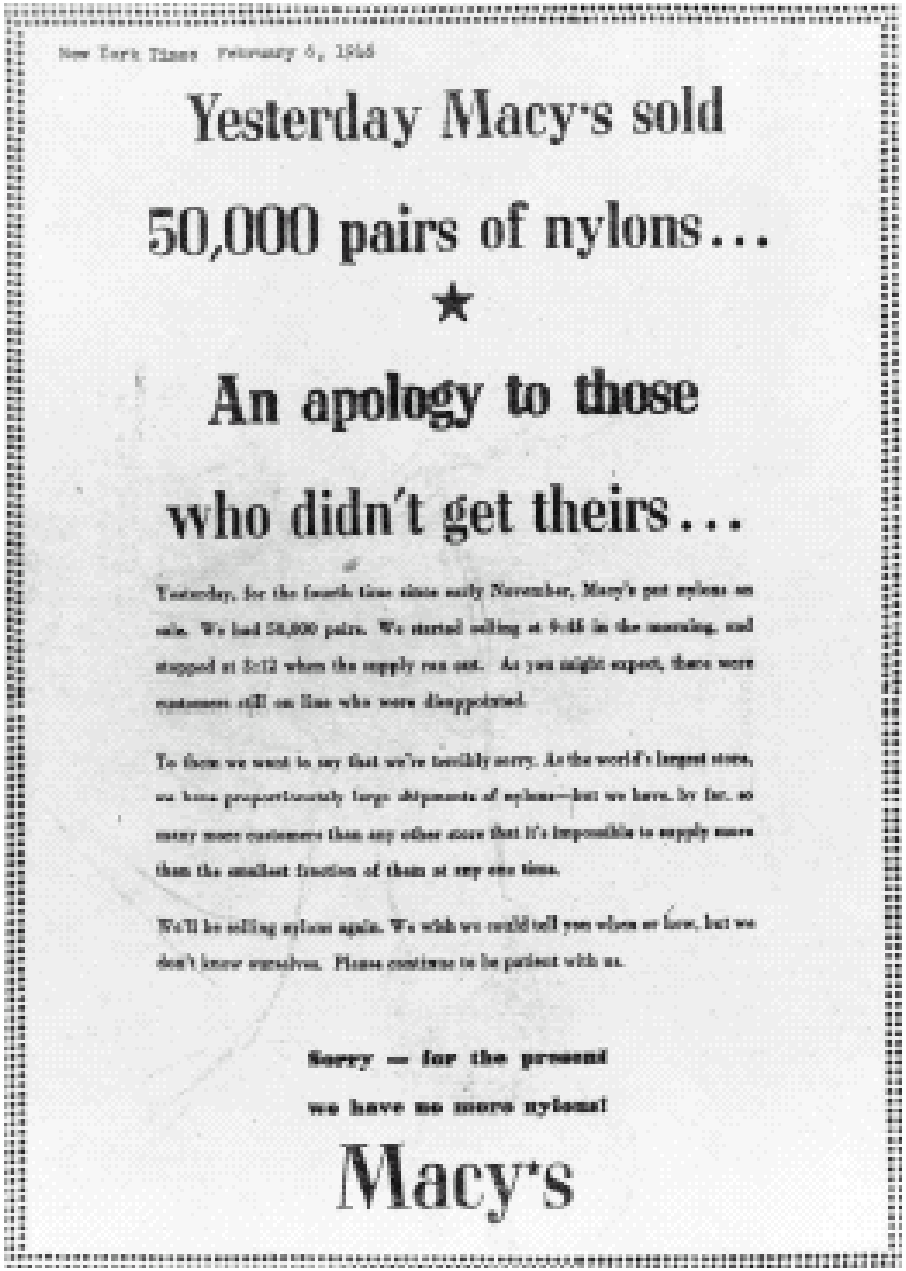
Betty Grable auctions her stockings for the war effort.

Post WWII stocking sale, NYC.

She couldn't wait!

Post WWII stocking sale, San Francisco.

Sold Out!



New York Times February 6, 1958

Yesterday Macy's sold

50,000 pairs of nylons...

★

An apology to those

who didn't get theirs...

Yesterday, for the fourth time since early November, Macy's put nylons on sale. We had 50,000 pairs. We started selling at 9:48 in the morning, and stopped at 9:52 when the supply ran out. As you might expect, there were customers still on line who were disappointed.

To them we want to say that we're terribly sorry. As the world's largest store, we have proportionately large shipments of nylons—but we have, by far, so many more customers than any other store that it's impossible to supply more than the smallest fraction of them at any one time.

We'll be selling nylons again. We wish we could tell you when we know, but we don't know ourselves. Please continue to be patient with us.

Sorry — for the present

we have no more nylons!

Macy's

A Tragic End

Carothers in happier times.

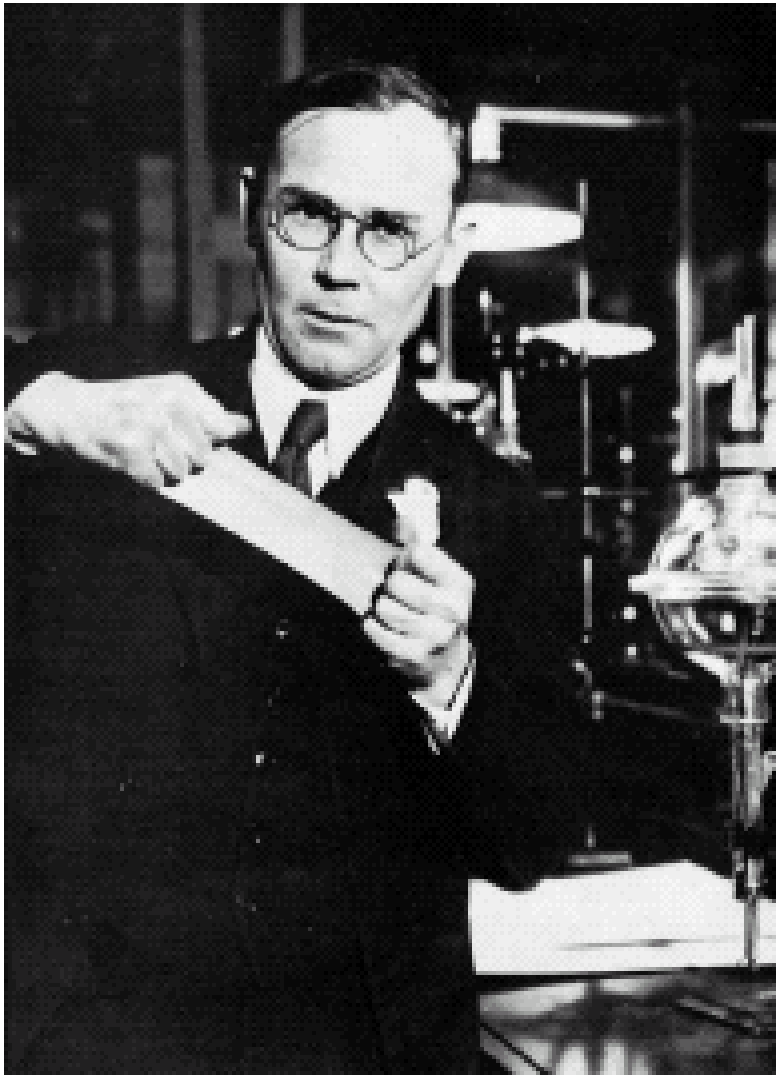
Polymer Synthesis - Classification

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

- *Condensation*
- *Addition*

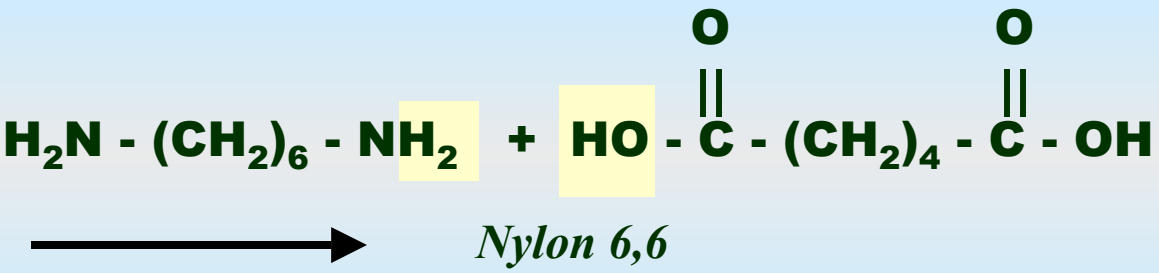
As you will see, a better classification may be;

- *Step-growth*
- *Chain*



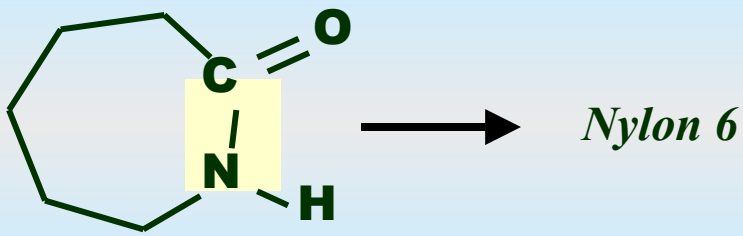
Types of Reactions

Condensation

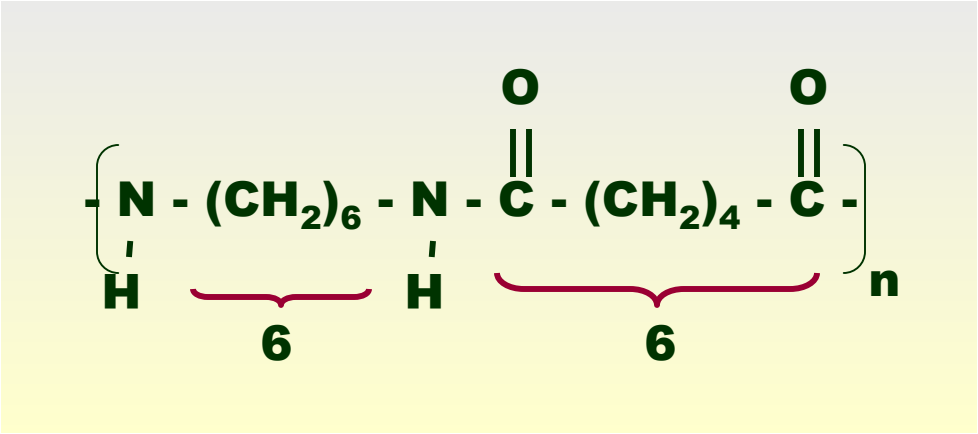


Addition

Ring opening



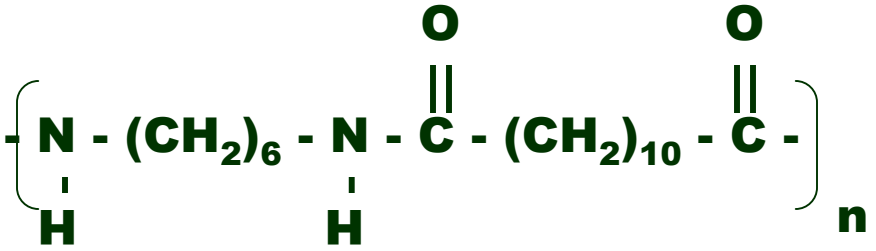
Nylon 6,6



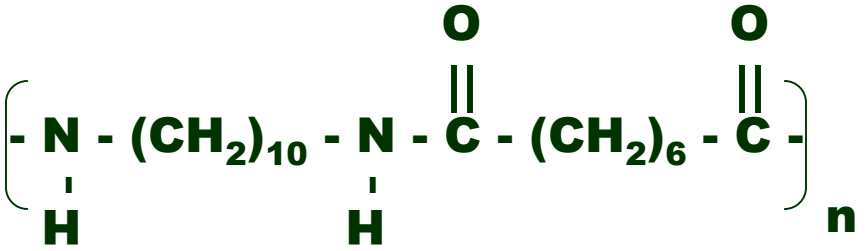
Nylon 6,10

What would nylon 6,10 look like?

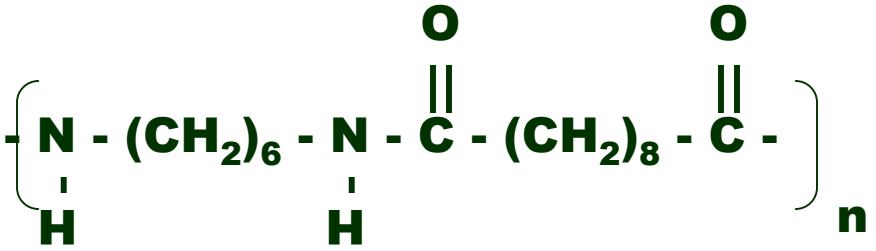
A



B



C



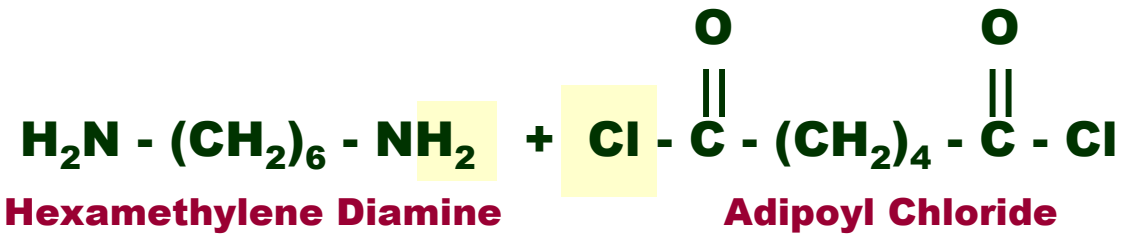
More on Nylons

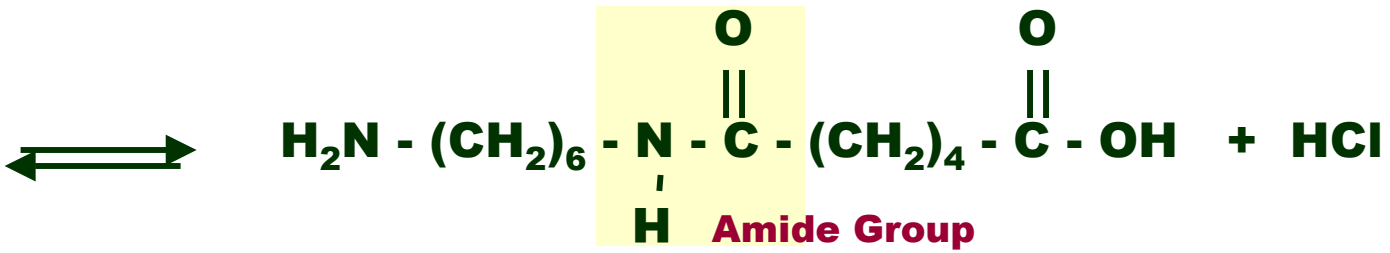
Applications

- *Carpet Fibers*
- *Clothes*
- *Gear wheels*
- *Etc.*

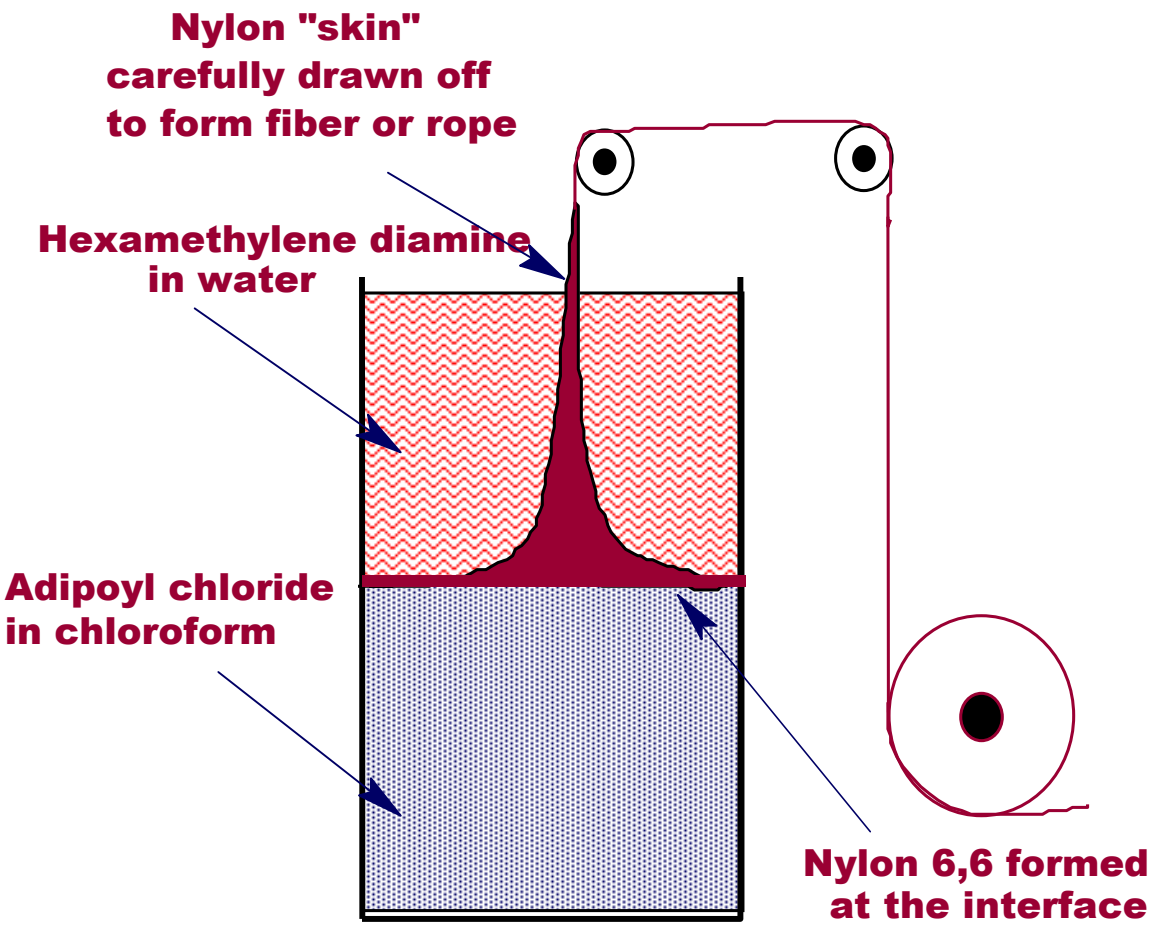
Back to Condensation

Is a molecule of water always split out?





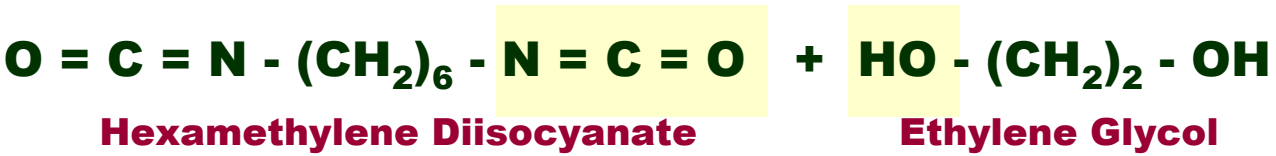
The Nylon Rope Trick



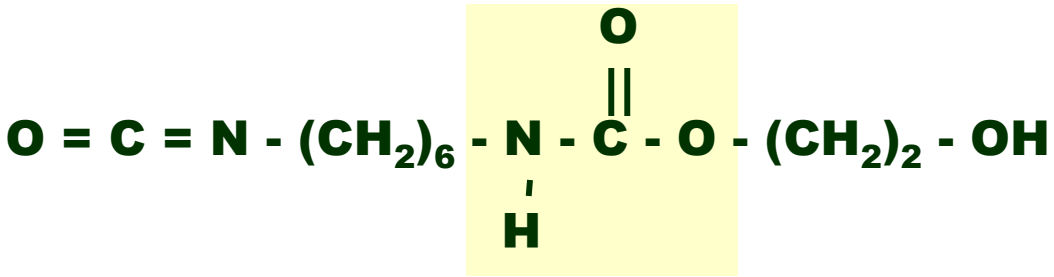
The Nylon Rope Trick

Polyurethanes

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



Hexamethylene Diisocyanate Ethylene Glycol



Urethane Linkage

Network Formation

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

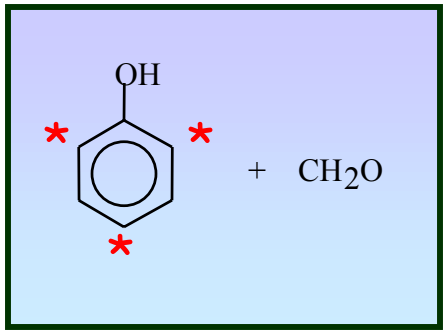
A. *Use a mixture of bifunctional and monofunctional units*

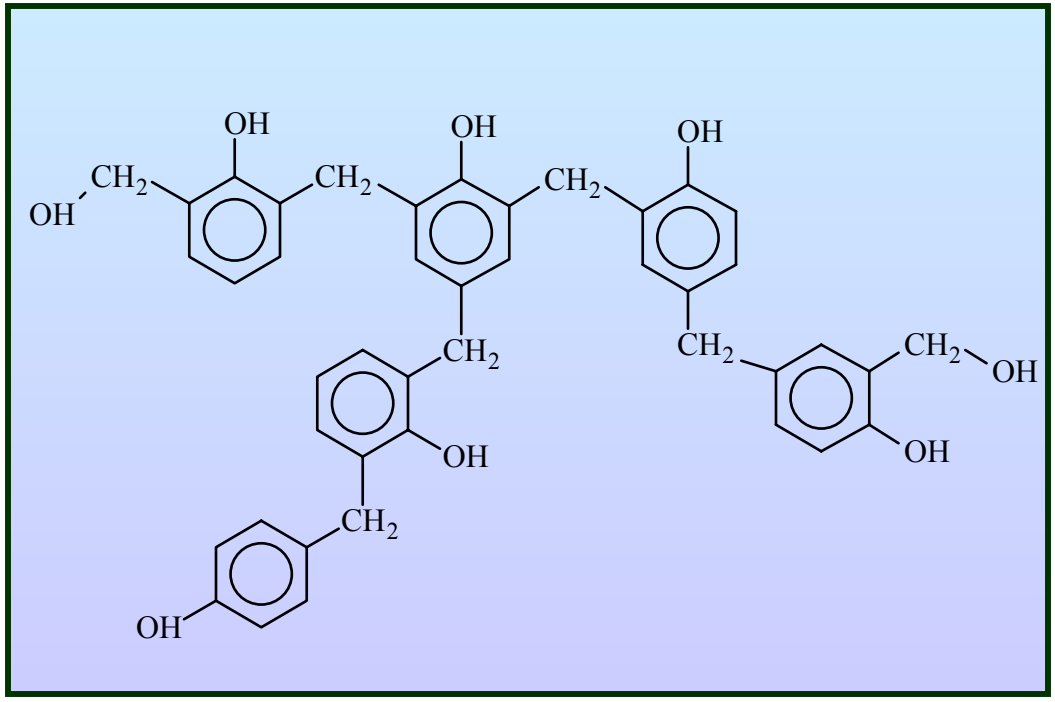
B. *Get a tube of Molecular Super Glue and stick a bunch of chains together*

C. *Use multifunctional (f>2) monomers*

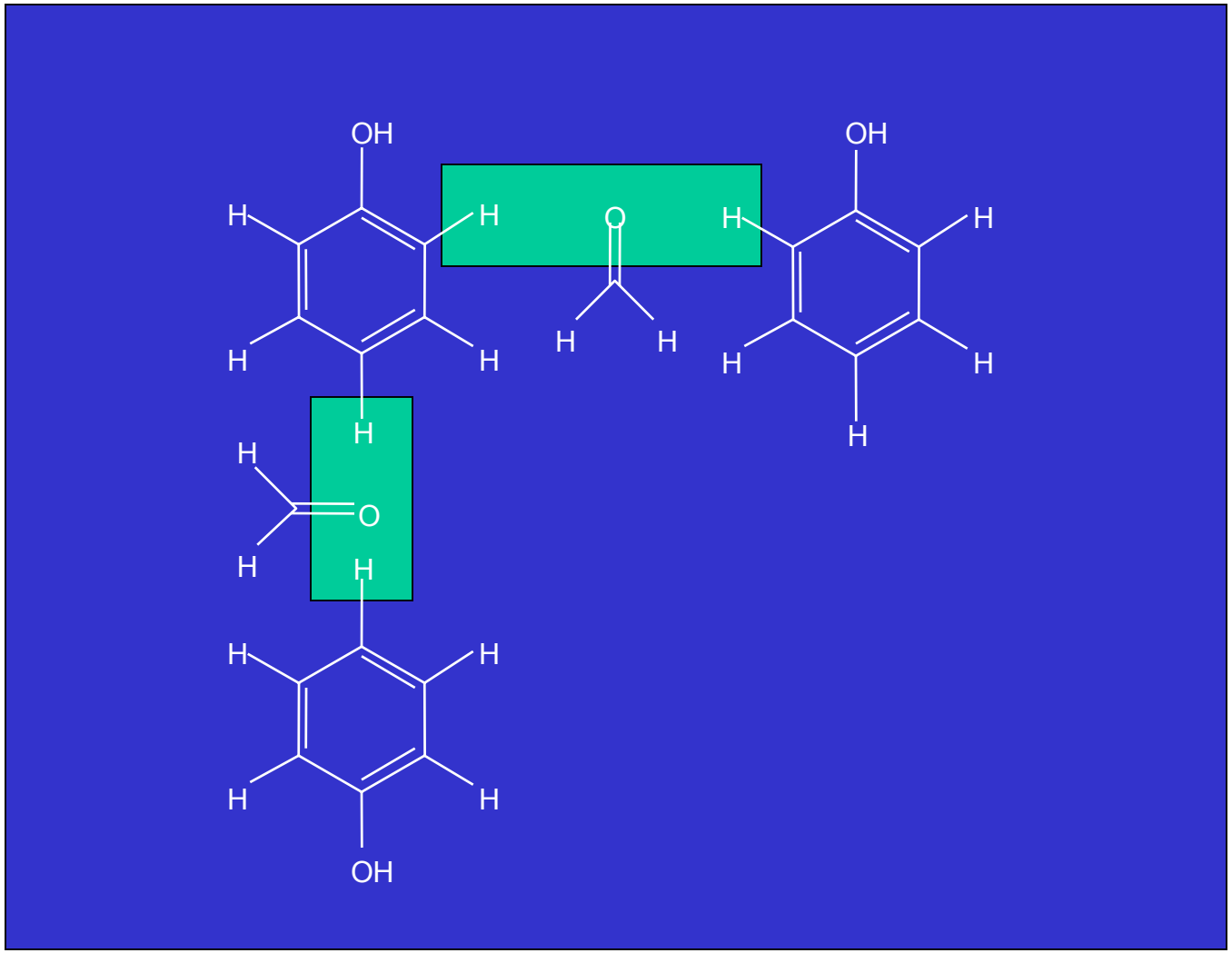
Network Formation

*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.*

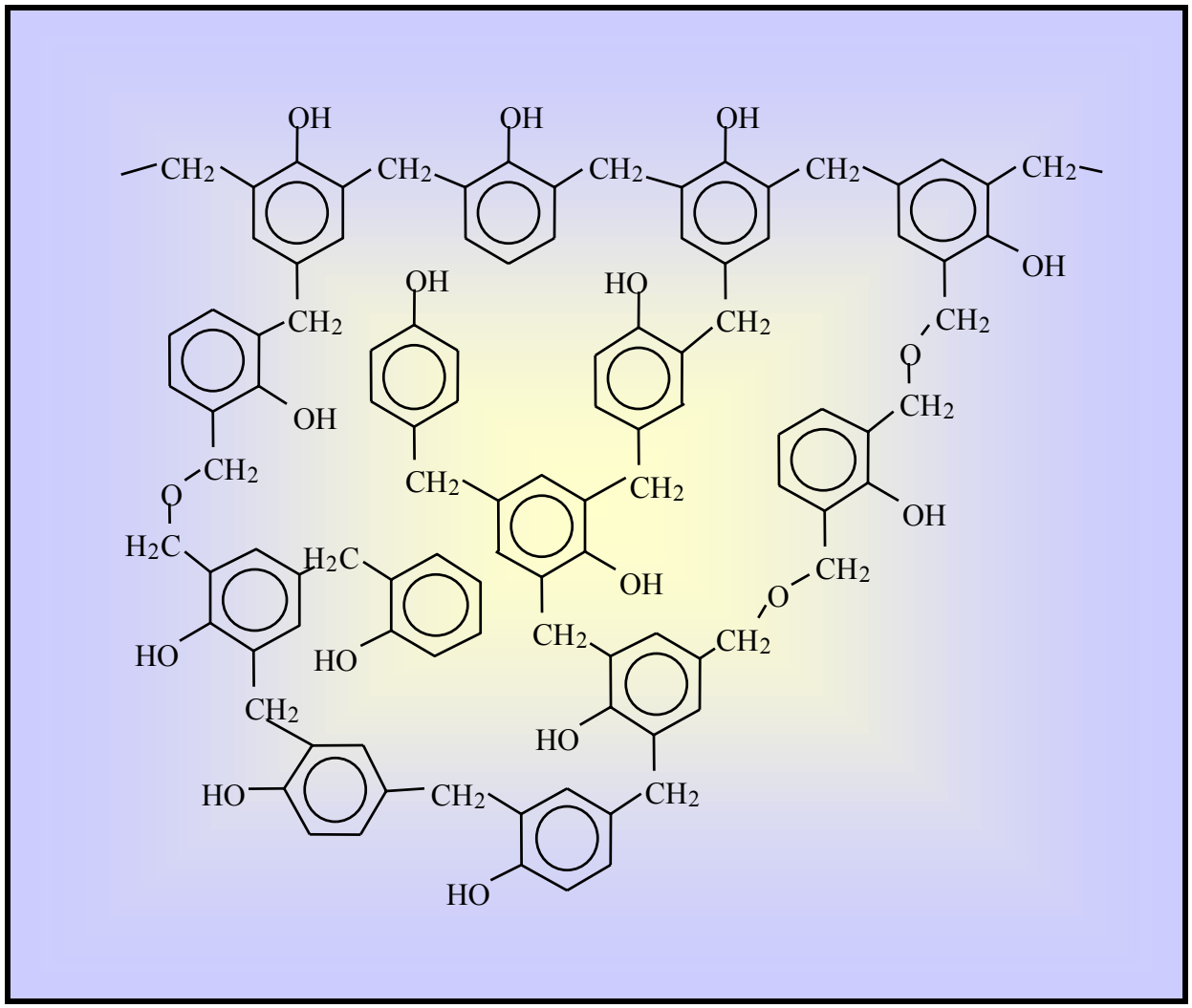




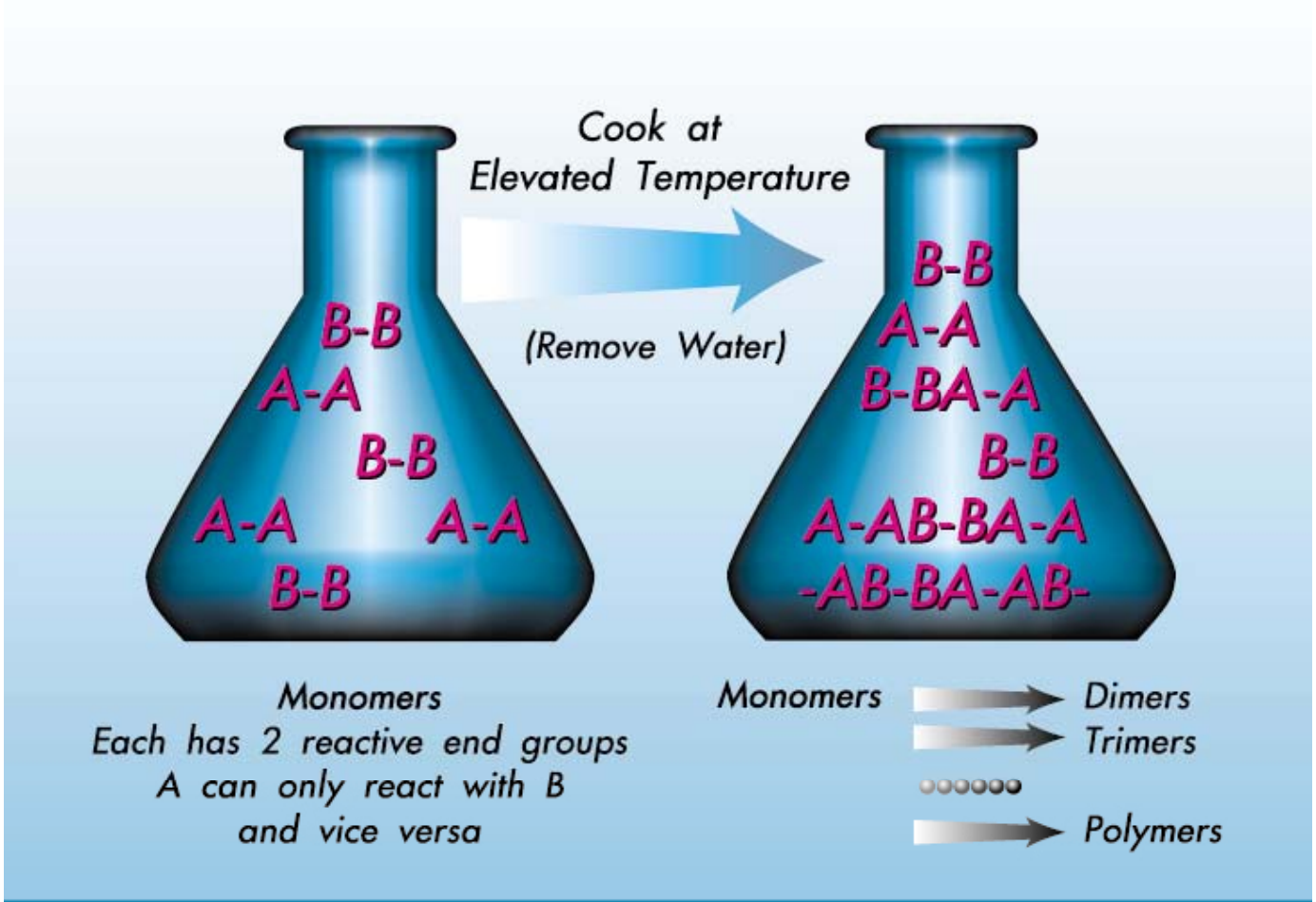
Another Condensation Reaction



Network Formation



Step-Growth Polymerization ; Summary

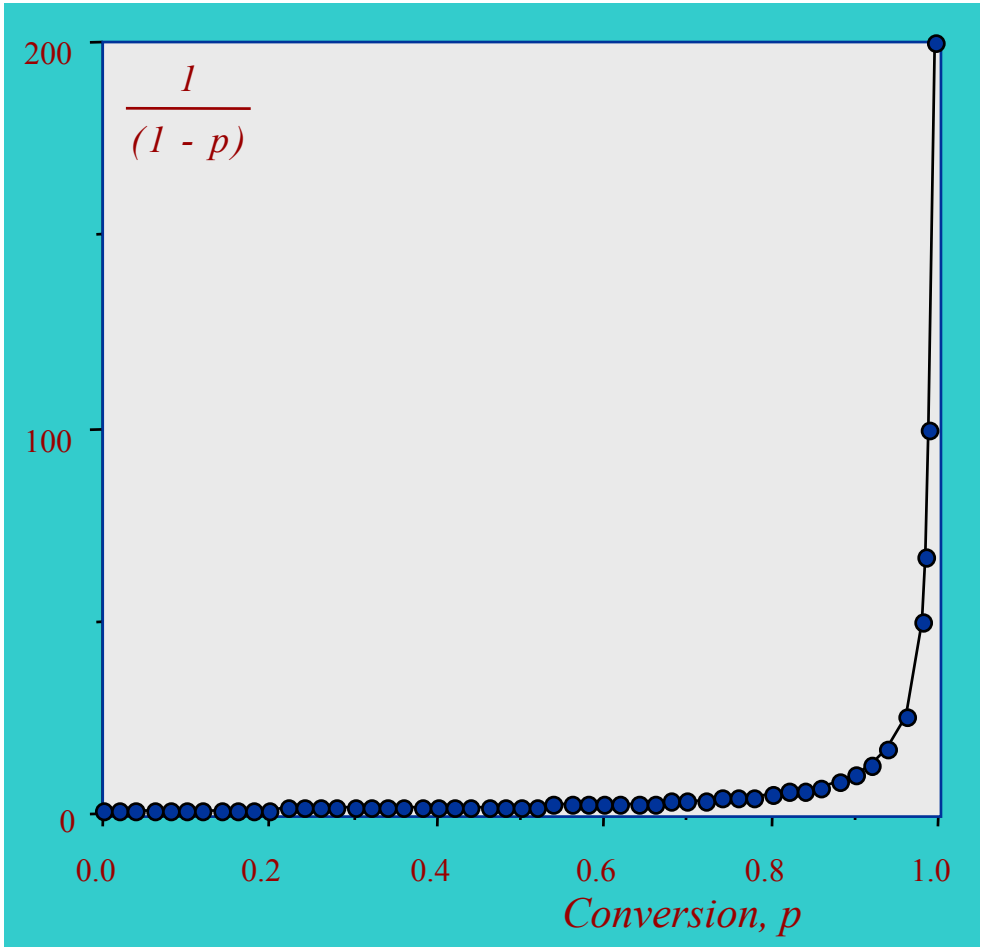


Schematic representation of step-growth polymerization

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