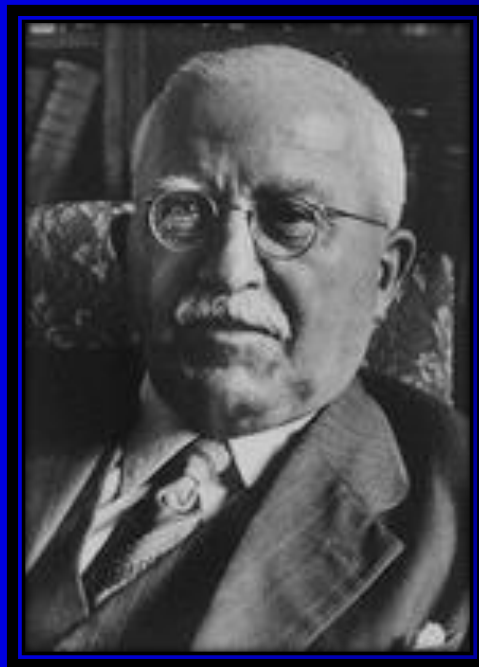


Lecture 24 *POLYMERS*



Jöns Jacob Berzelius
(1779-1848)



Hermann Staudinger
(1881-1965)



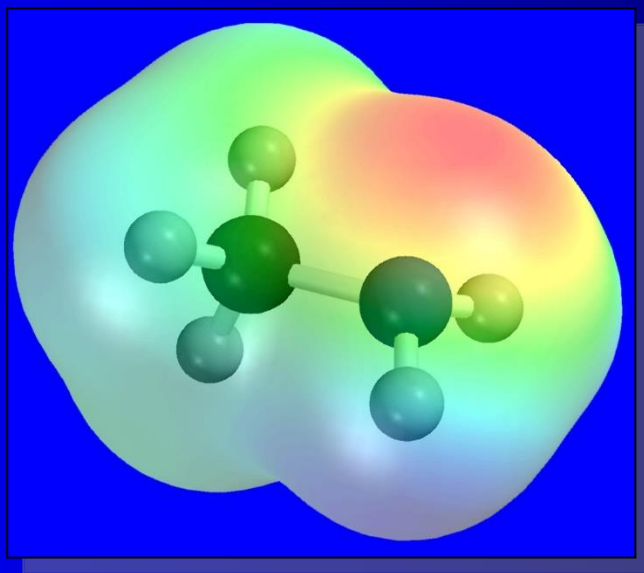
Wallace Hume Carothers
(1896-1937)

April 13, 2016

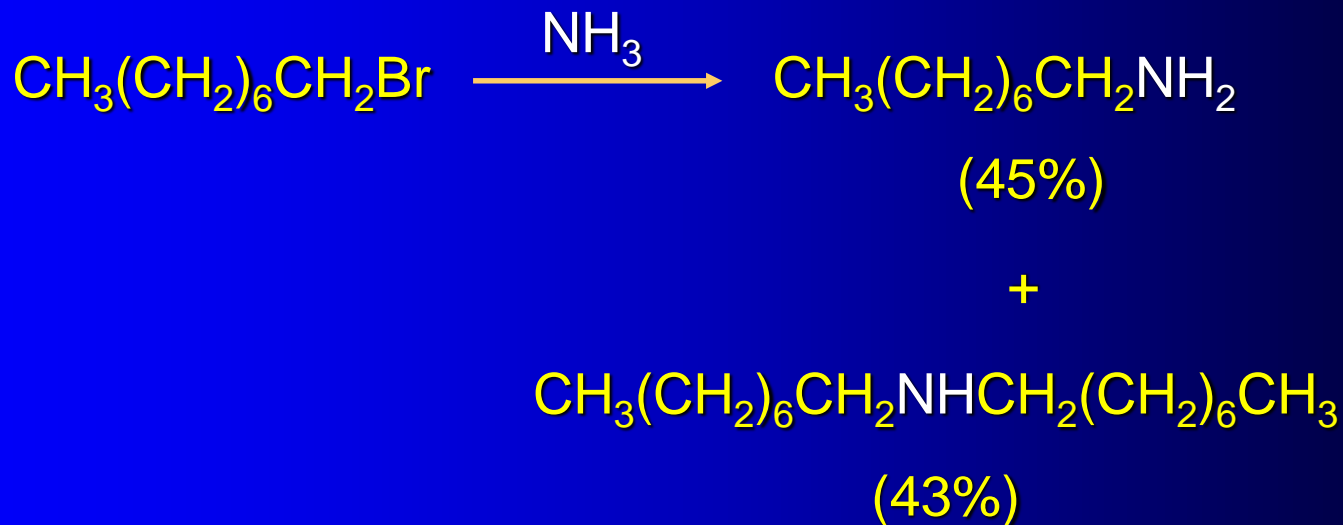
Chemistry 328N



Synthesis of Amines



Example

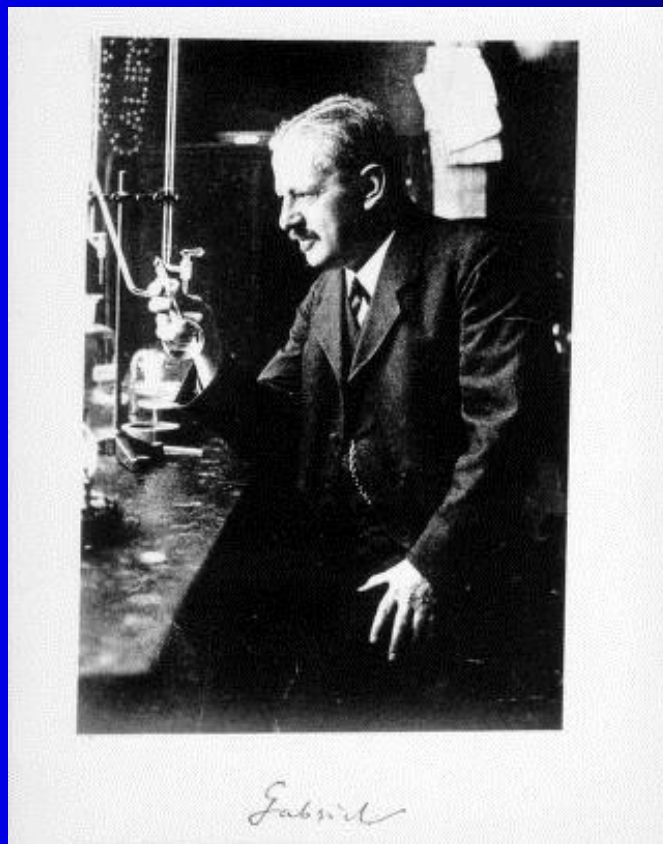


- As octylamine is formed, it competes with ammonia for the remaining 1-bromooctane. Reaction of octylamine with 1-bromooctane gives *N,N*-dioctylamine.



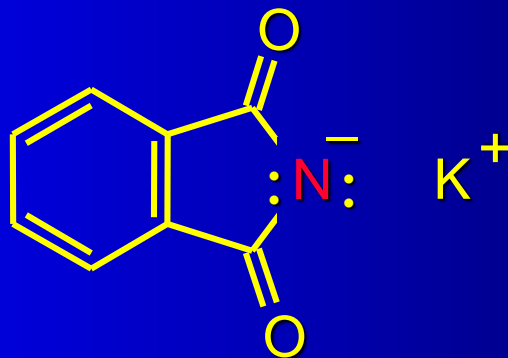
Siegmund Gabriel

1851-1924



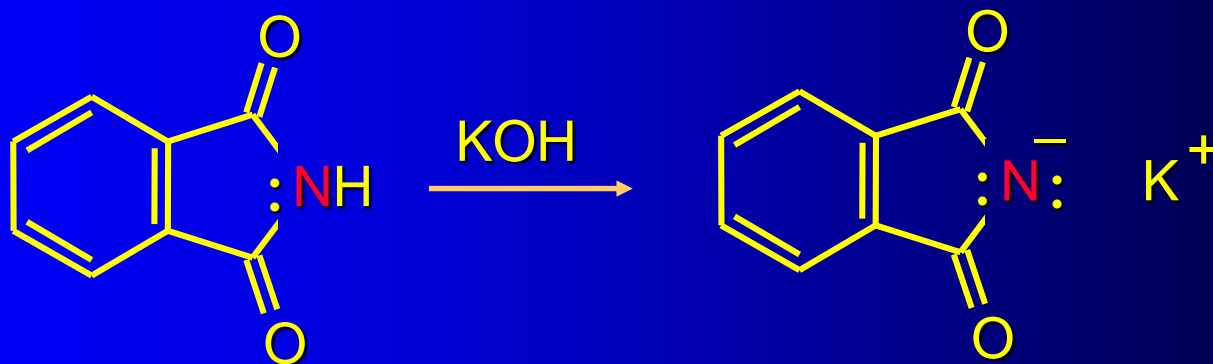
The Gabriel Synthesis

- Gives primary amines without formation of secondary, etc. amines as byproducts
- Uses an S_N2 reaction on an alkyl halide to form the C—N bond
- The nitrogen-containing nucleophile is *N*-potassiophthalimide

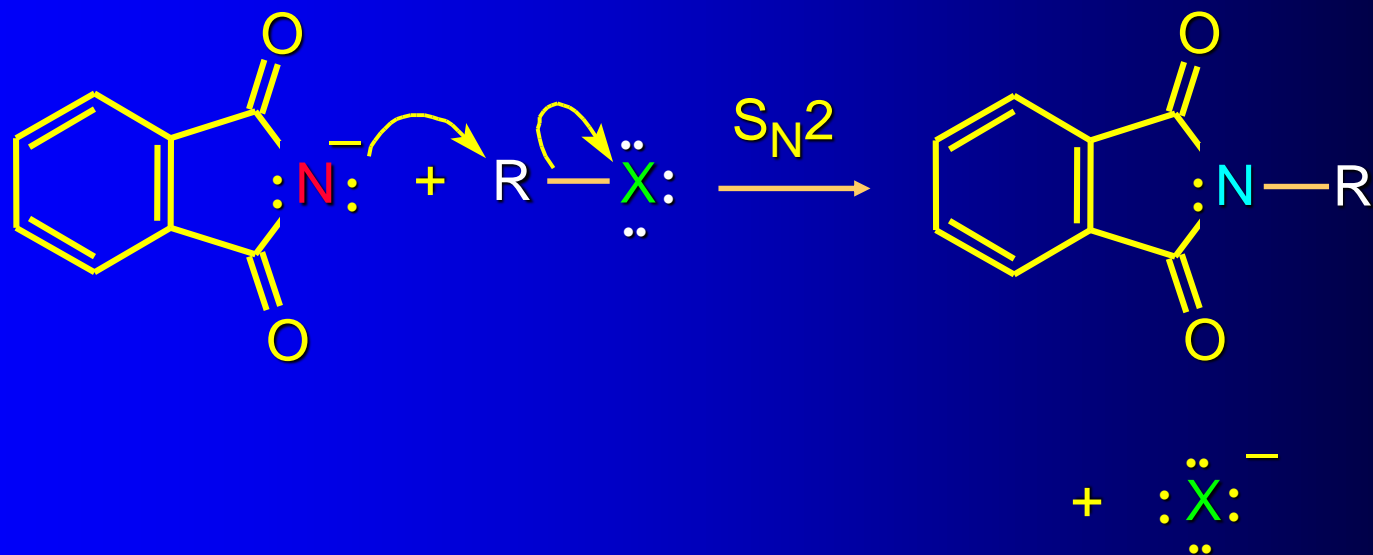


N-Potassiophthalimide

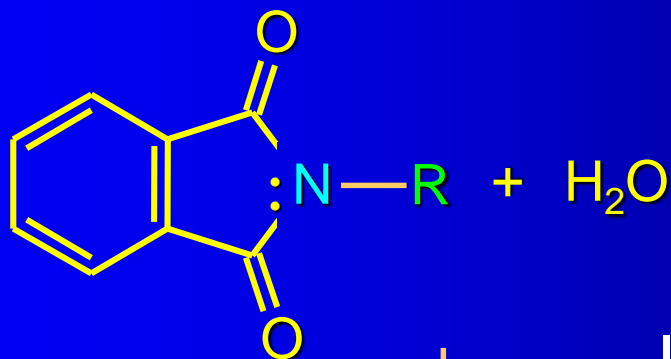
- the pKa of phthalimide is 8.3
- *N*-potassiophthalimide is easily prepared by the reaction of phthalimide with KOH



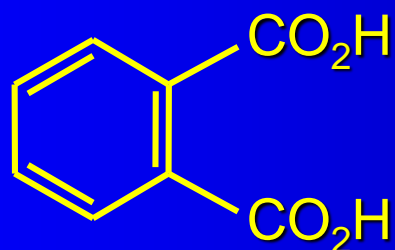
N-Potassiophthalimide as a nucleophile



Cleavage of Alkylated Phthalimide



acid or base

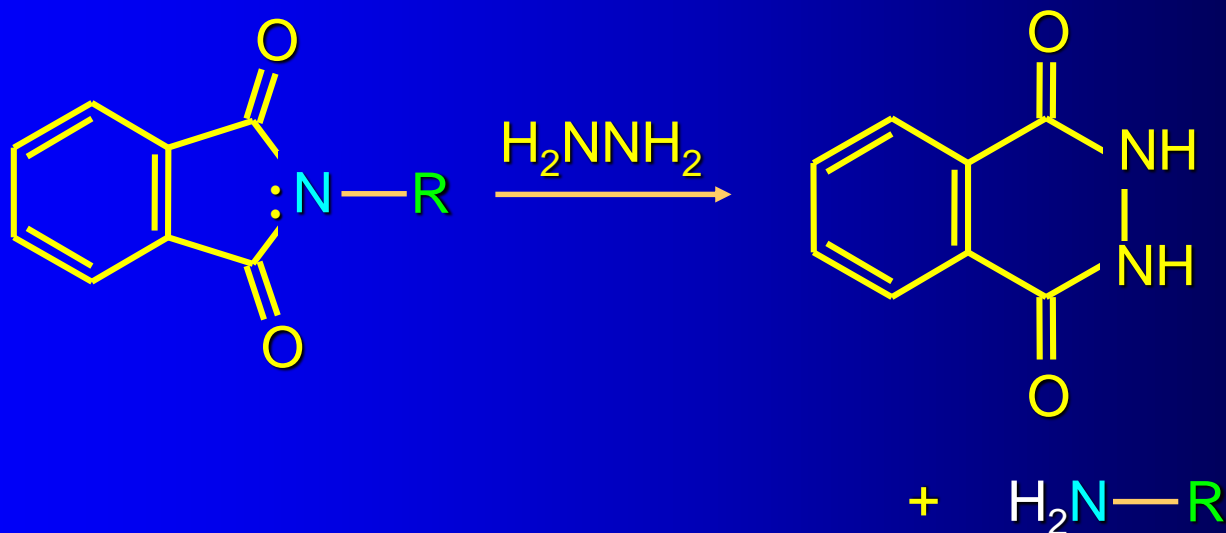


Imide hydrolysis is
nucleophilic acyl
substitution !!

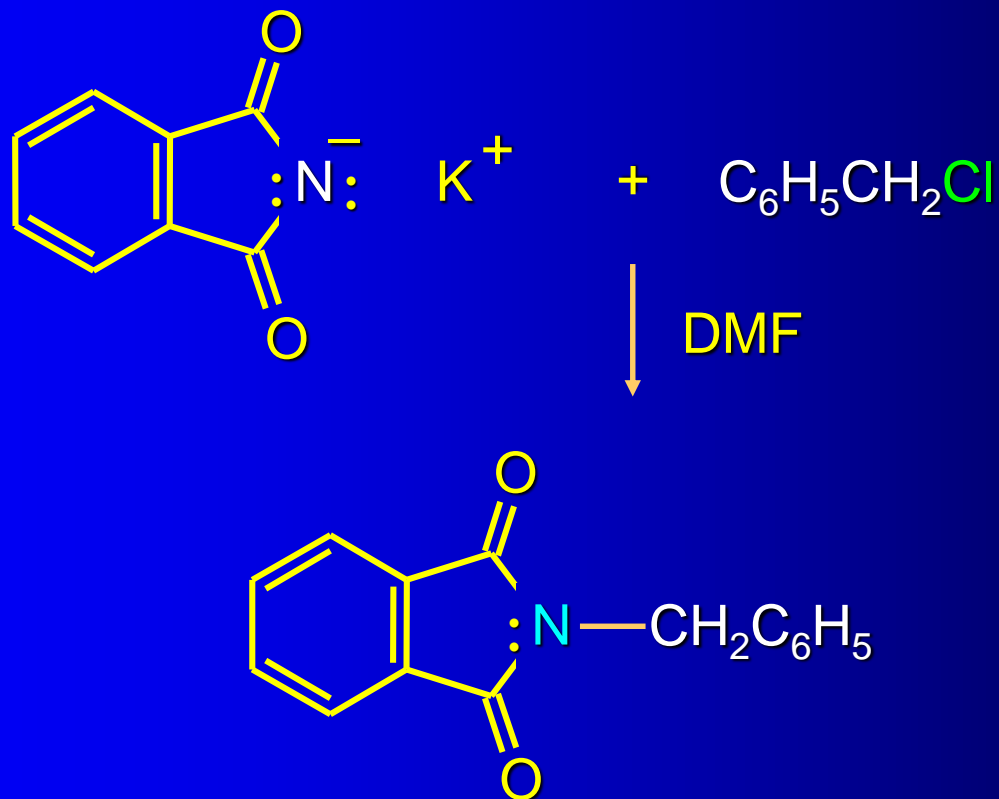


Cleavage of Alkylated Phthalimide

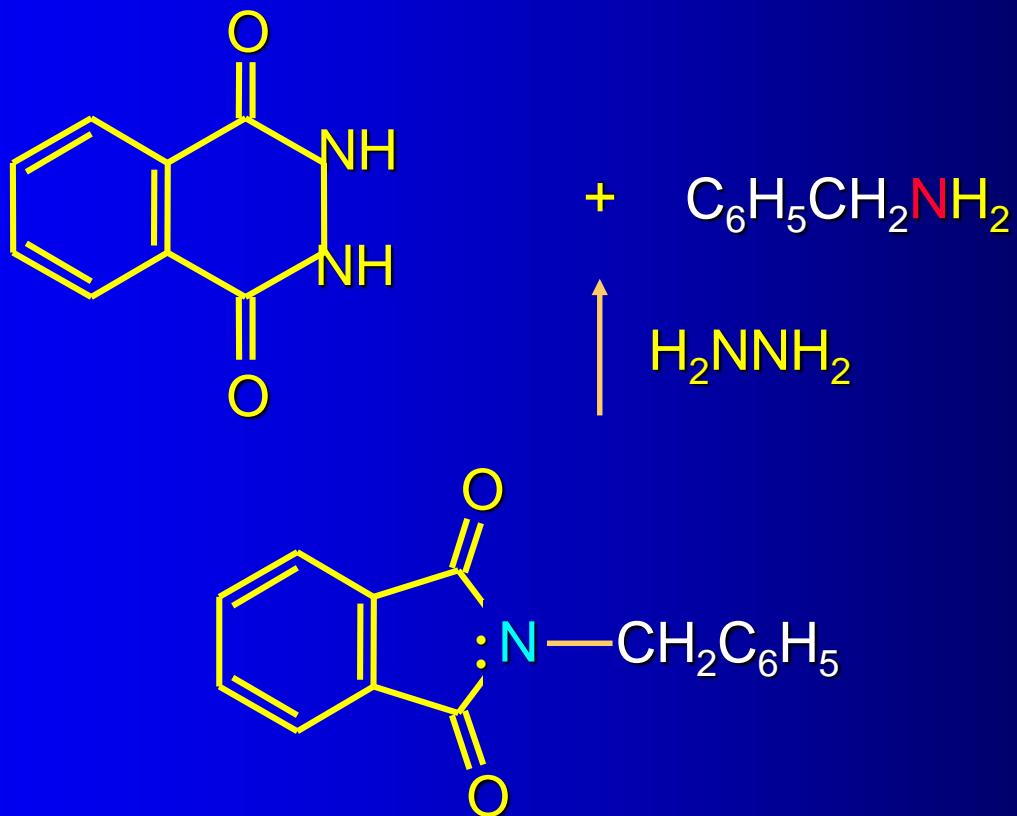
- Hydrazinolysis is an alternative method of releasing the amine from its phthalimide derivative



Example



Example



Preparation of Amines by Reduction

- Almost any nitrogen-containing compound can be reduced to an amine, including: nitriles, nitro-substituted benzene derivatives and amides

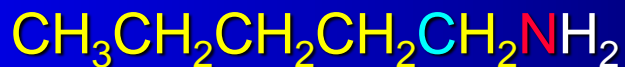


Synthesis of Amines via Nitriles

- S_N2 reaction, followed by reduction, gives a primary alkylamine.



nitriles can be reduced by lithium aluminum hydride



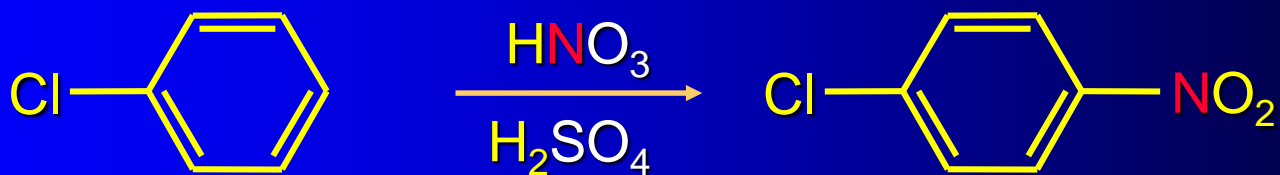
Synthesis of Amines via Nitriles



the reduction also works with cyanohydrins

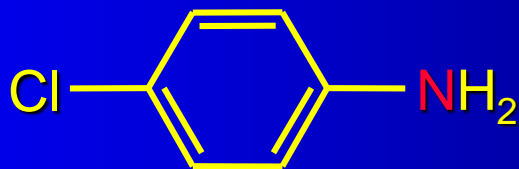


Synthesis of Amines via Nitroarenes

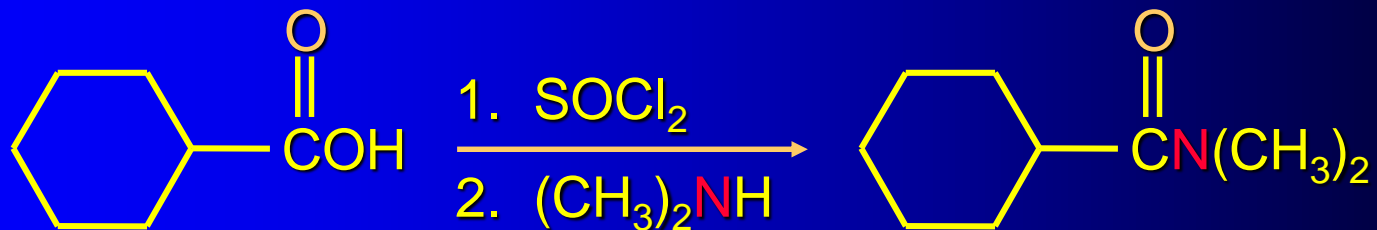


nitro groups may also be reduced with tin (Sn) + HCl or by catalytic hydrogenation

1. Fe, HCl
2. NaOH

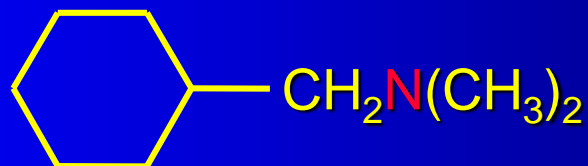


Synthesis of Amines via Amides



only $LiAlH_4$ is an appropriate reducing agent for this reaction

1. $LiAlH_4$
2. H_2O



Plastics !!!!

The Graduate (1967): Recent college graduate Benjamin Braddock is trapped into an affair with Mrs. Robinson, who happens to be the wife of his father's business partner and then finds himself falling in love with her teenage daughter, Elaine.



[The Graduate](#)

Chemistry 328N



Polymer Chemistry

- I encourage you to take ChE 355
Introduction to Polymers (Dr. Ellison)
- Most chemical engineers will work with organic materials in their career
- Nearly all of you will encounter polymer materials issues in you work.
- If you are going to be a chemical engineer, you are going to work with polymers in some way!







A Polyethylene Plant
500,000 Metric Tons / year

Supplemental Problem

- The world wide production of polyethylene in 2015 was on the order of 100 million metric tons.
- Austin ranks No. 9 nationally for largest home sizes. A typical house in Austin is 1,837 square feet.
- Assuming a density of 1 gram/cc, no interior walls or other complexity, how many 1,837 square foot homes with 8 foot ceilings would be required to contain all of this polymer???



What are Polymers??



Jöns Jacob Berzelius
(1779-1848)

Berzelius coined the term "polymer" in 1833 to describe organic compounds that share identical empirical formulas but differ in overall molecular weight ...a kind of "isomer".. acetylene cyclobutadiene, benzene and styrene, for example.

This concept lasted until Carothers.



Organic Polymer Chemistry

- Polymer: from the Greek, poly + meros, many parts. Any long-chain molecule synthesized by linking together repeat units called monomers
- Monomer: from the Greek, mono + meros, single part. The simplest non-redundant unit from which a polymer is synthesized
- Plastic: a polymer that can be molded when hot and retains its shape when cooled...also more precisely called a thermoplastic



“Plastics” ...

- **Thermoplastic:** a polymer that can be melted and molded into a shape that is retained when it is cooled
- **Thermoset:** a polymer that can be molded when it is first prepared, but once it is cooled, hardens irreversibly and cannot be remelted



Natural Polymers

- Natural polymeric materials have been used throughout history for clothing, decoration, shelter, tools, weapons, and writing materials
- Examples of natural polymers:
 - Shellac
 - Cellulose (wood)
 - Hair
 - Silk
 - Rubber
- Modified natural polymers
 - Nitrocellulose (lacquer, smokeless powder)
 - Rayon, etc



Shellac



Bug



Bug “do do”



Lots of bug “do do”

It takes 100,000 lac bugs
to make 500 g of shellac

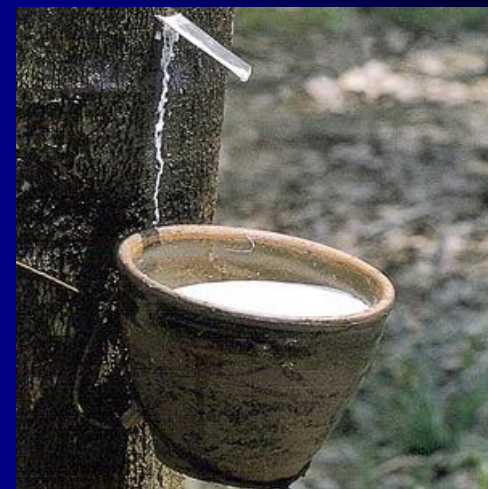


Shellac

- natural polymer secreted by a southeast Asian lac beetle
- Excellent quality of molding detail leads to:
- Early 78 rpm records
 - 25% "shellac", cotton filler, powdered slate, and a small amount of wax



Natural Rubber



The Mayan Ball Game: life or death with a little rubber ball...



- The Ball Court was used for symbolic religious games.
- It is formed of two parallel walls.



Cotton



Wool



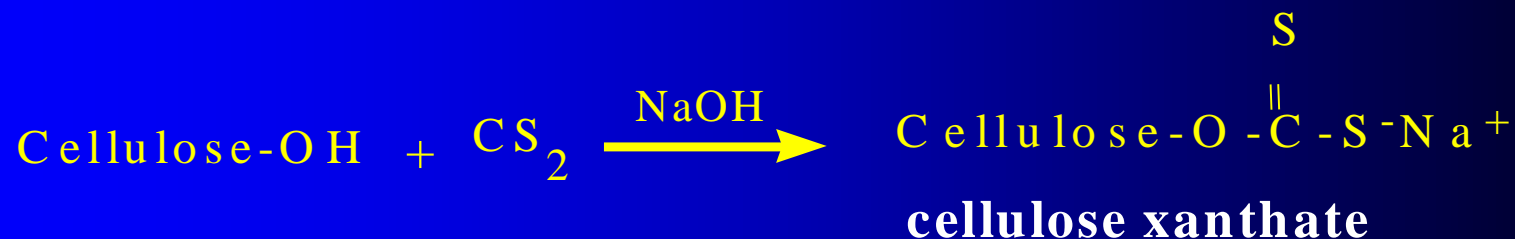
Cellulose

- The average MW of cellulose is 400,000 g/mol, corresponding to about 2200 D-glucose units per molecule.
- Cellulose molecules act a lot like stiff rods and align themselves side by side into well-organized water-insoluble fibers. The -OH groups form numerous intermolecular hydrogen bonds adding strength to the network.
- This arrangement leads to high mechanical strength and water insolubility, hence the strength and utility of wood and cotton fiber.



Rayon

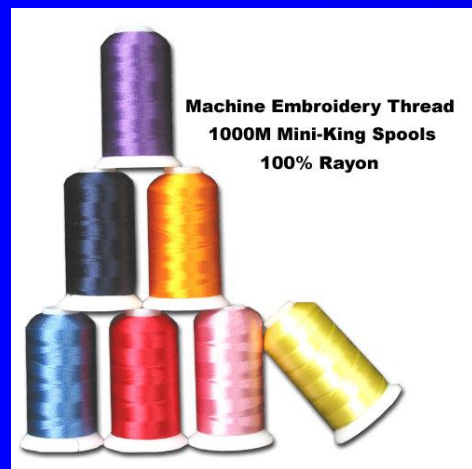
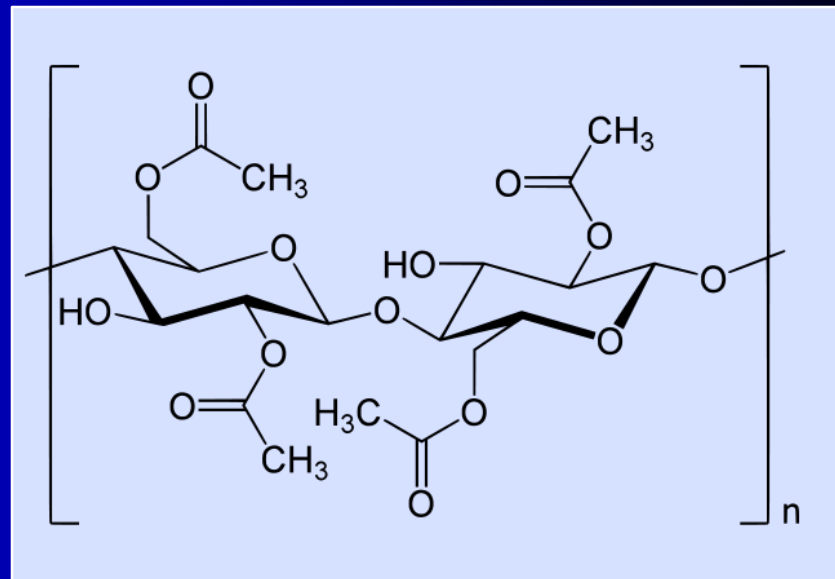
Rayon is made by first treating cellulose with carbon disulfide in base solution.



Then the solution of cellulose xanthate is passed through a small Orifice or slit into an acidic solution.



Cellulose acetate



Rayon



The Association People



Thomas Graham

1805-1869

Graham thought that cellulose and other colloids consisted of large numbers of structurally simple molecules held together by "association."also called "partial valency" ???!





Hermann Staudinger

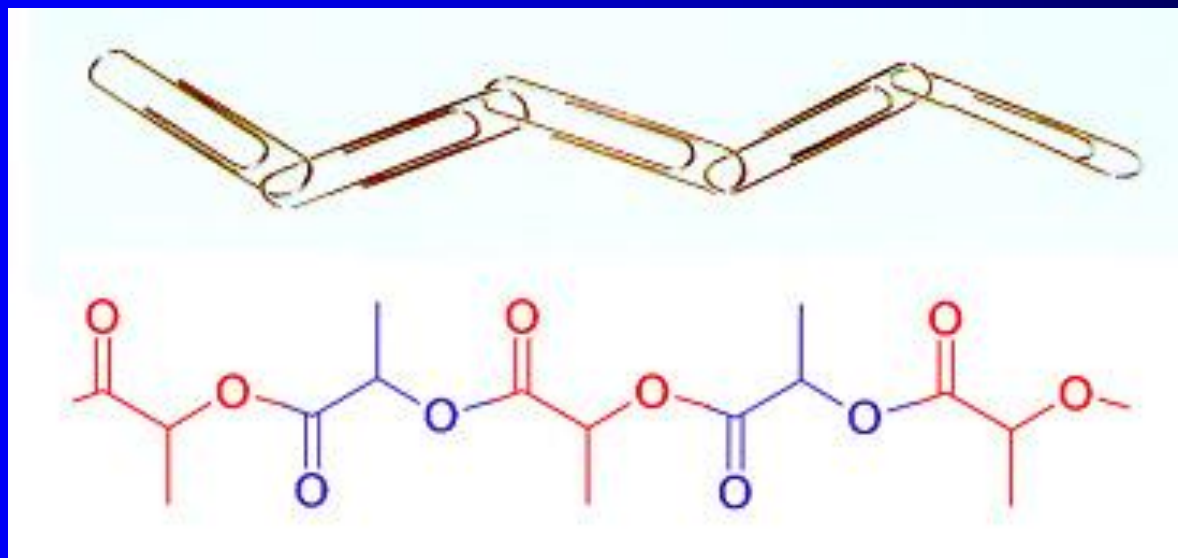
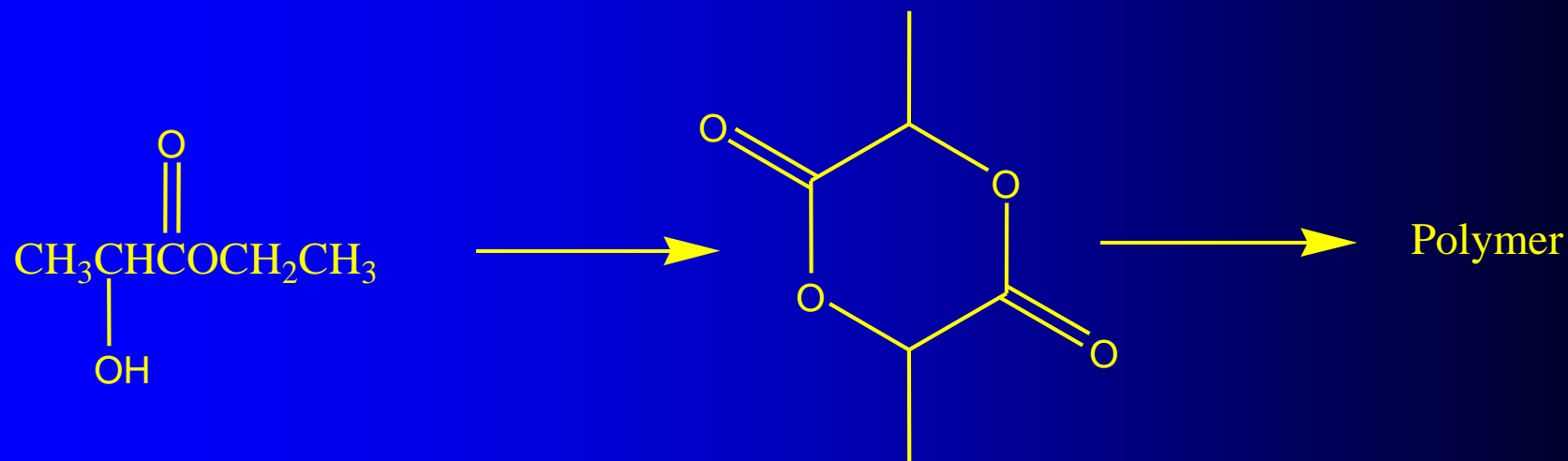
1881-1965

The statement of a German chemist after a debate with Staudinger in 1926: 'We are shocked like zoologists would be if they were told somewhere in Africa an elephant was found who was 1600 feet long and 300 feet high'. Staudinger received the Nobel Prize in chemistry in 1953.



Staudinger's Heretic Proposal

Macromolecules



Science Wins

If the total mass of dissolved material is known, depression of freezing point, elevation of boiling point, and osmotic pressure, **colligative** properties give an easy way to estimate the molecular weight of the substance. Eventually, the tiny osmotic pressures and freezing point depressions seen in polymer solutions could no longer be ignored, or attributed to small amounts of a low molecular weight impurity.



Freezing Point Depression

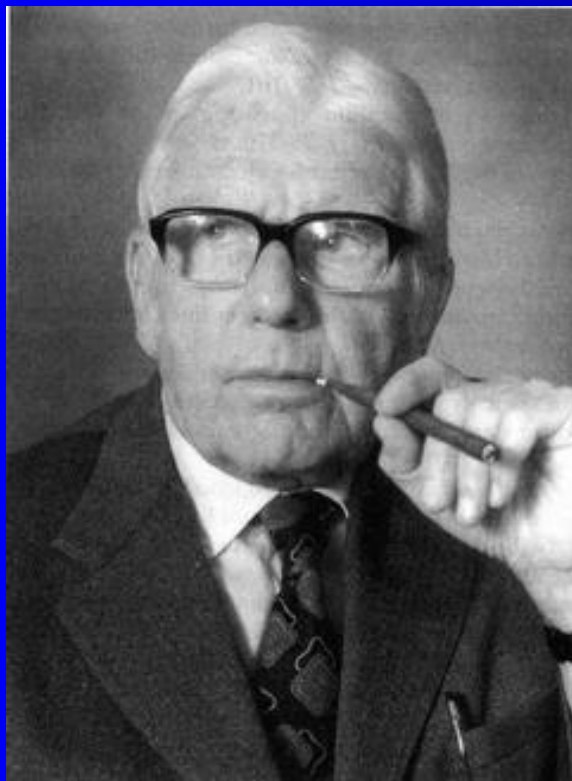
$$\Delta T_f = - i K_f C_m$$

- freezing point depression ΔT_f is a colligative property of the solution, and for dilute solutions is found to be proportional to the molal concentration C_m of the solution. K_f is called the freezing-point-depression constant for the solvent (1.86 °C/kg/mol for H₂O) and i is the the van't Hoff factor which represents the number of dissociated moles of particles per mole of solute
- For sucrose, $i = 1$; for NaCl, $i = 2$ and for CaCl₂, $i = 3$



Herman Francis Mark

May 3, 1895 — April 6, 1992

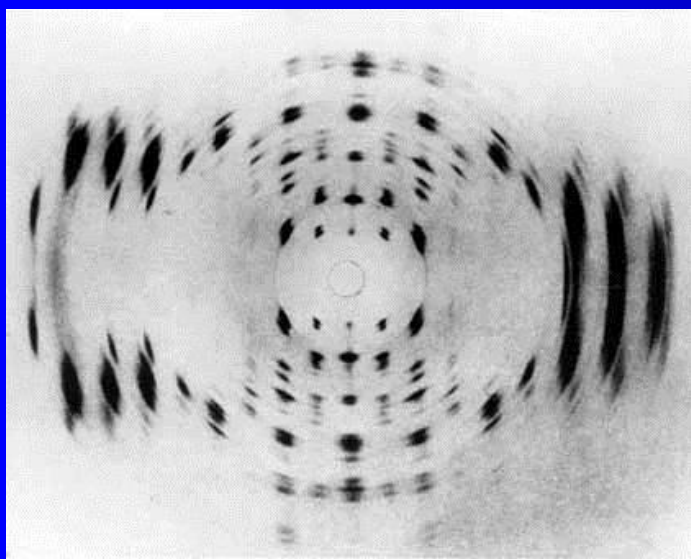


Hans Mark

H. F. Mark



X-Ray Crystal Structures



Mark and Staudinger fight over stiffness



Wallace Hume Carothers 1896-1937



Inventor of Nylon ... US patent 2,130,947

see http://www.invent.org/hall_of_fame/28.html

