# Topics to be Covered

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

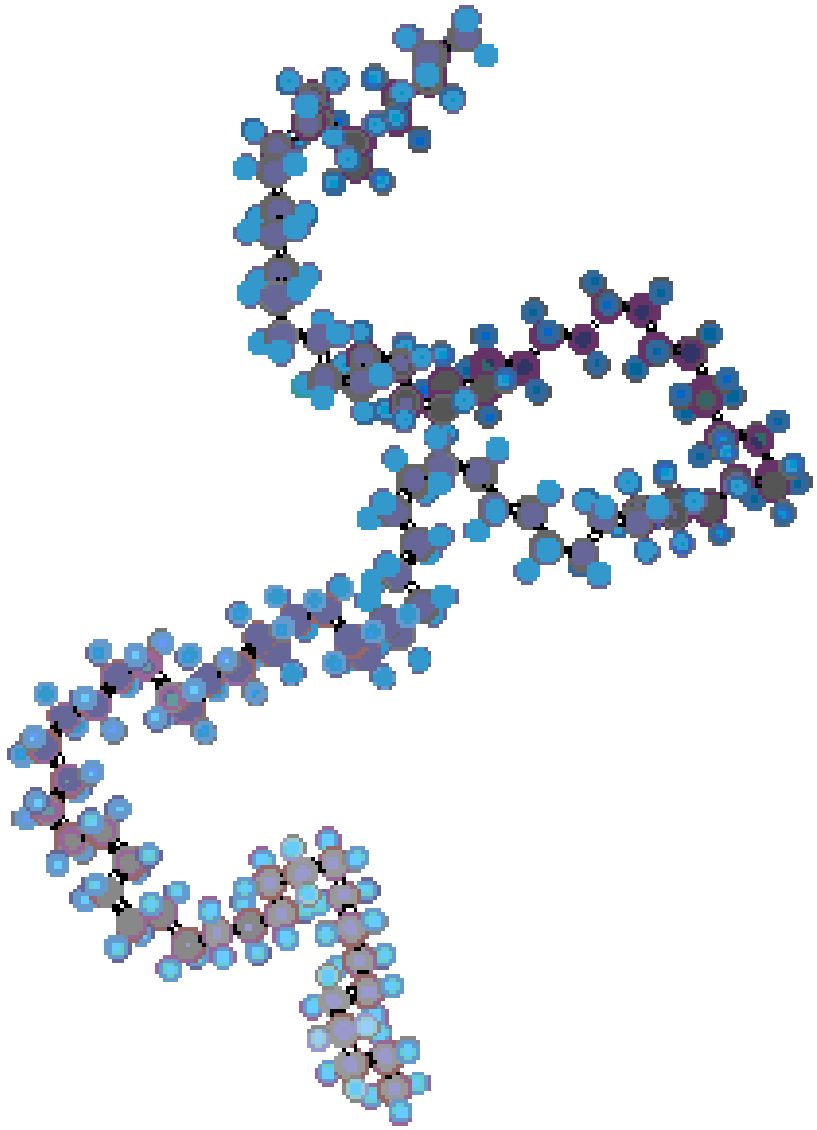
*Chapters 1 & 2 in CD (Polymer Science and Engineering)*

# 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"*

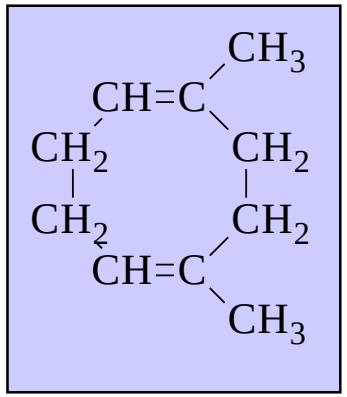
**—Lord Todd,1980**

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

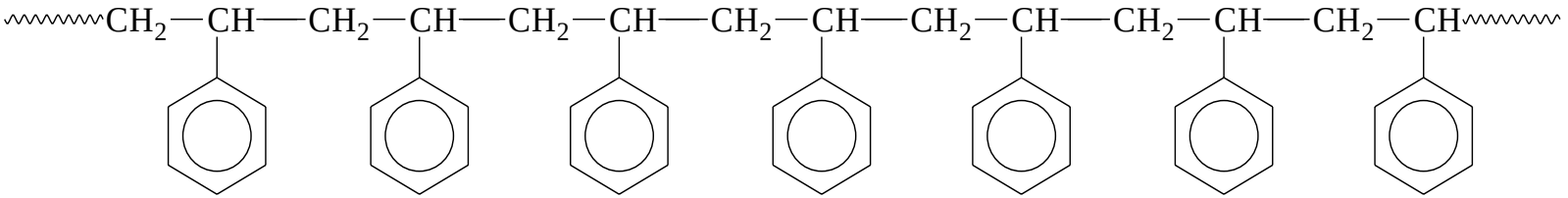


# Staudinger

*"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*

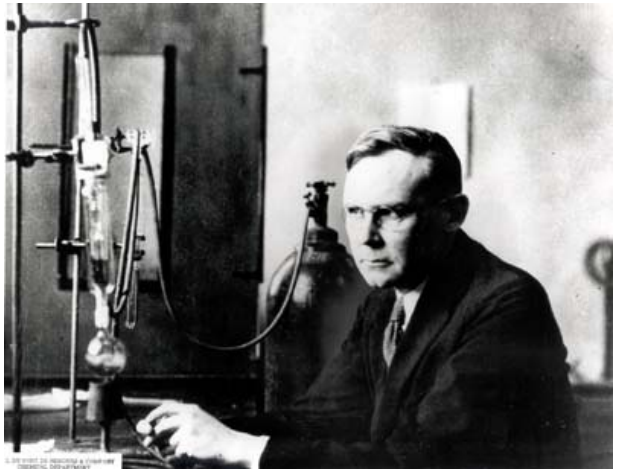


# Timeline

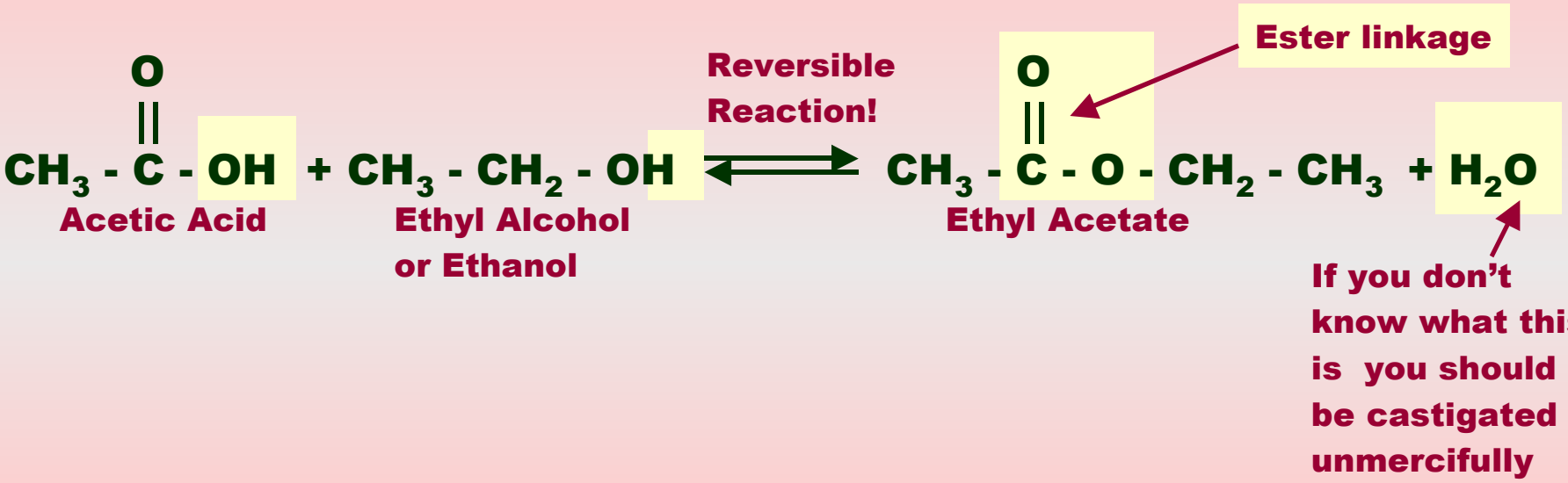
1920 – STAUDINGER;
*The macromolecular hypothesis.*

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

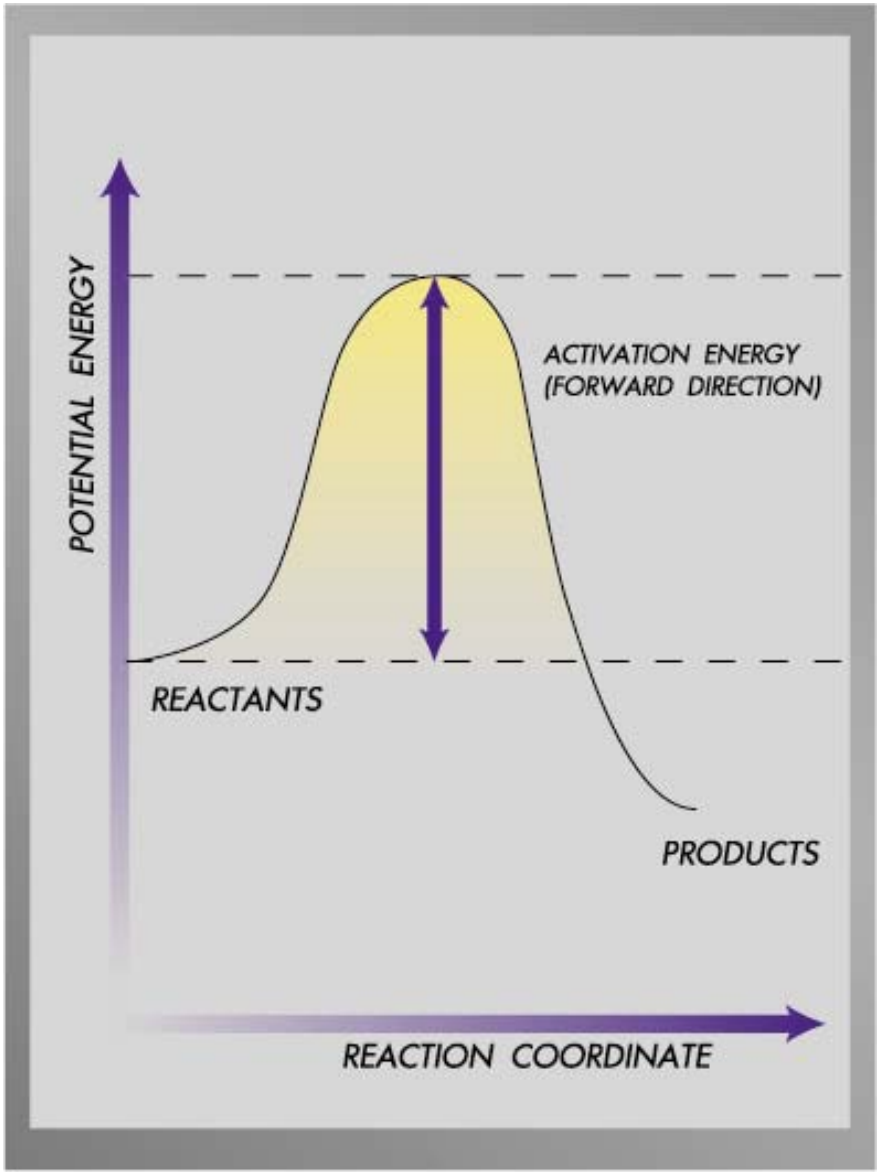
LATE 1920's – CAROTHERS;
*Set out to prove the existence of macromolecules by systematically building them from small molecules using well known chemistry.*



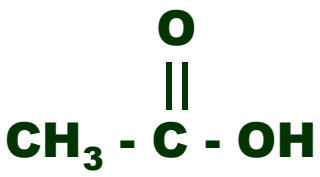
# Condensation Reactions



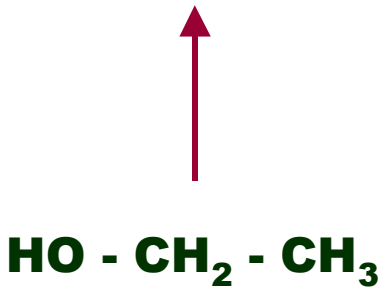
# Why do Molecules React ?




**Acetic Acid**

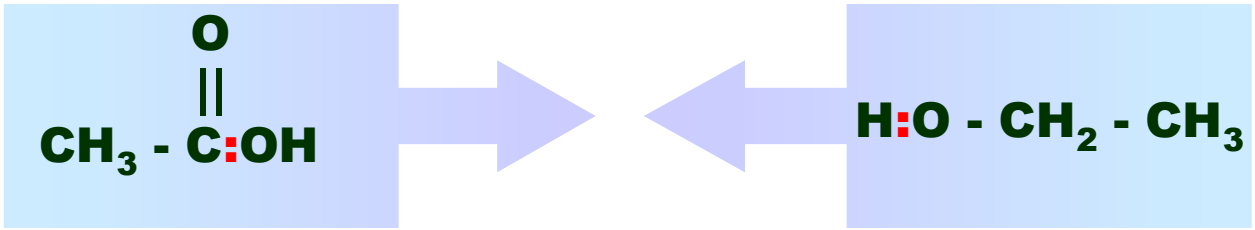



**kersplat!**




**Ethyl Alcohol**
**or Ethanol**

# Why do Molecules React ?

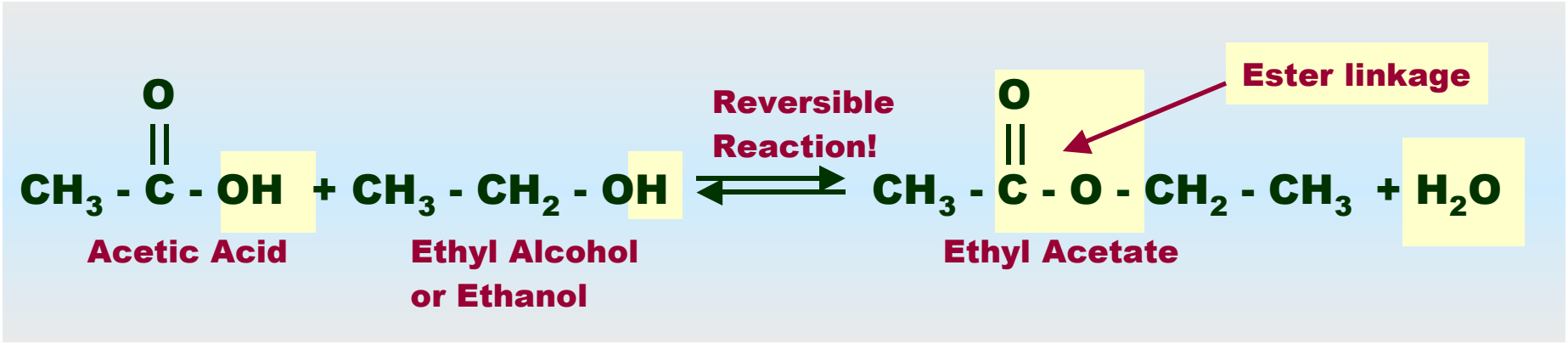



$$HO\cdot + \cdot H \longrightarrow HO{:}H \sim H_2O$$

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

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

# Making a Polymer

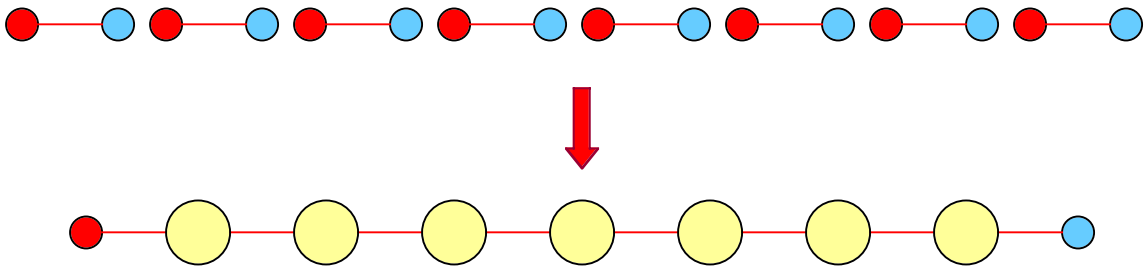



*If we heat acetic acid and ethanol up to just over 100$^0$C, to get the reaction going and drive off water, why don't we form polymer?*

# Making a Polymer

*The molecules are monofunctional;*

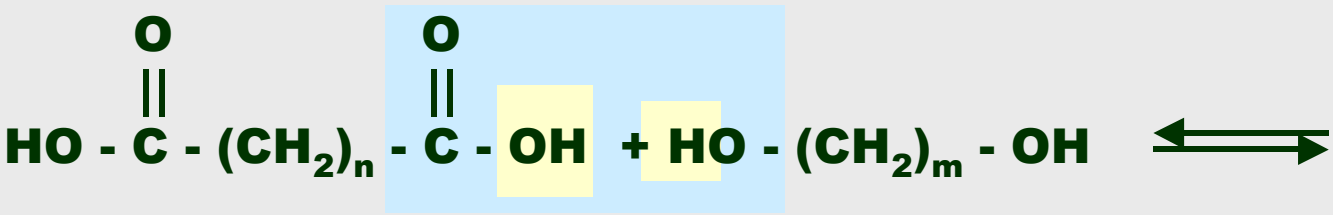
*To make linear chains we need bifunctional molecules;*

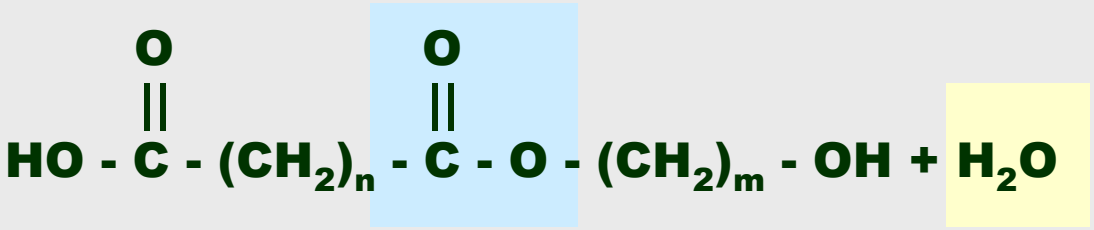


*Except the reaction doesn't happen all in one go, like this, but in a step- growth fashion.*

# Making a Polyester

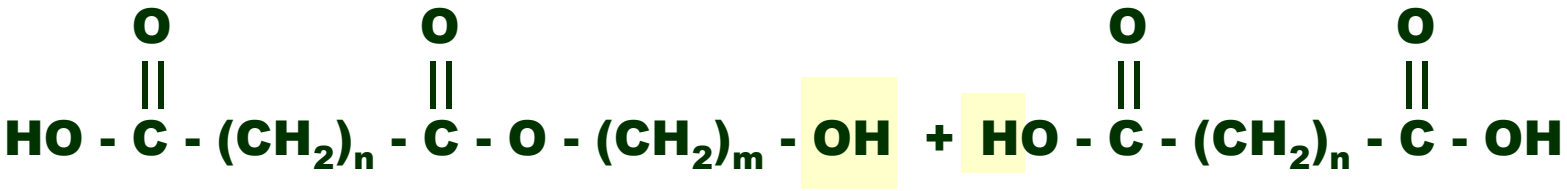
*Monomers*

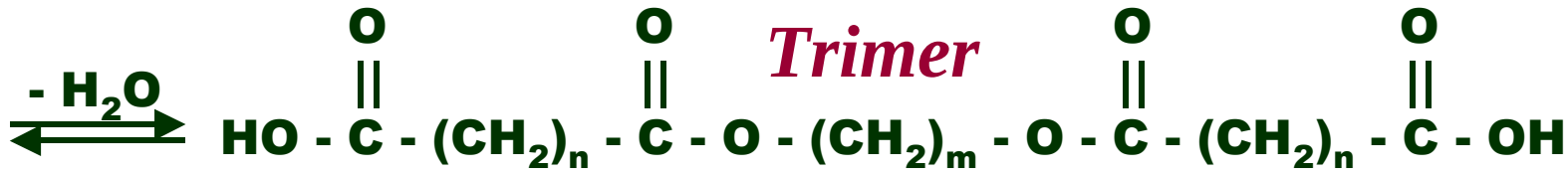



*Dimer*

# Making a Polyester




*Trimer*

*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.

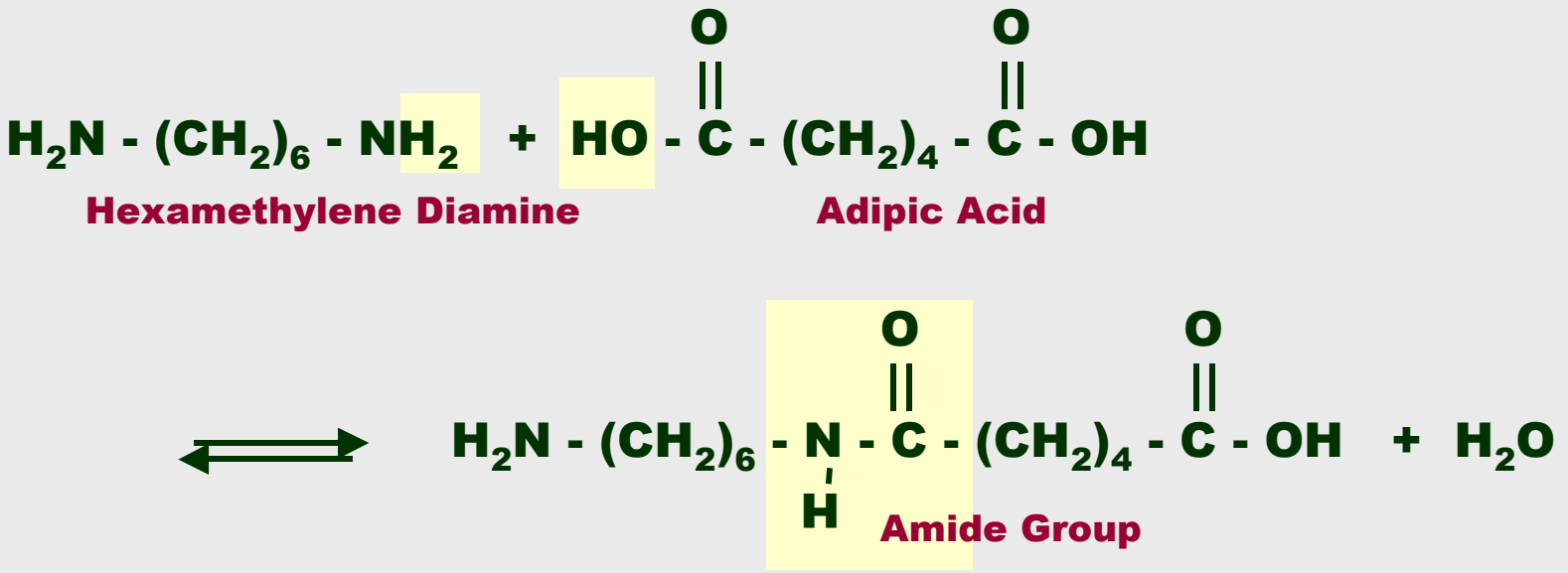
# The Invention of Nylon

*1927 - Stine offers Carothers a job.*

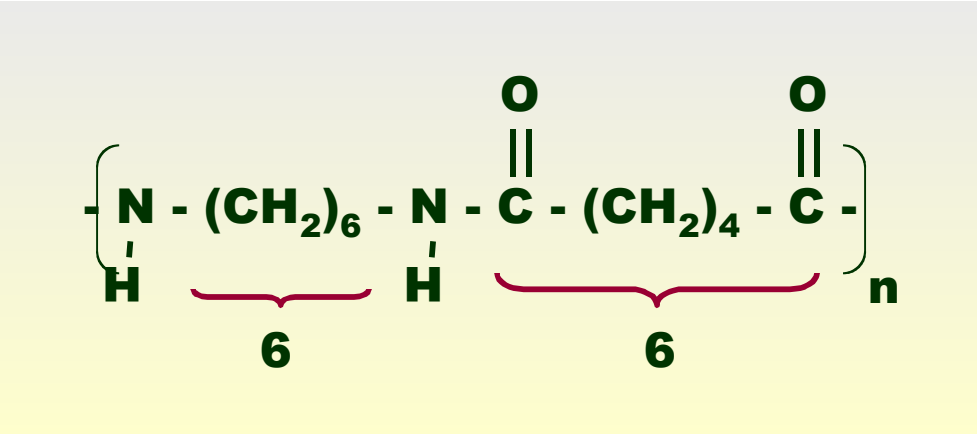
*1929 - Carothers and his group succeed in making low molecular weight aliphatic polyesters*

***The molecular still and the shift to polyamides***

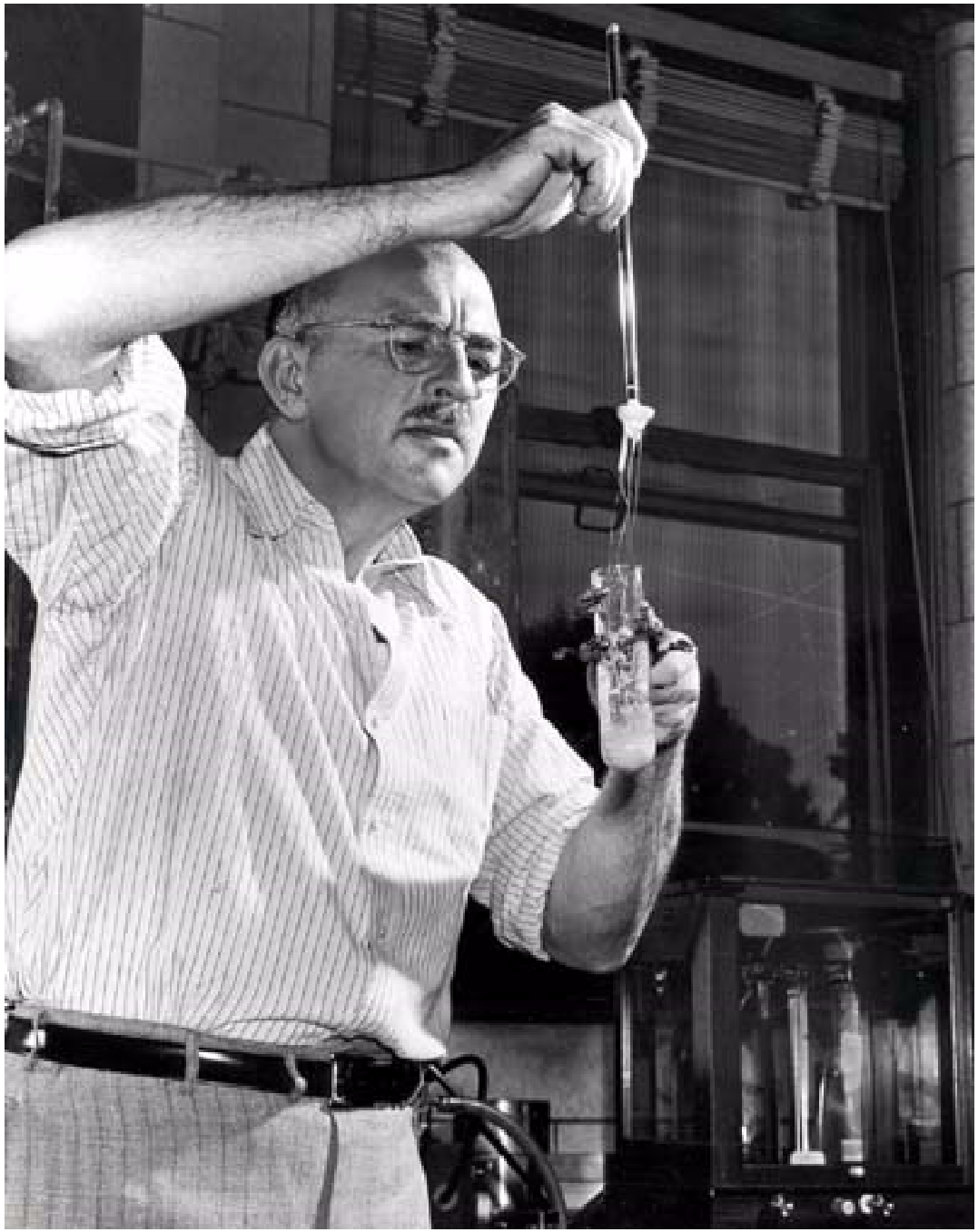
# Nylons


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

NO BETTER EXAMPLE of the fruits of research could be found than nylon—so new a material that a name had to be coined by Du Pont for it—so vast in the number of its possible uses that no list, however farseeing at present, can include them all—so promising in its first uses that Du Pont will spend $8,000,000 on a plant employing approximately 1,000 people.

Nylon is the generic name for all materials defined scientifically as synthetic fiber-forming polymeric amides having a protein-like chemical structure; derivable from coal, air and water, or other substances, and characterized by extreme toughness and strength and the peculiar ability to be formed into fibers and into various shapes, such as bristles, sheets, etc.

*This is the newest of the synthetic materials. In its development a group of Du Pont chemists have been occupied for years. Nylon, though it springs from common raw materials that exist in abundance, can be fashioned into filaments possessing a beautiful luster, strong as steel, delicate as the fiber of a spider's web, yet more elastic than any of the natural fibers.*

Toothbrushes with "Exton" bristles made from nylon are now available. Soon other forms of this new product will reach the public as a result of experimental work in progress.

Out of continued research in synthetic chemistry has come this development, as will others, to aid in the building of the World of Tomorrow.

### Jobs...Jobs...

Still another important result comes from this contribution—as from other chemical developments. From these fruits of chemical research spring jobs for the men who build plants and machinery—jobs for the men who make the raw material—jobs for the men who convert it into numerous articles for everyday service. Thus science doubly aids man in his search for better living.

### The Past Gives a Clue to the Future

During the past ten years, Du Pont developments have included (among many other uniquely useful products) such contributions as these:

*Moistureproof "Cellophane" cellulose film to protect foodstuffs from dirt and germs, and to preserve freshness and flavor.*

*"Cordura" rayon yarn, the super-tough fiber for truck and auto tires.*

*Nitrogen compounds made from the air, to return vital elements to the soil.*

*Neoprene chloroprene rubber with the resilience, strength and toughness of natural rubber, yet superior in its resistance to gasoline, oils, sunlight, heat and aging.*

*Improved fire retardants to reduce fire hazards in home and industry.*

*"Zerone" anti-rust anti-freeze to protect automobile radiators from freezing in winter . . . from rusting and corroding in summer.*

*"Dulux" enamels, the tough, long-lasting finishes now used on automobiles, trucks, streamlined trains, ships, bridges, home appliances, interior walls, refrigerators.*

### Higher Wages...Lower Prices

Since 1929, Du Pont has developed scores of new products. Today Du Pont employs more people than in 1929, pays higher wages, and sells its goods in greater quantities and at lower prices. Last year, forty percent of Du Pont's entire sales was on twelve lines of products developed or improved since 1929.

Scientists believe this record of accomplishment, these contributions to better living, are a promise of things to come—a promise for the World of Tomorrow and for those who will inherit it.

### Your Preview of a Better World

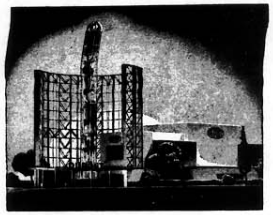
At the New York World's Fair, Du Pont's "Wonder World of Chemistry" exhibit will present some of the more spectacular chemical achievements. Here will be shown, for the first time, many of the intricate processes used in the development and manufacture of Du Pont products. Here those who look hopefully to the future will find proof of what orderly research has done to contribute to better living and more continuous employment for everyone.

### Where to Tomorrow, Mr. Chemist?

And the chemist answers: "To a thousand untouched shores. To a land of tomorrow where rain won't wet your clothes, where everyone gets his vitamins, where fire won't burn your home, where insects won't steal your wealth, where life is easier, happier, and more complete in ways that can't even be dreamed of today."

How soon, Mr. Chemist? And the chemist answers: "Just as soon as I can make it come true. I build for the tomorrow that will be yours, and your children's and your grandchildren's. And when each of these tomorrows becomes a 'today'—there will still be tomorrows to work for!"

Such is the spirit and the meaning of the Du Pont pledge: "Better Things for Better Living . . . through Chemistry."



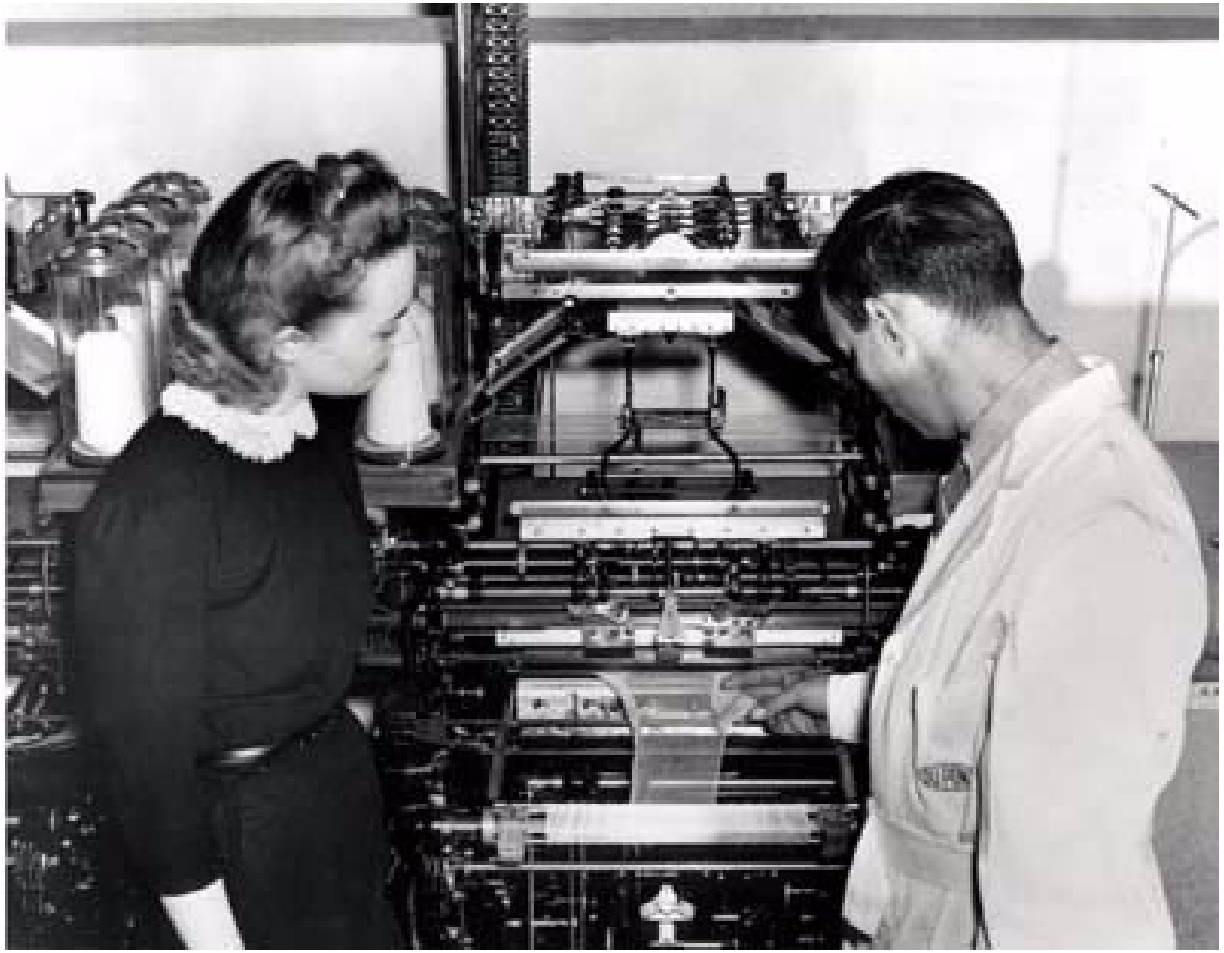
*When you visit New York's World Fair in 1939, you will find nothing more fascinating than a tour through this building—The Wonder World of Chemistry, presented by Du Pont to give you a glimpse of the world of tomorrow.*

DU PONT
REG. U.S. PAT. OFF.

E. I. du Pont de Nemours & Company, Inc., Wilmington, Delaware

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.*

Journal-Every Evening, Wilmington, Delaware, Monday, May 13, 1940

# *Nylon Parachute*
# *WWII*

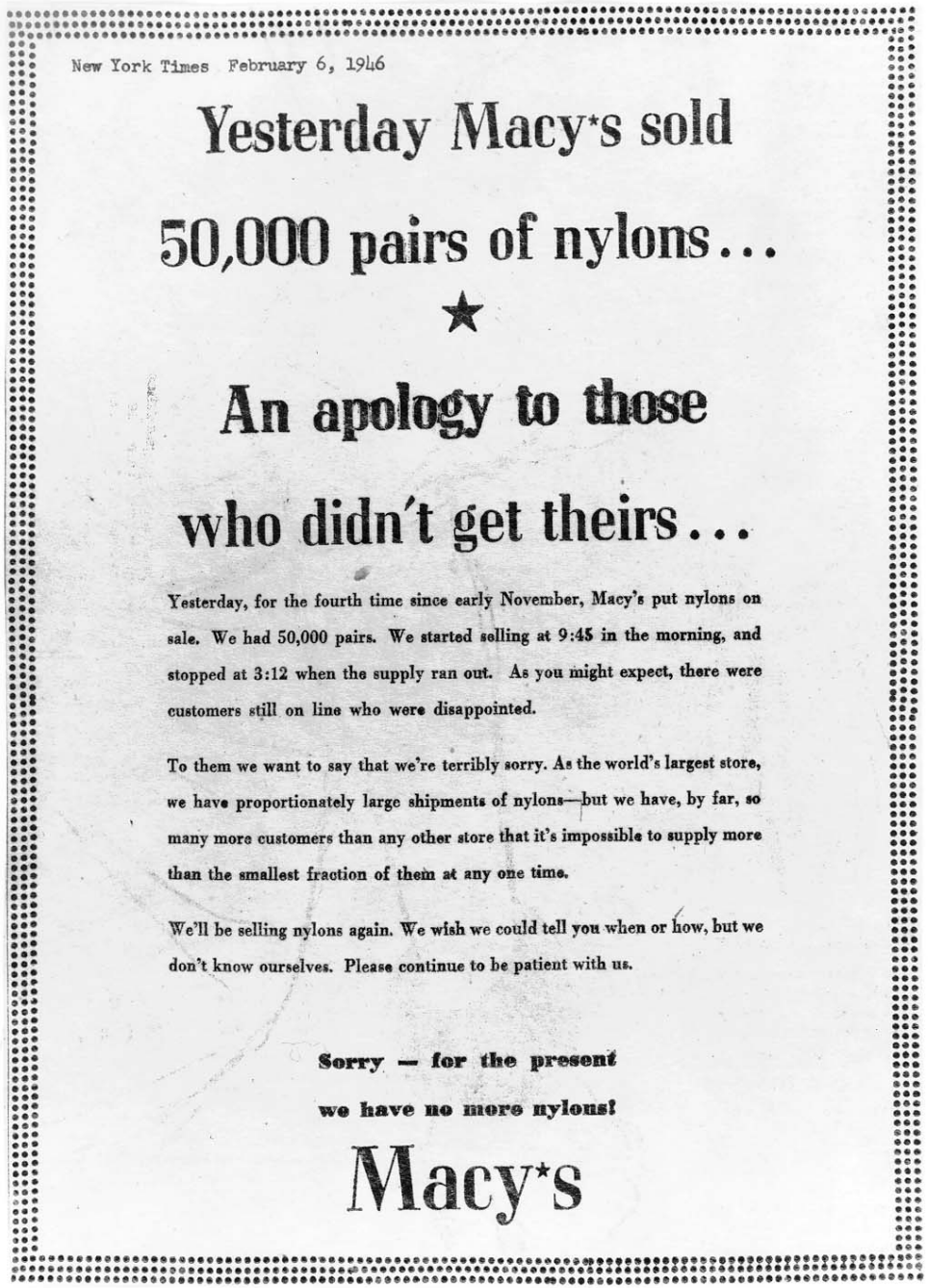
***Betty Grable auctions her stockings for the war effort.***

***Post WWII stocking sale, NYC.***


***She couldn't wait!***

# *Post WWII stocking sale, San Francisco.*

# Sold Out!



New York Times February 6, 1946

## 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 9:45 in the morning, and stopped at 3:12 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 or how, 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.

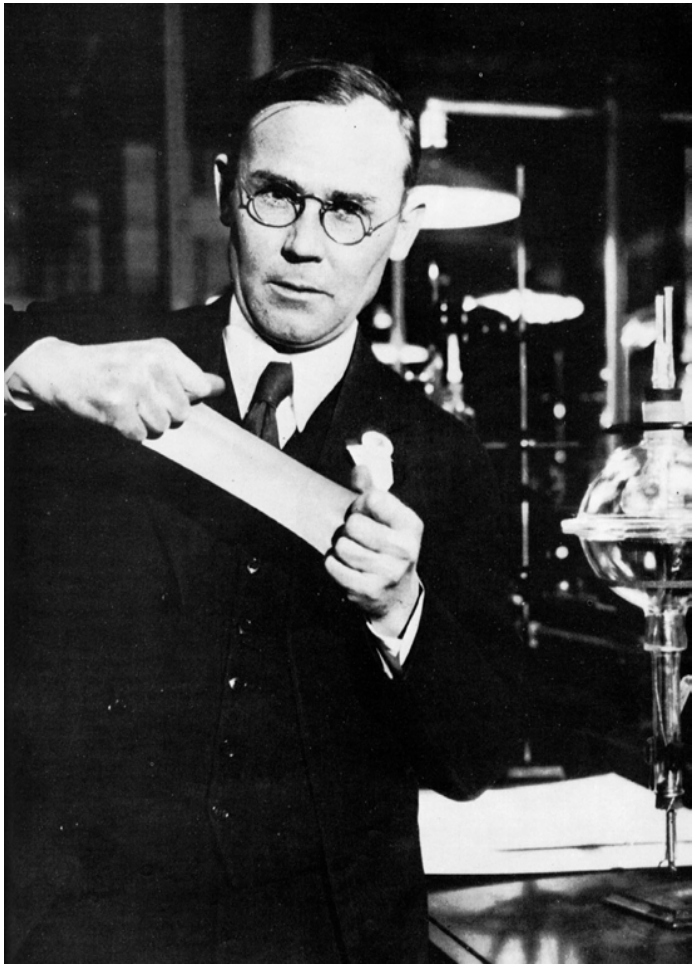
# Polymer Synthesis - Classification

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

- *Condensation*
- *Addition*

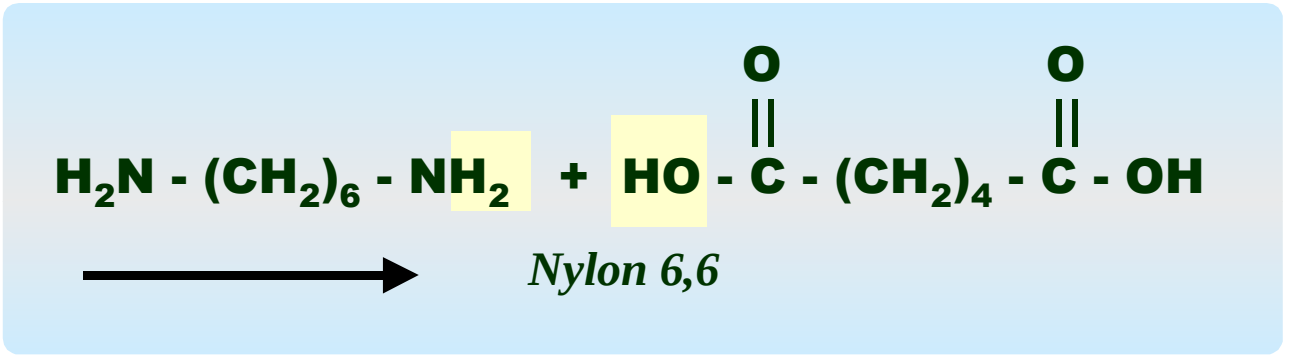
As you will see, a better classification may be;

- *Step-growth*
- *Chain*

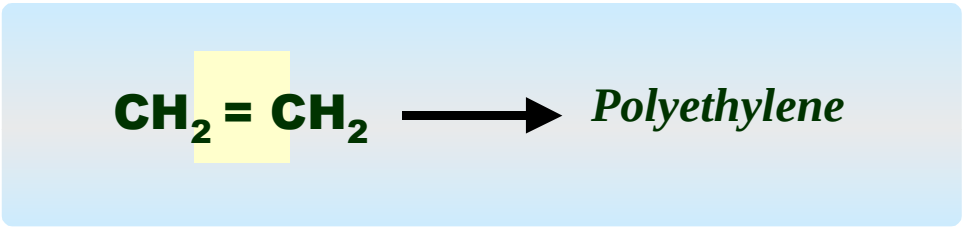


# Types of Reactions

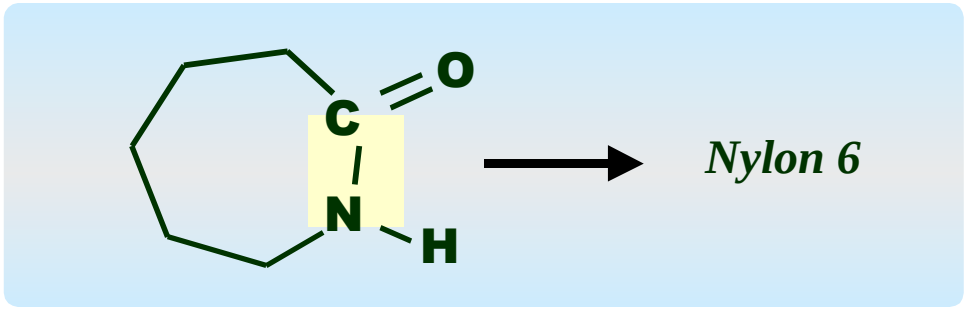
*Condensation*



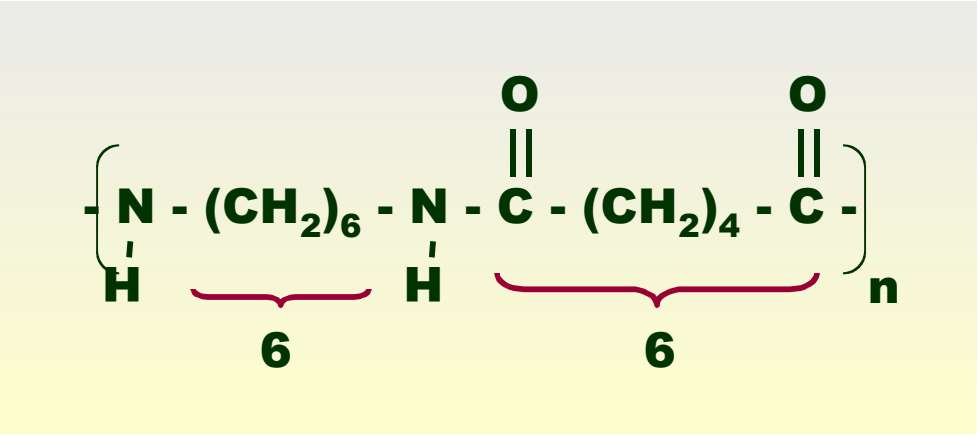

*Addition*




*Ring opening*



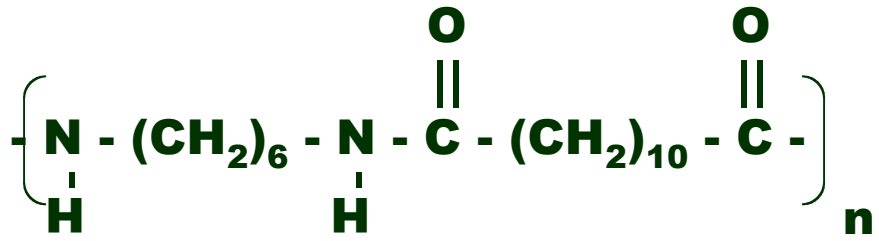
# Nylon 6,6



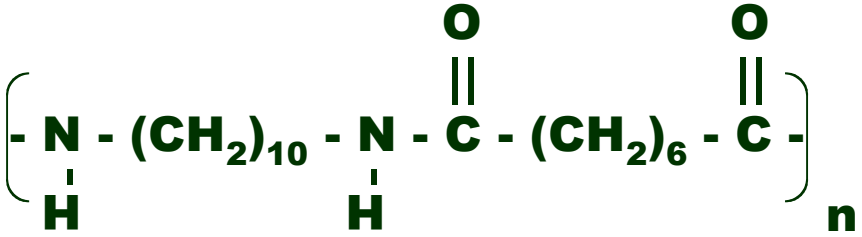
# Nylon 6,10

*What would nylon 6,10 look like?*

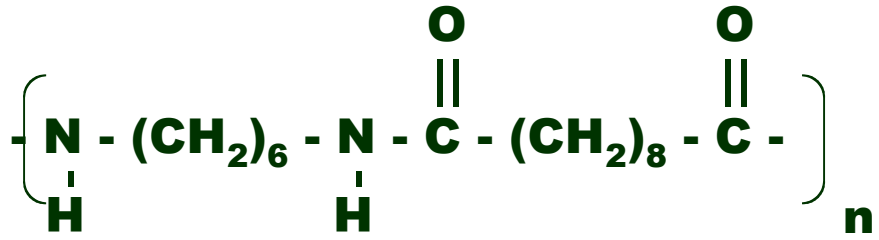
**A**



**B**



**C**



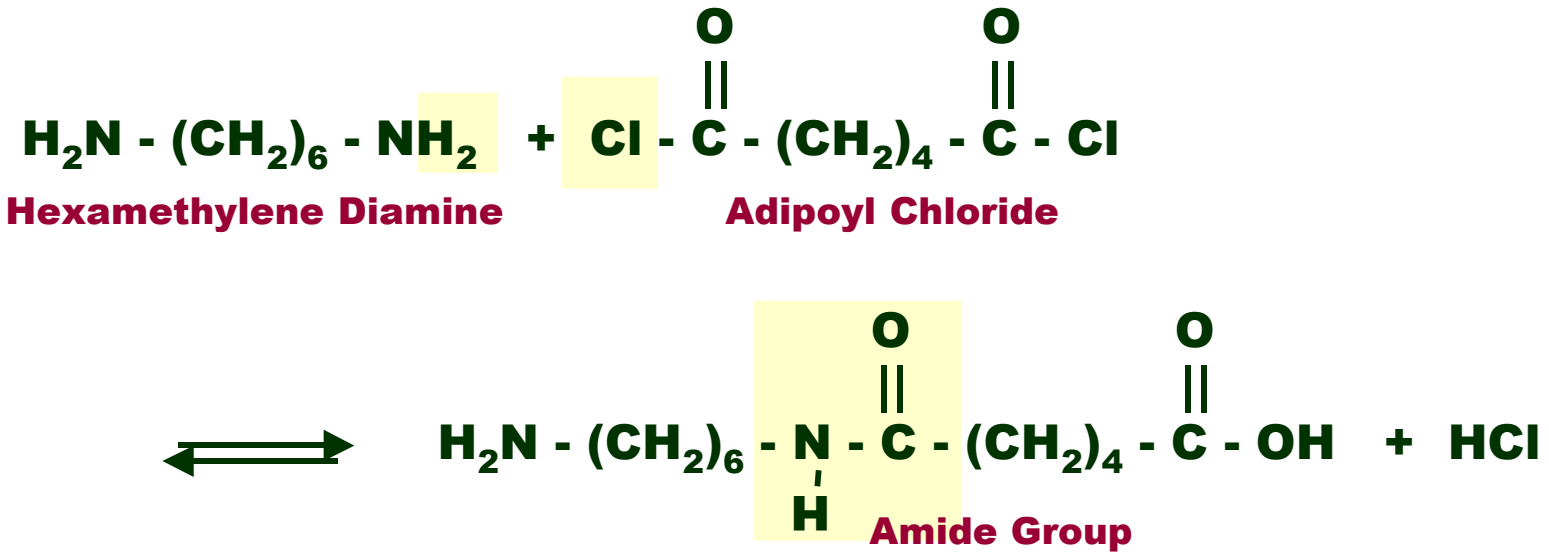
# More on Nylons

*Applications*

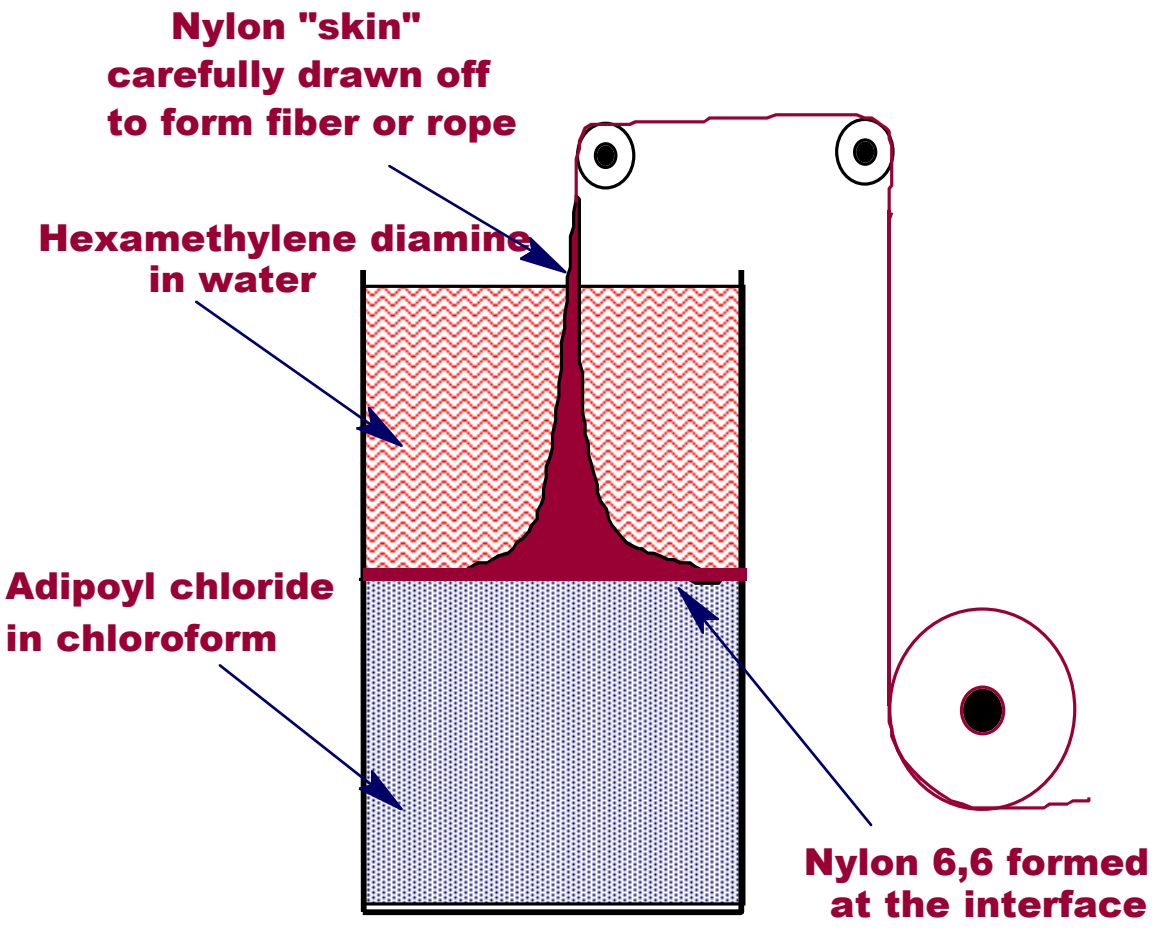
- *Carpet Fibers*
- *Clothes*
- *Gear wheels*
- *Etc.*

# Back to Condensation

*Is a molecule of water always split out?*



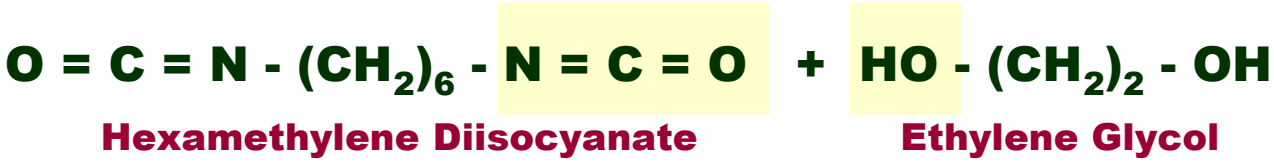
# The Nylon Rope Trick



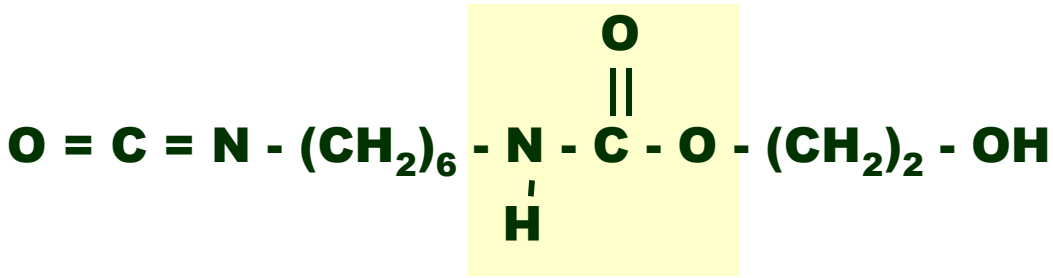
# The Nylon Rope Trick

# 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?*

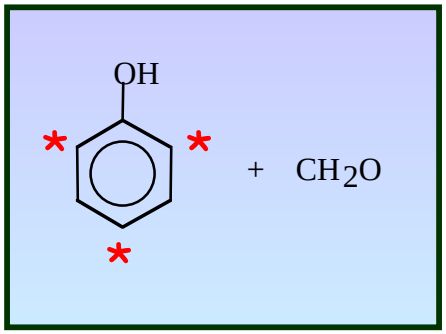
A. *Use a mixture of bifunctional and monofunctional units*

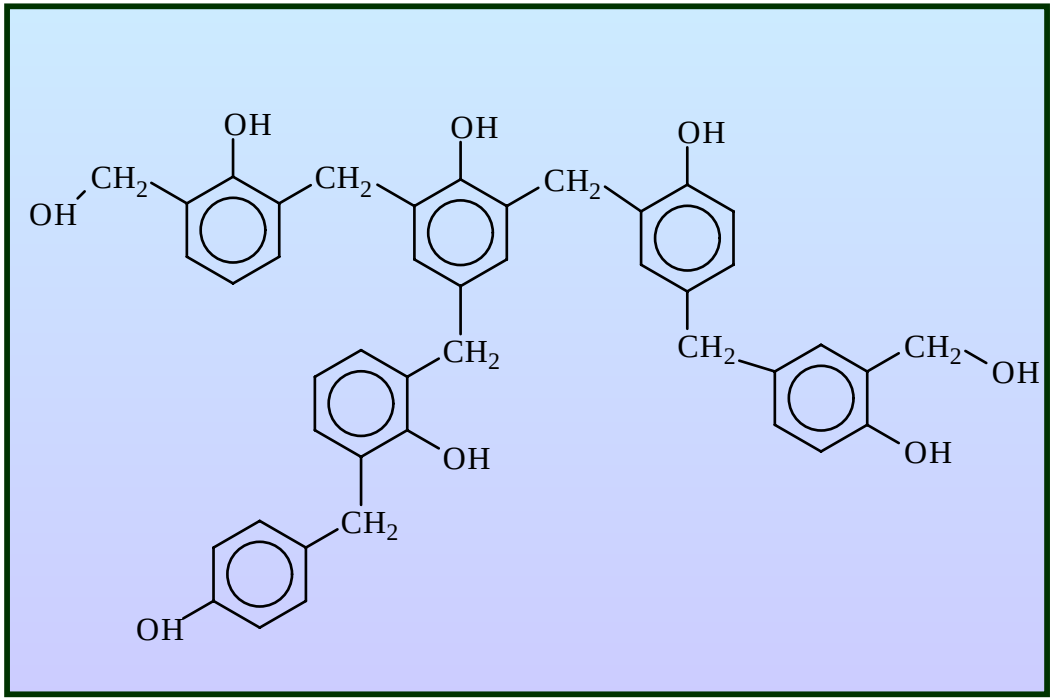
B. *Get a tube of Molecular Super Glue and stick a bunch of chains together*

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

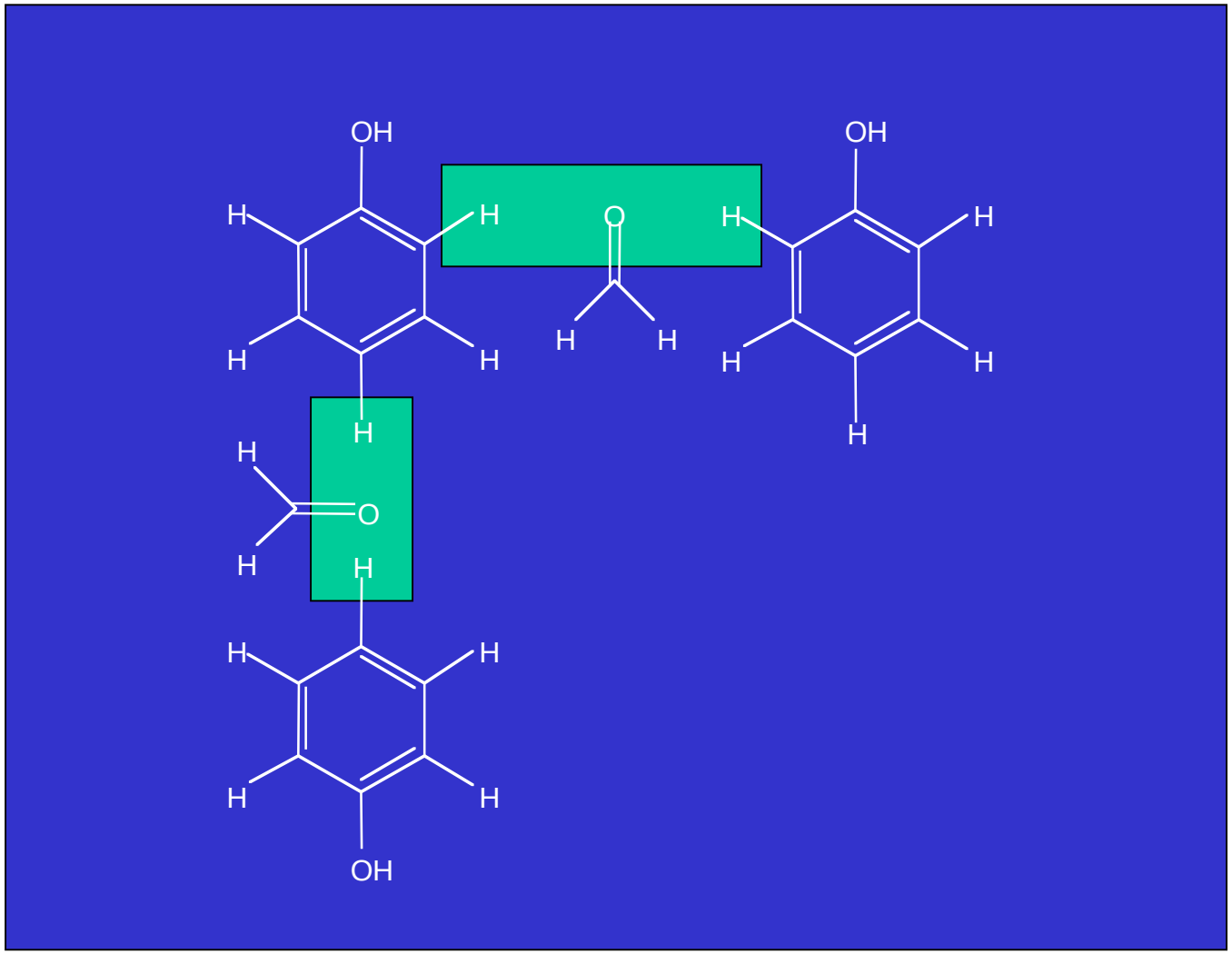
# Network Formation

*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.*

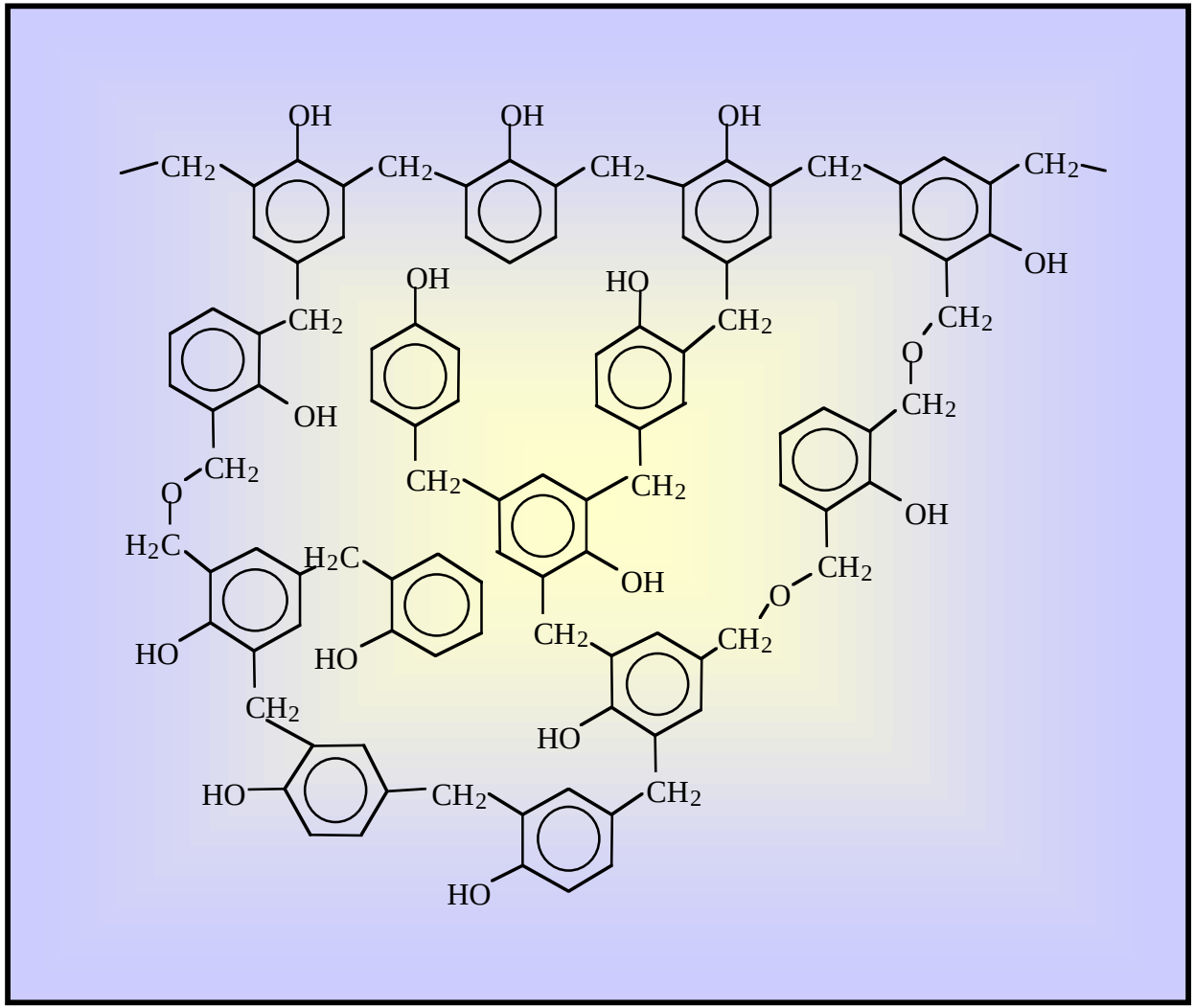


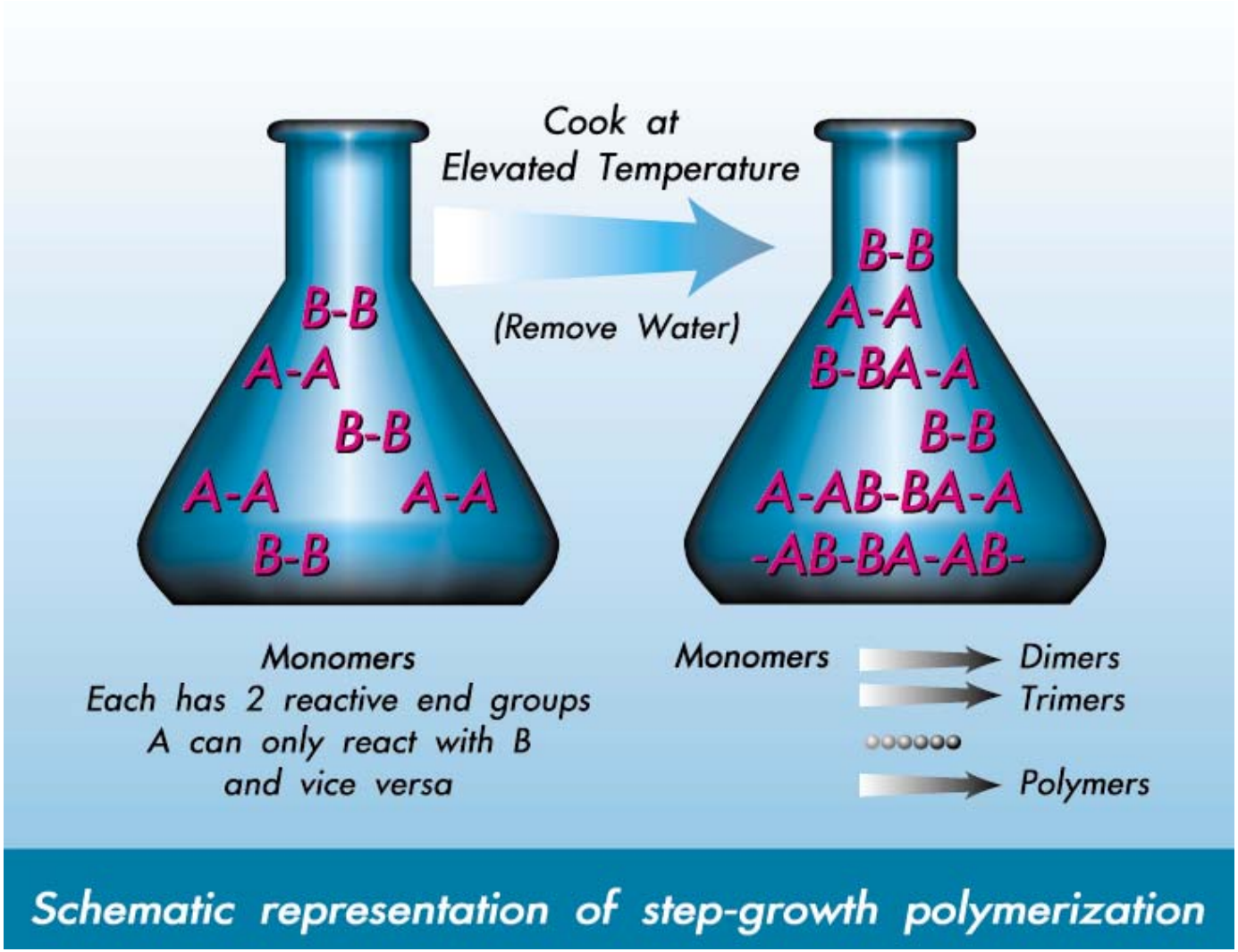
# Another Condensation Reaction



# Network Formation



# Step-Growth Polymerization ; Summary

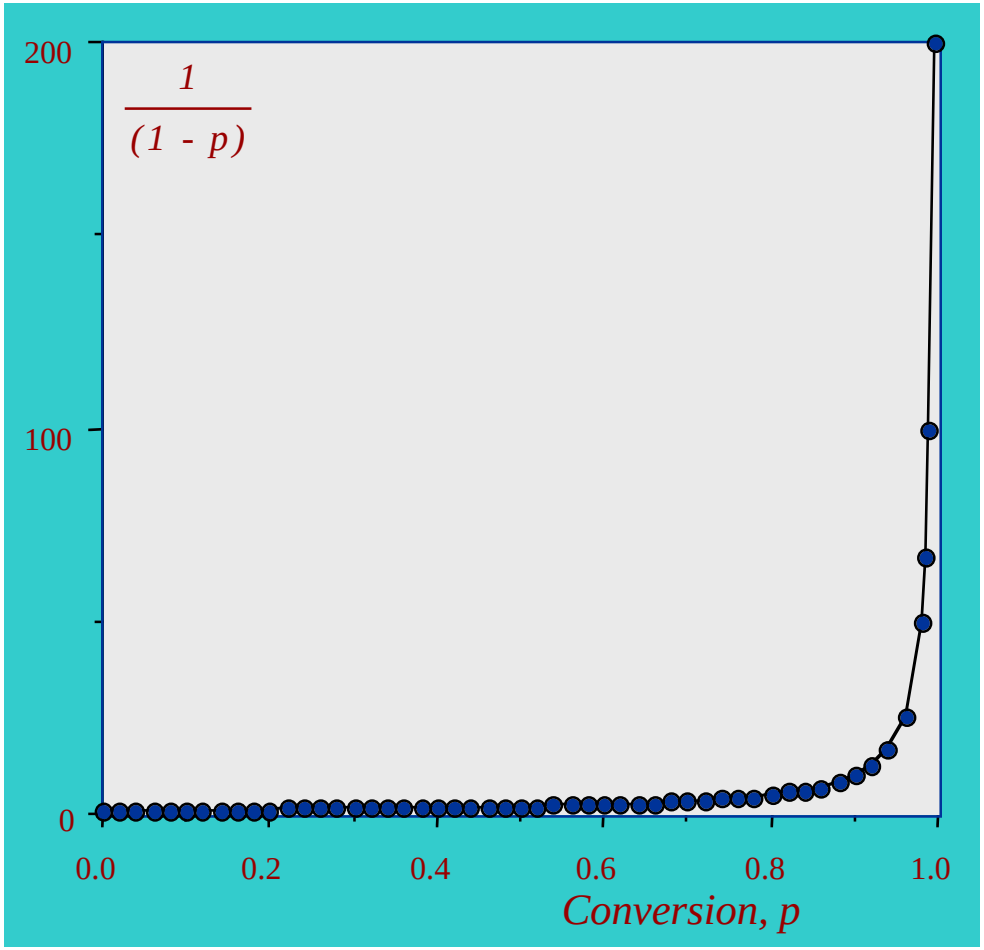



Schematic representation of step-growth polymerization

# 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*