Lecture 24

Next..... *POLYMERS*

Jöns Jacob Berzelius
(1779-1848)

Hermann Staudinger
(1881-1965)

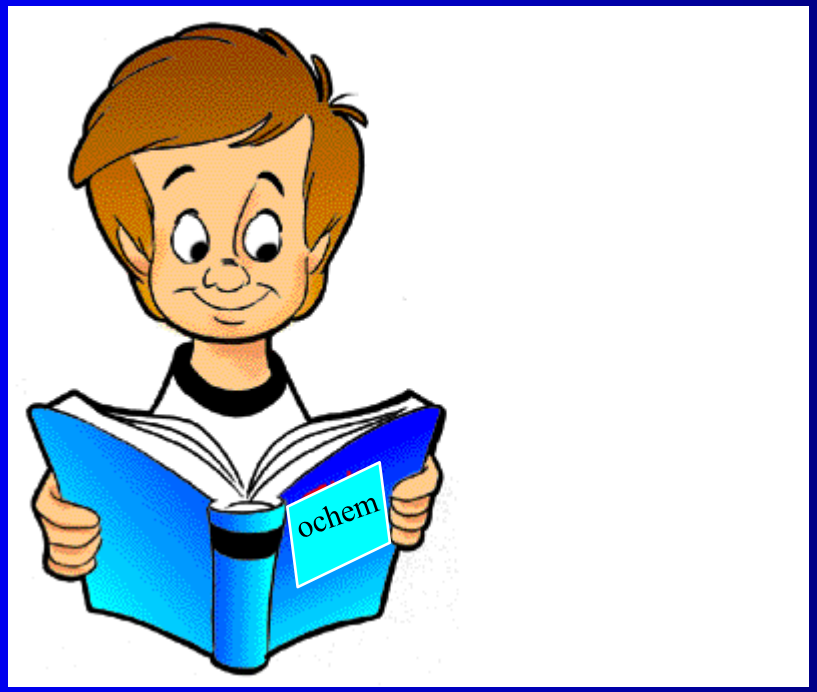
Wallace Hume Carothers
(1896-1937)

Exam III - Wed April 24

- PAI 3.02
- 7-9 PM
- Covers thru 4/18
- Homework
- Hydrolysis
- Reactions
- Synthesis
- Get an A!!!

Review Session

- Where: Here
- When: Tuesday April 23 at 5PM
- Bring questions from your studies



Polymer Chemistry

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


FINN TOYS
1235

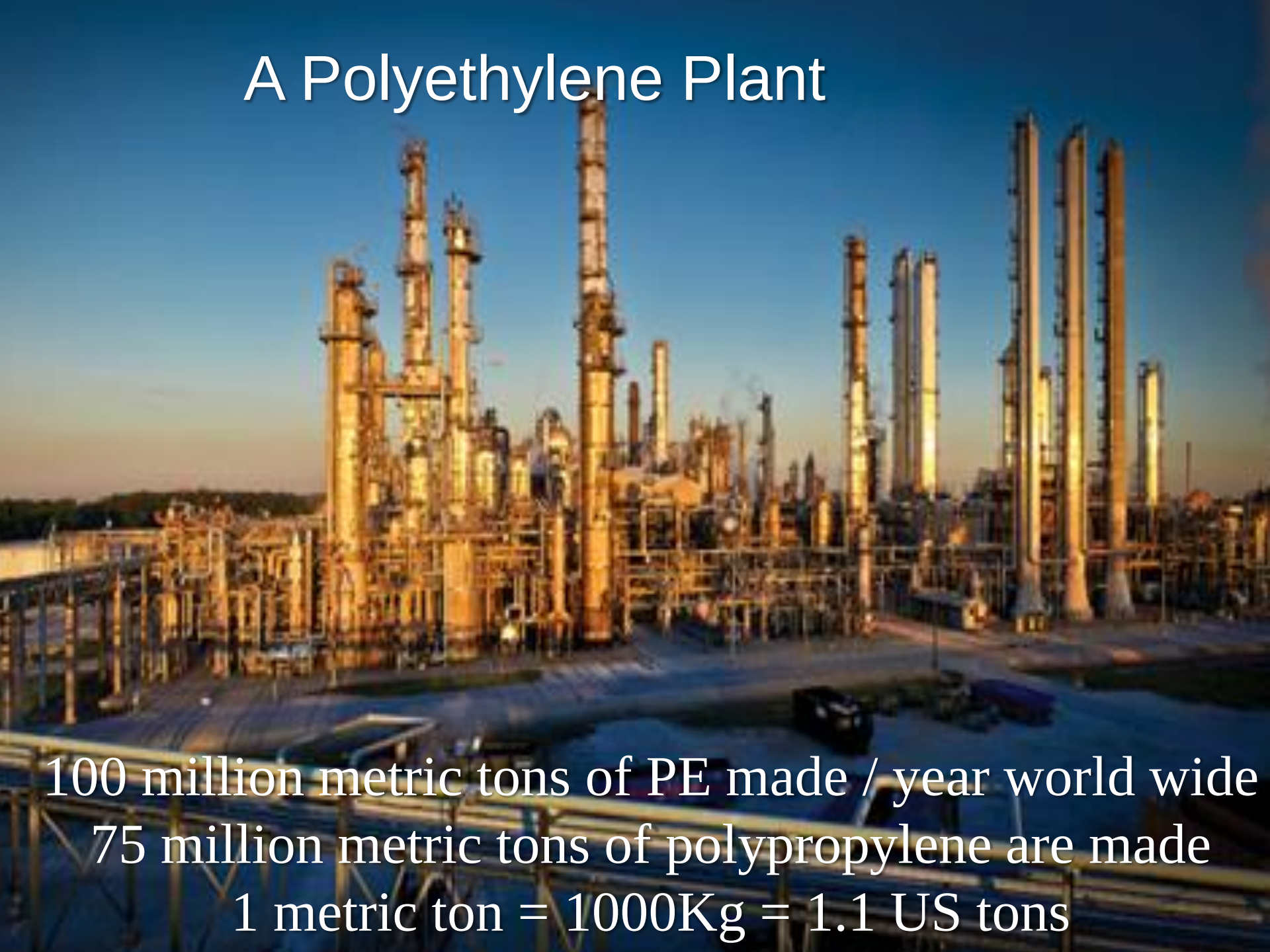

A SONG

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

A Polyethylene Plant



100 million metric tons of PE made / year world wide

75 million metric tons of polypropylene are made

1 metric ton = 1000Kg = 1.1 US tons

Supplemental Problem

- The world wide production of polyethylene in 2018 was approximately 100 million metric tons and there were 75 metric tons of polypropylene produced.
- Austin ranks No. 9 nationally for largest home sizes. A typical house in Austin is 2,068 square feet.
- Assuming a density of 1 gram/cc, no interior walls or other complexity, how many 2068 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 are all CH_n.

This concept lasted near;y a century!

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…Wax is a familiar example.

"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

From 1921 to 1928, 18,000 tons of shellac were used to create 260 million records for Europe

Natural Rubber

The current global natural rubber market is >15 million tons and demand exceeds supply.

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.

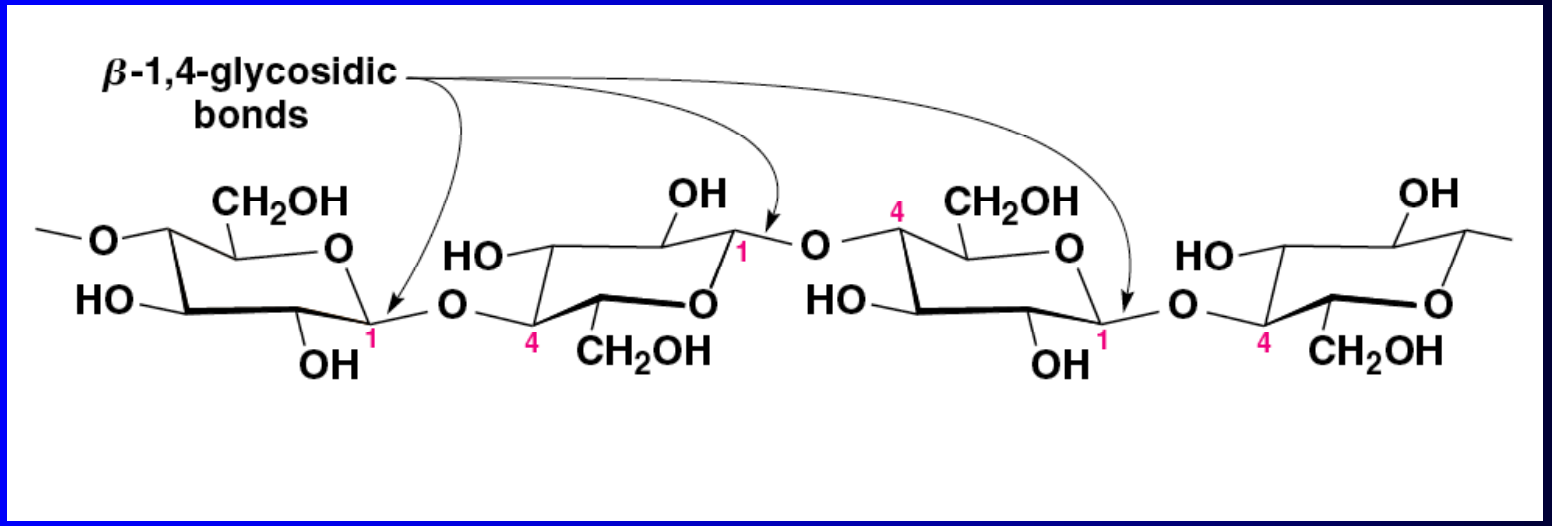
Cotton

Wool

Cellulose

Cellulose is the most widely distributed plant skeletal polysaccharide. It constitutes over half of the cell wall material of wood. Cotton is almost pure cellulose.

Cellulose is a linear polysaccharide of D-glucose units joined by b-1,4-glycosidic bonds.



Cellulose

- The average MW of cellulose in 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.

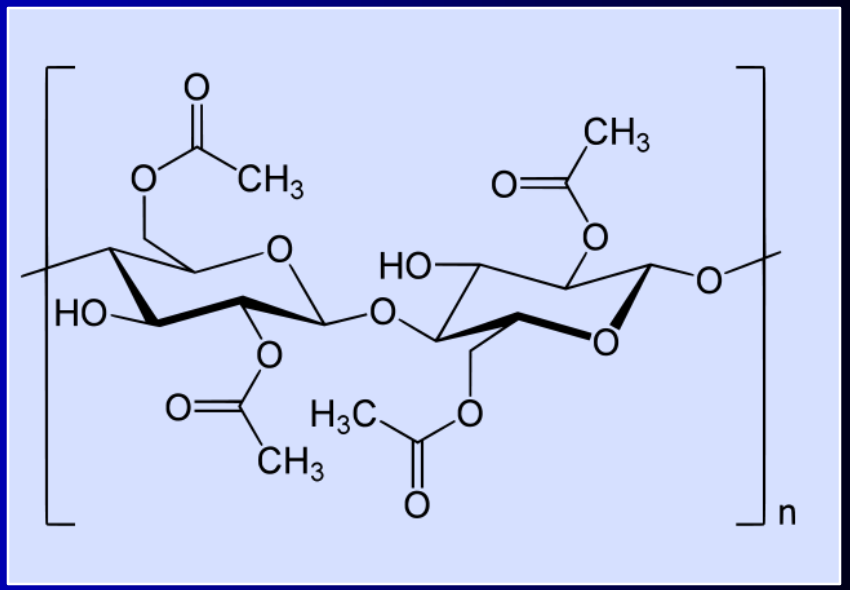
Rayon

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

cellulose xanthate

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

Cellulose acetate



Rayon

Some History and Philosophy

???

The Vitalist People

Friedrich Wöhler
1800 - 1882

Prior to 1828, all **organic compounds** had been obtained from organisms or their remains. ... A theory known as "Vitalism" stated that a "vital force" from living organisms was necessary to make an **organic compound**.

In 1828 Friedrich Wöhler made the organic product urea from NH_4OCN by heating…that finally ended Vitalism

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” ??!!☹

This misconception persisted for nearly a century… very bad!!

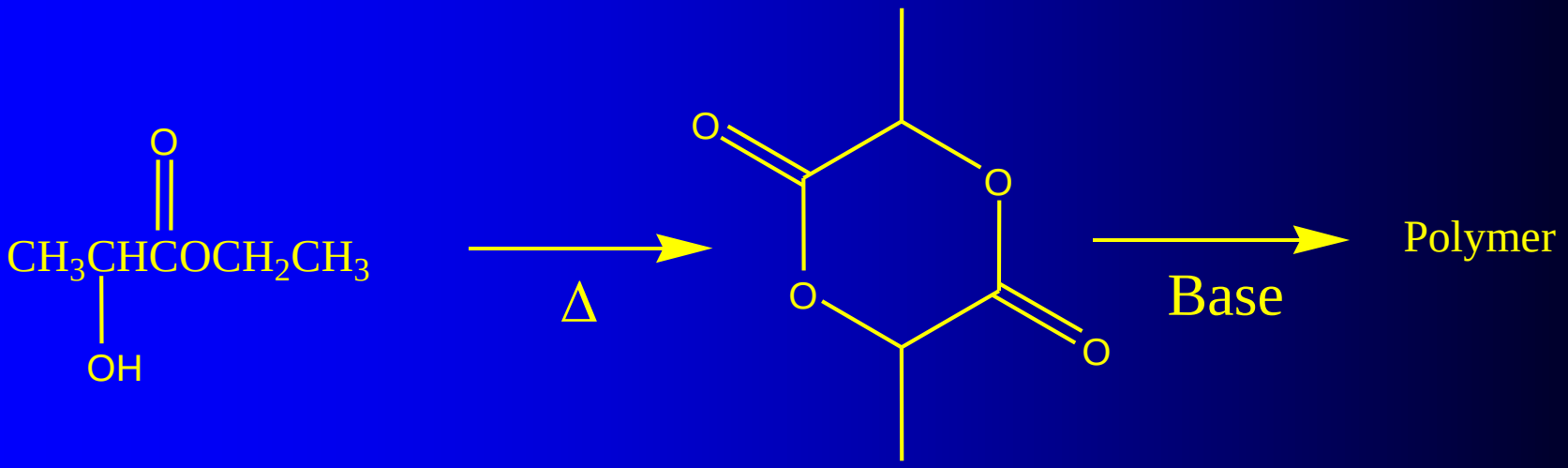
Hermann Staudinger

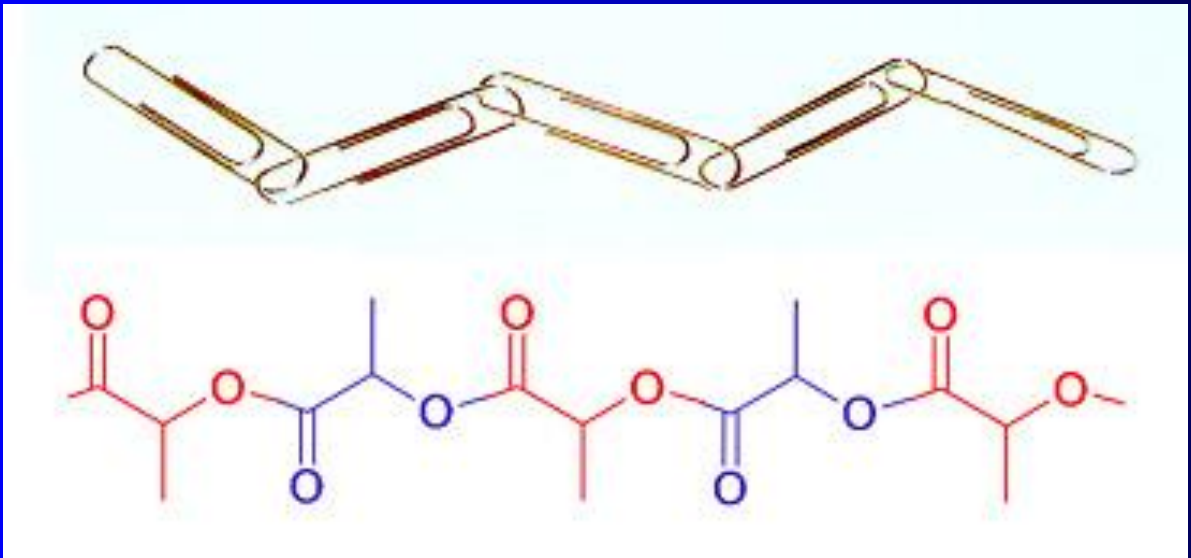
1881-1965

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, depresssion 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

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

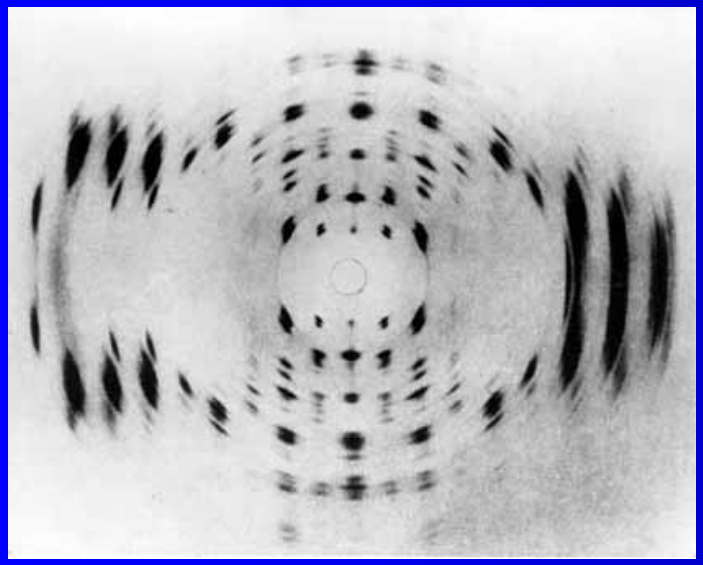
- freezing point depression ΔT_f is a colligative property of the solution, and for dilute solutions is found to be proportional to the molal concentration C_m of the solution. K_f is called the freezing-point-depression constant for the solvent (1.86 ºC/kg/mol for H_2O) and i is the the van't Hoff factor which represents the number of dissociated moles of particles per mole of solute
- For sucrose, i = 1; for NaCl, i = 2 and for $CaCl_2$, i = 3

Herman Francis Mark

May 3, 1895 — April 6, 1992

Hans Mark

X-Ray Crystal Structures



Mark and Staudinger fight over stiffness