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Introduction to Polymers

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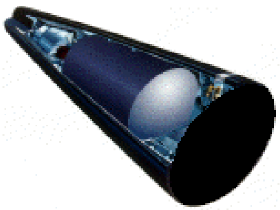

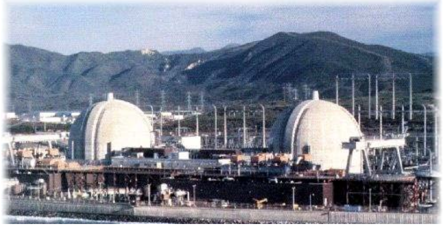

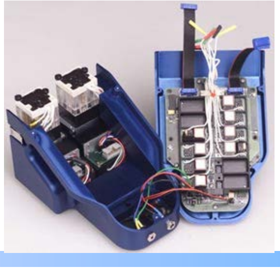

June 2011

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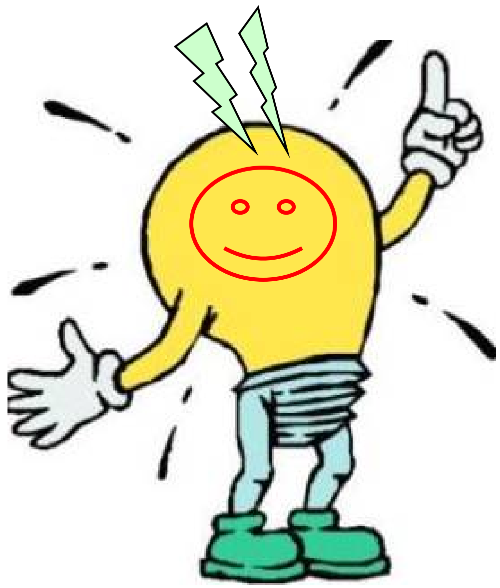
What makes reactions go?

No, it's not just the pure love or hate between molecules

Something has to come out of it, nature requires something more

Life or chemistry ain't free or cheap



Energy !
Reactions are often exotherm
Others require a lot of help

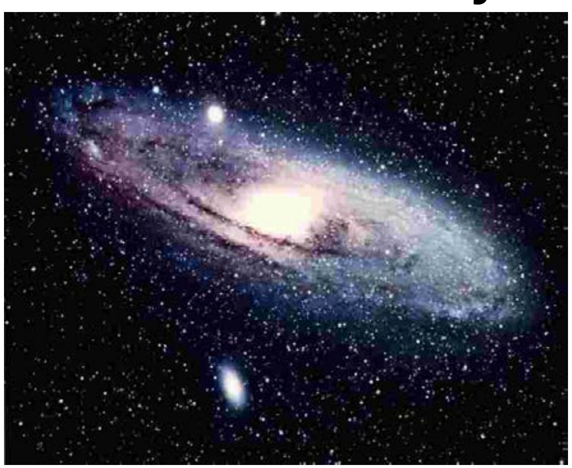
Thermodynamics can tell us whether reactions may go forward or if "we pay or get paid"

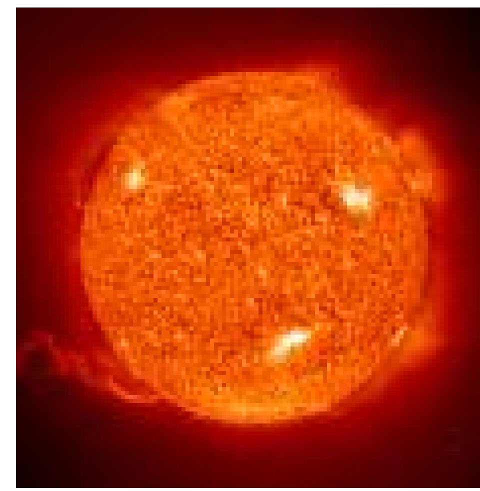
Two things are certain, what ?

- **Death and taxes**
- **There is action and reaction**
- **There are physicists and chemists in science**

Plasma, particles, no chemistry

-273C, frozen in space, no more chemistry



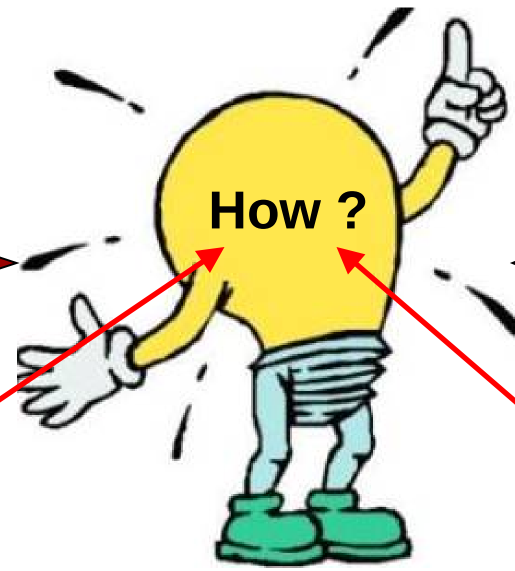


In between is chemistry
The exchange of energy
that rules the world we live in

Applied organic chemistry

'101' of all you ever wanted to know about polymers

Gaseous precursors



Liquid precursors

Catalysts and polymerization technology

POLYMERS
$$$$

Polymer chemists

Cash $

Rubbers, glues, fibers, foams, glasses, anti-stick, carbon composites, contact lenses, body parts

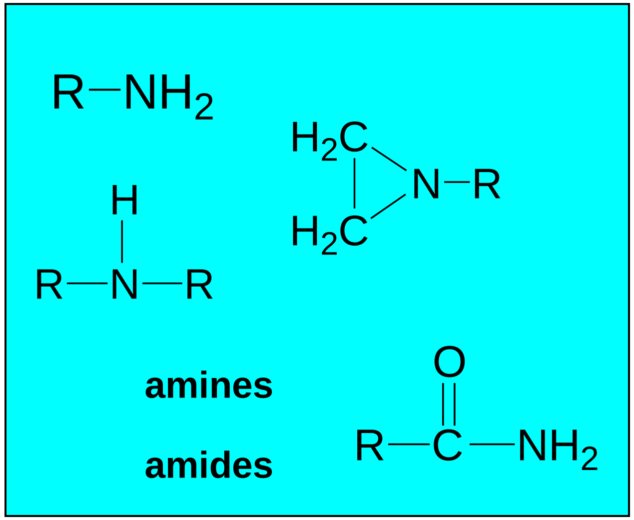
Some basic reactive groups

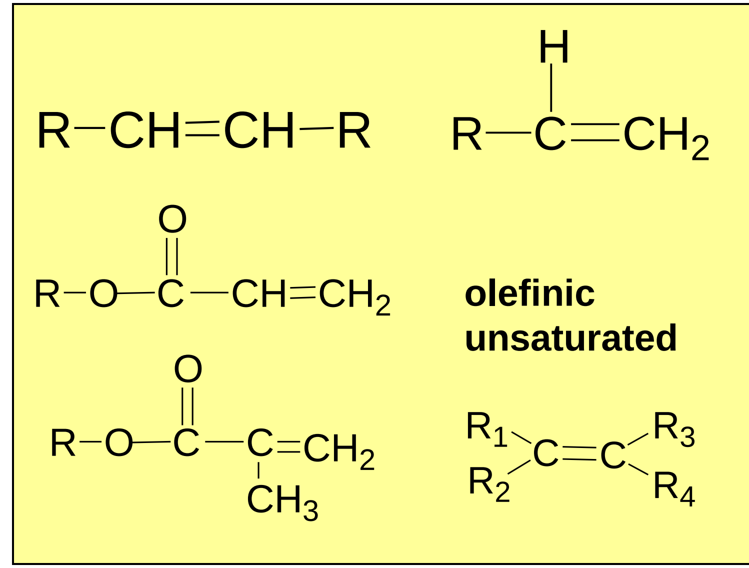
Chemical building blocks

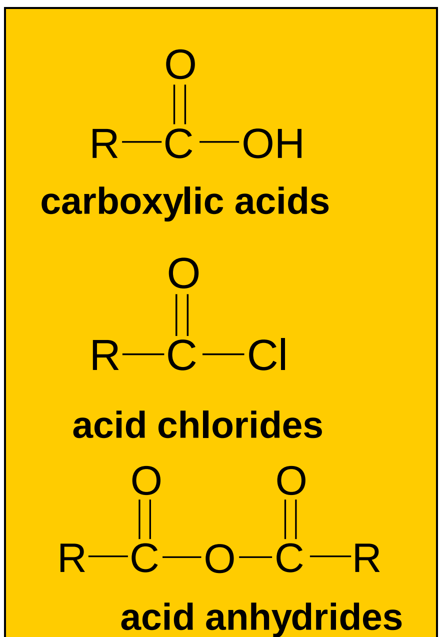
$R-OH$

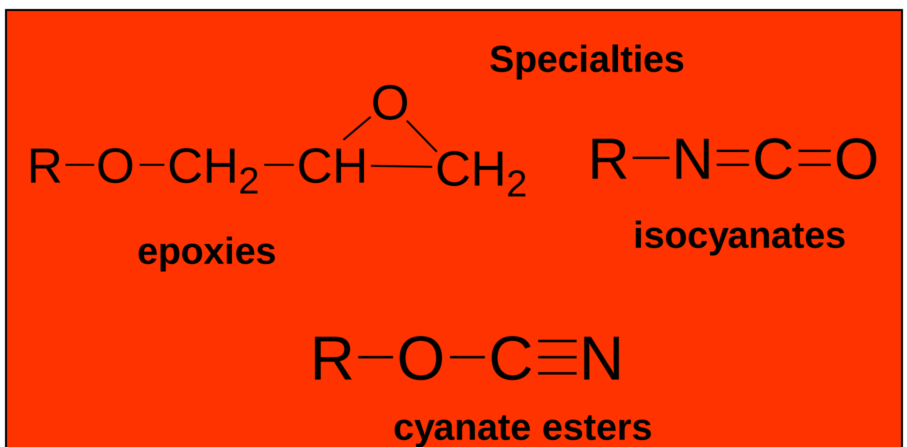
$R-SH$

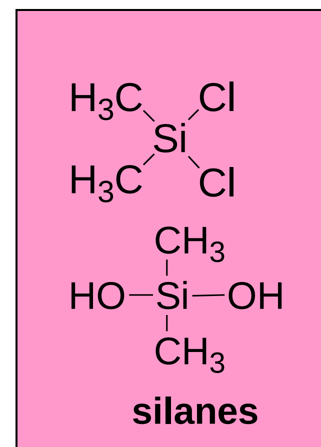
alcohols, thiols



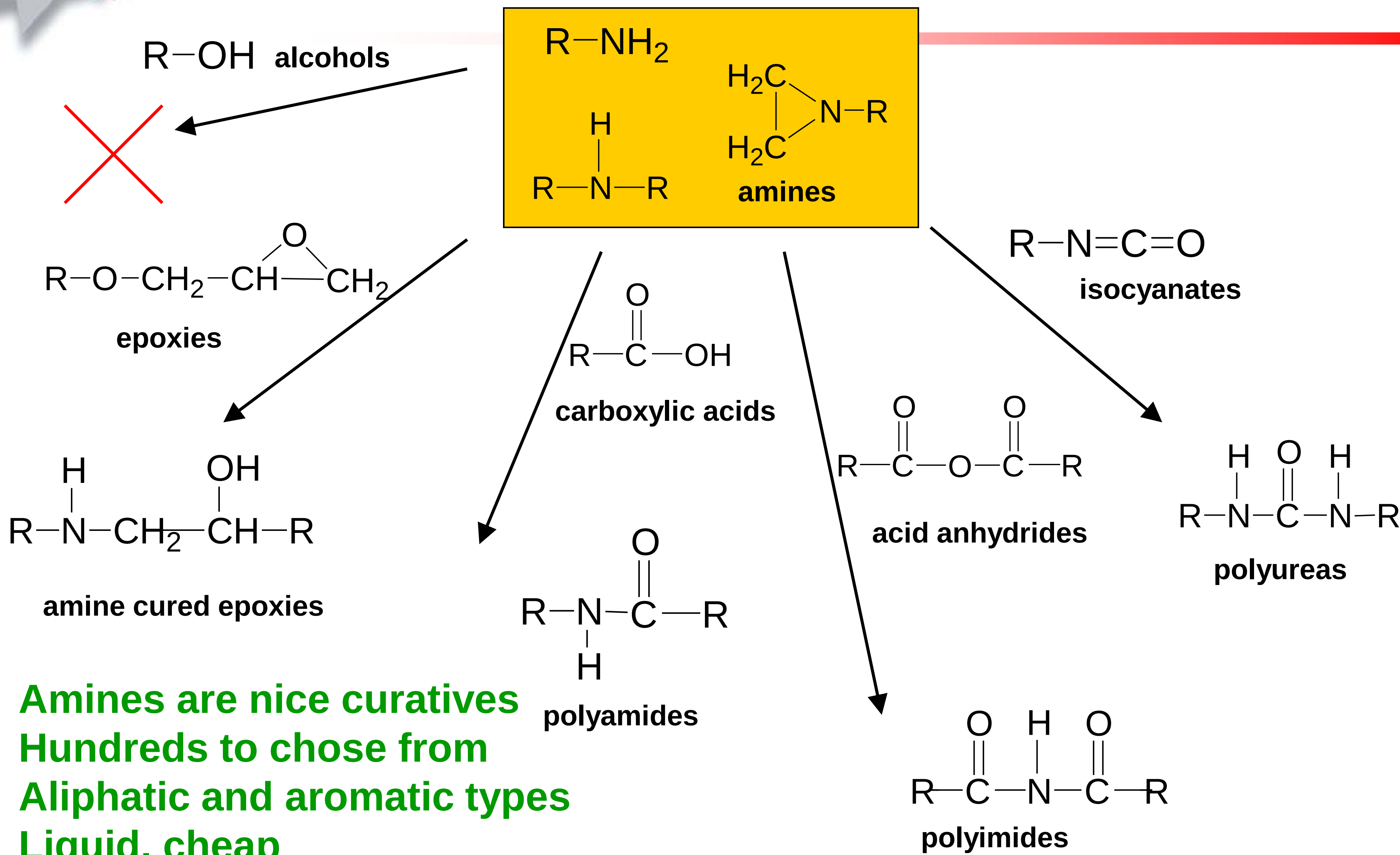






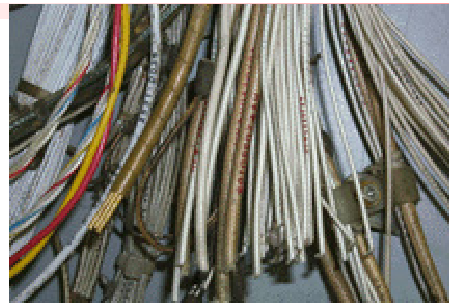


Amine groups (very versatile)



Amines are nice curatives
Hundreds to chose from
Aliphatic and aromatic types
Liquid, cheap

Polymeric materials



Elastomers

Polymer chemists have one business "Polymers Are Us"

Thermoplastics

Thermosets,thermal cure

Engineering materials

Foams

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Polymers

Definition

- **Polymer**: *High molecular weight molecule made up of a small repeat unit (monomer or "mer"). Molecular weight 10^3 - 10^7 gm/mole*
  - » A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A or $-[A-A]_n-$

DP = n

- **Monomer**: Low molecular weight compound that can be connected together to give a polymer

- **Oligomer**: Short polymer chain

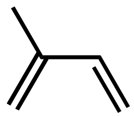
- **Copolymer**: polymer made up of 2 or more monomers
  - » Random copolymer: A-B-B-A-A-B-A-B-A-B-B-B-A-A-B
  - » Alternating copolymer: A-B-A-B-A-B-A-B-A-B-A-B-A-B
  - » Block copolymer: A-A-A-A-A-A-A-A-B-B-B-B-B-B-B-B

Polymers

Natural

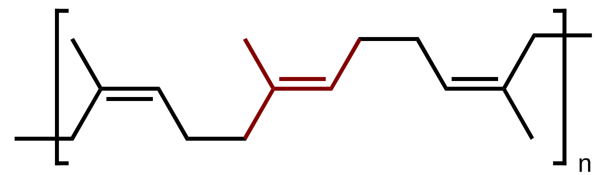
Monomer

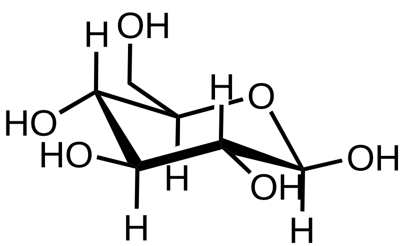
Polymer



Isoprene

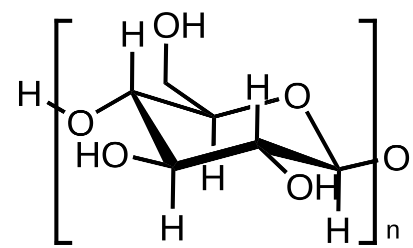
Polyisoprene:
Natural rubber

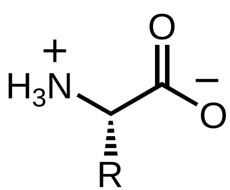




ß-D-glucose

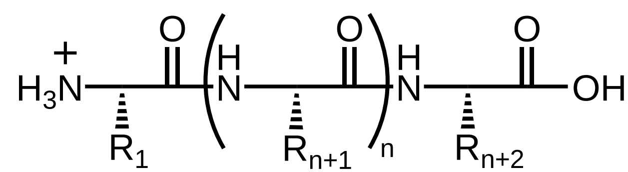
Poly(ß-D-glycoside):
cellulose

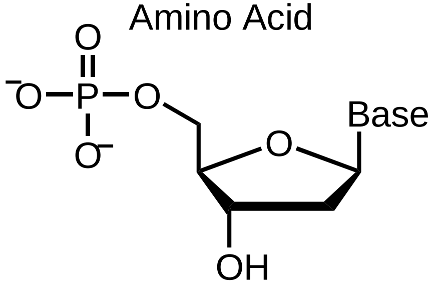




Amino Acid

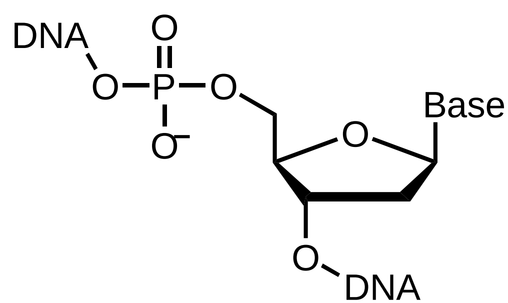
Polyamino acid:
protein





Nucleotide
Base = C, G, T, A

oligonucleic acid
DNA



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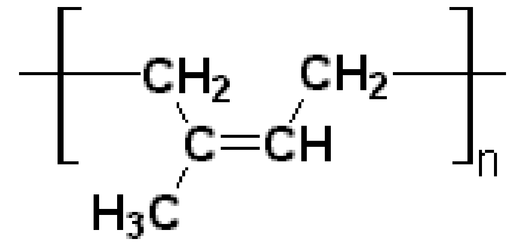
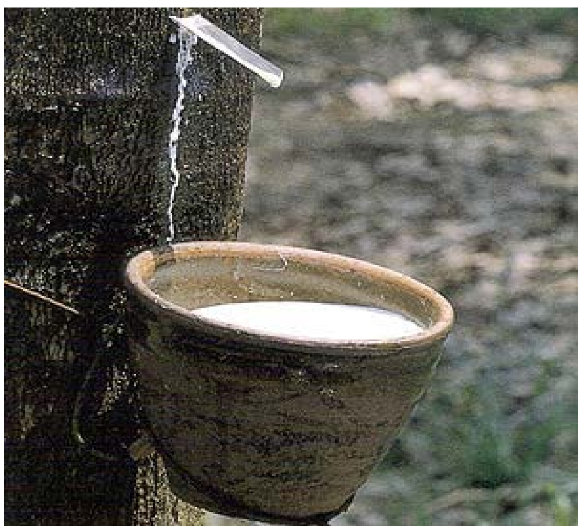
Polymers

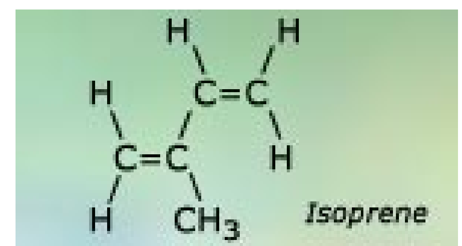
History

- *Manati* rubber balls (1600 BC – 1150 AD)
- Rubber tool handles and figures (600-900 AD)
- medicinal chewing gum, rubber boots and clothes (1400 AD)



El Manati Springs (Mexico)
Olmec 1500 BC



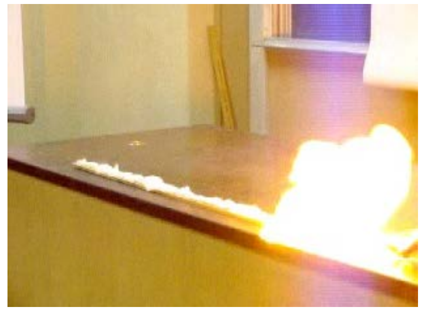


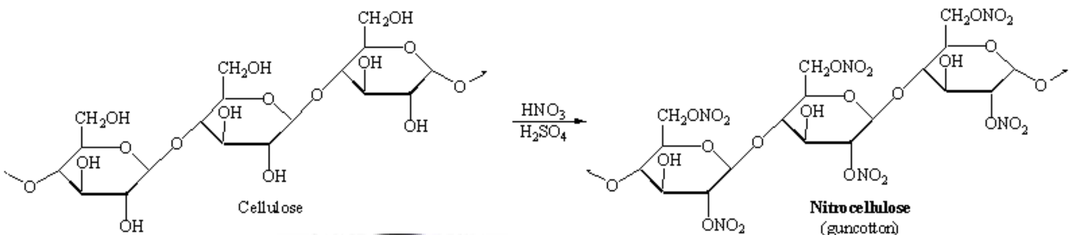
Erasers

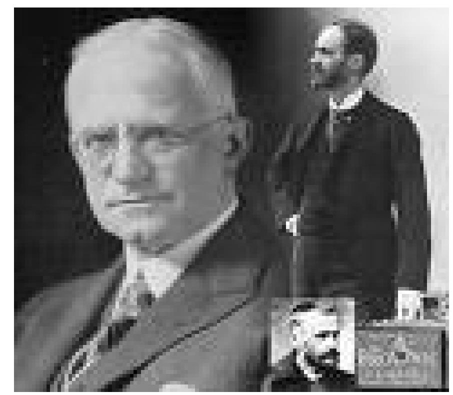
1600 BC – 1550 AD - Rubber

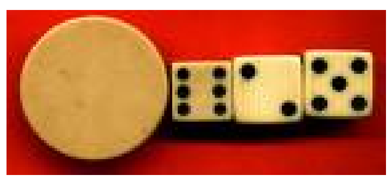
Polymers

History









1846 **–** *Gun Cotton* Christian Schönberg

1866 **–** *Celluloid* Christian Schönberg

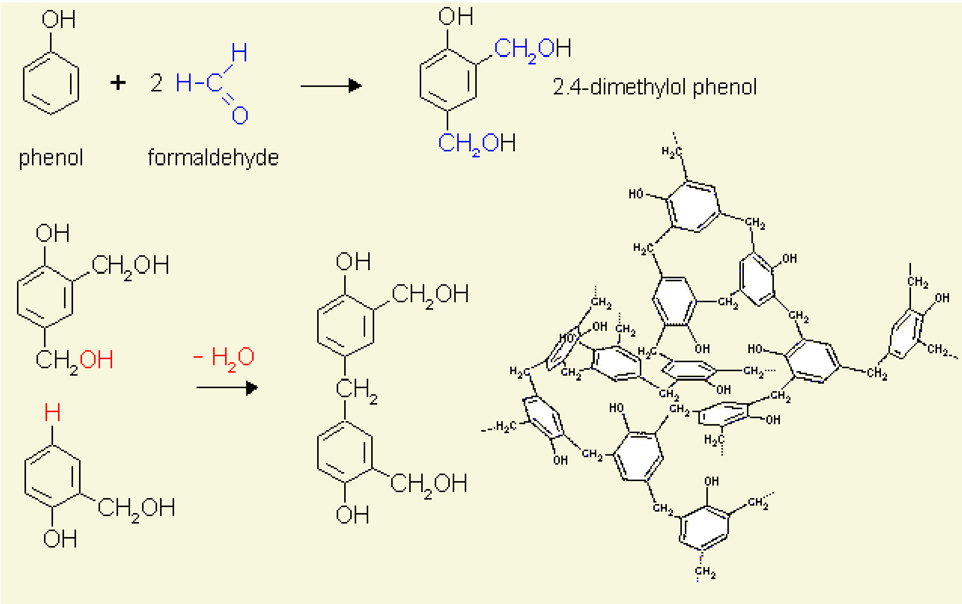
1885 **–** *Celluloid Photographic Film* Christian Schönberg

1908 **–** *Cellulose Acetate* George Eastman

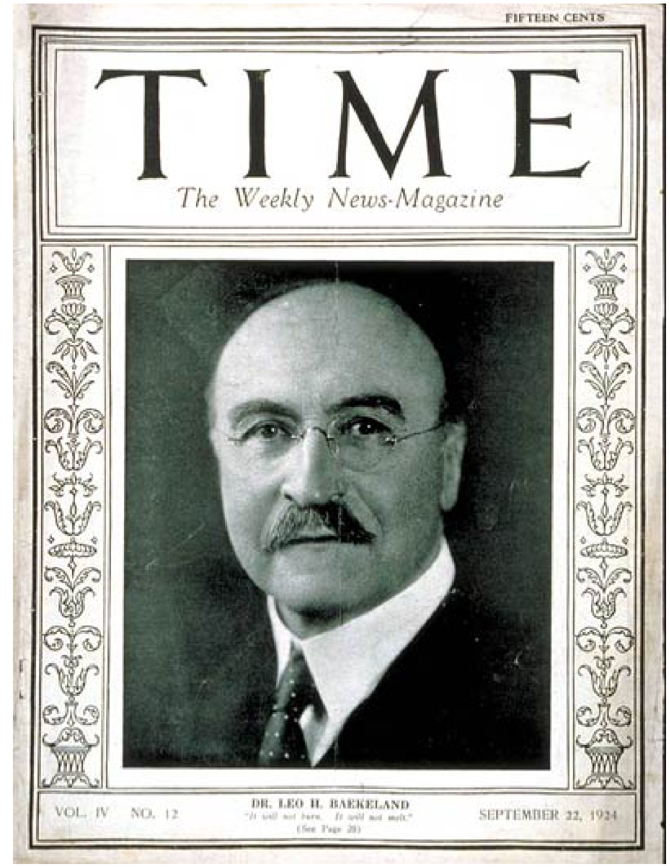
(1950 Oscar awarded to Eastman Company)

Polymers

History



section of the 3D structure of bakelite



1907 **-** *Bakelite* Leo Baekeland

Polymers

Growth of Research

*Macro*molecules were not recognized as such until the 1920s (Staudinger)

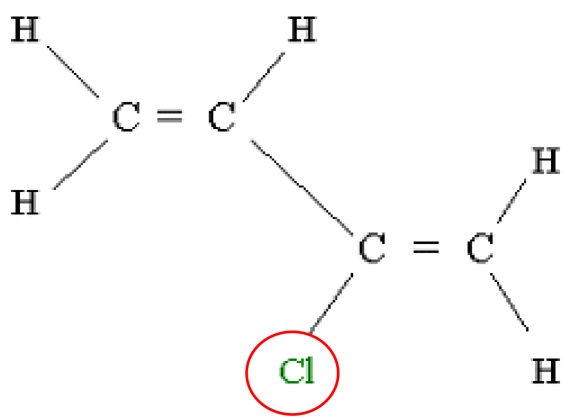
"*I just want to say one word to you -- just one word --* '***plastics***.'"

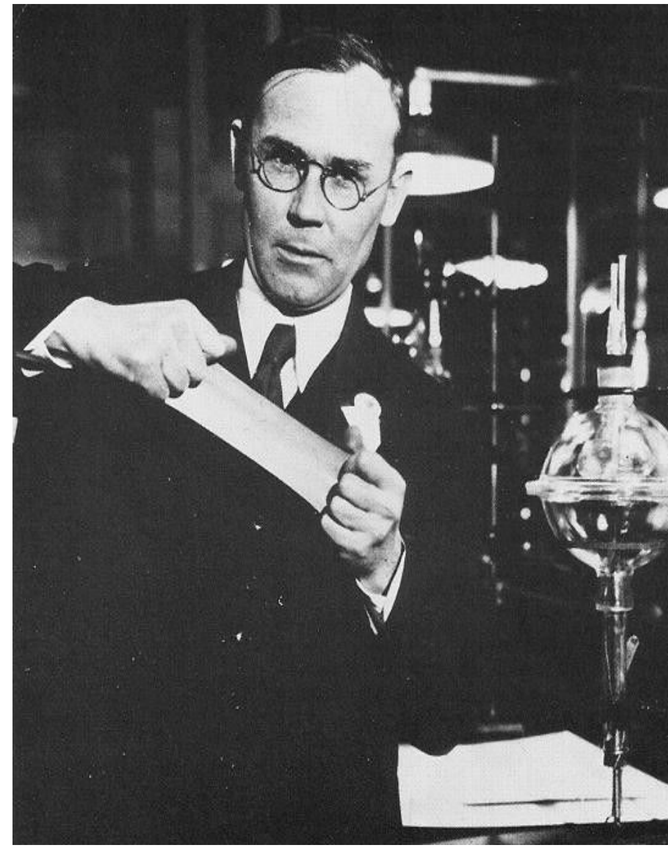
Advice to Dustin Hoffman's character in *The Graduate*

Polymers

Synthetic Polymers

Neoprene
(First Synthetic Rubber)





Polyesters

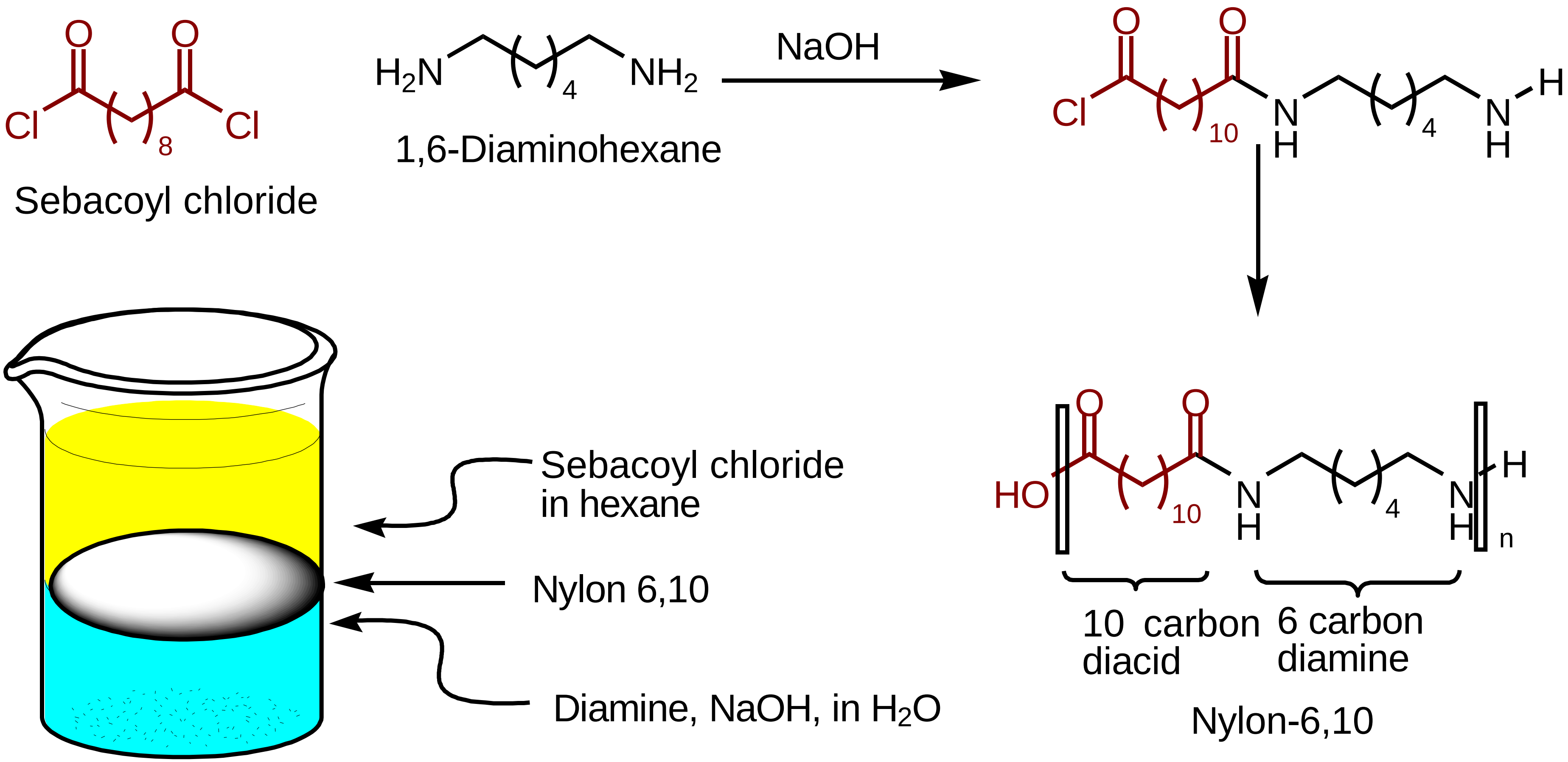
Nylons (Polyamides)

1929 **-** *Neoprene* Wallace H. Carothers
Developed Concepts for Step Growth and Chain Growth Polymerizations

Wallace H. Carothers. *J. Am. Chem. Soc*.; **1929**; *51(8);* 2548-2559. *Chem. Rev.;* **1931**; *8*(3); 353-426.

Polymers

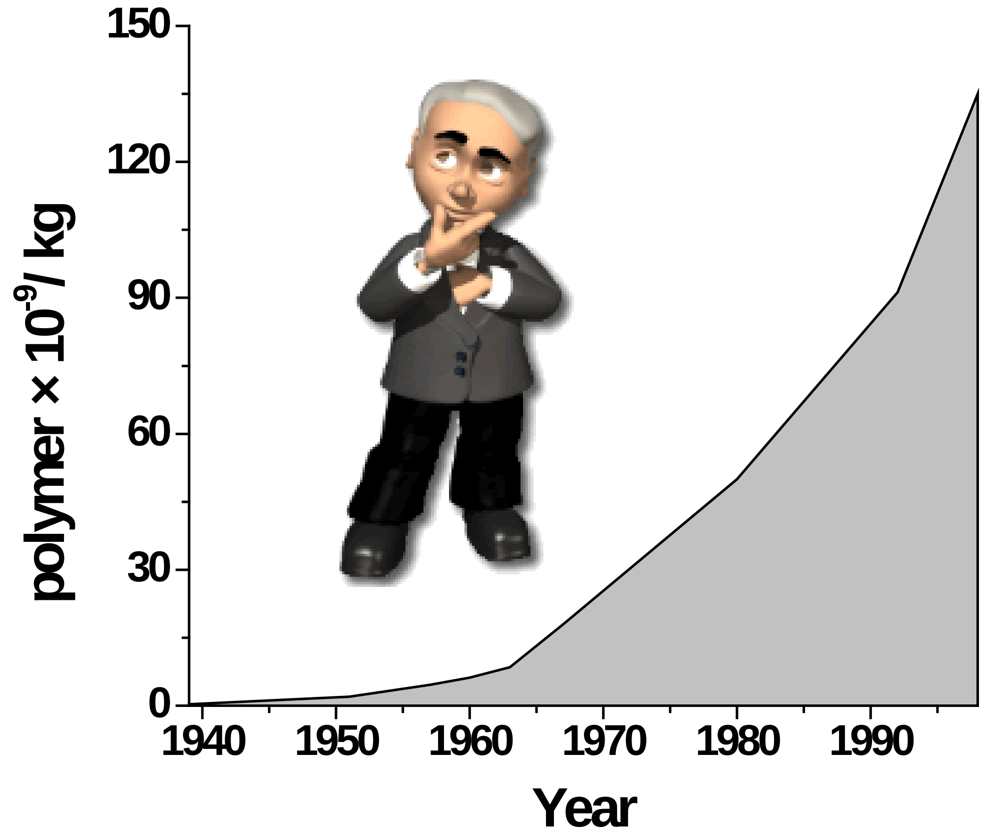
Synthesis: Nylon-6,10



Step growth or chain growth?

Polymers

Growth of Research



Exponential industrial growth since Worldwar II (1939-1945), silicones, epoxy, synthetic rubber, polyurethanes

Polymers

Types of Polymers

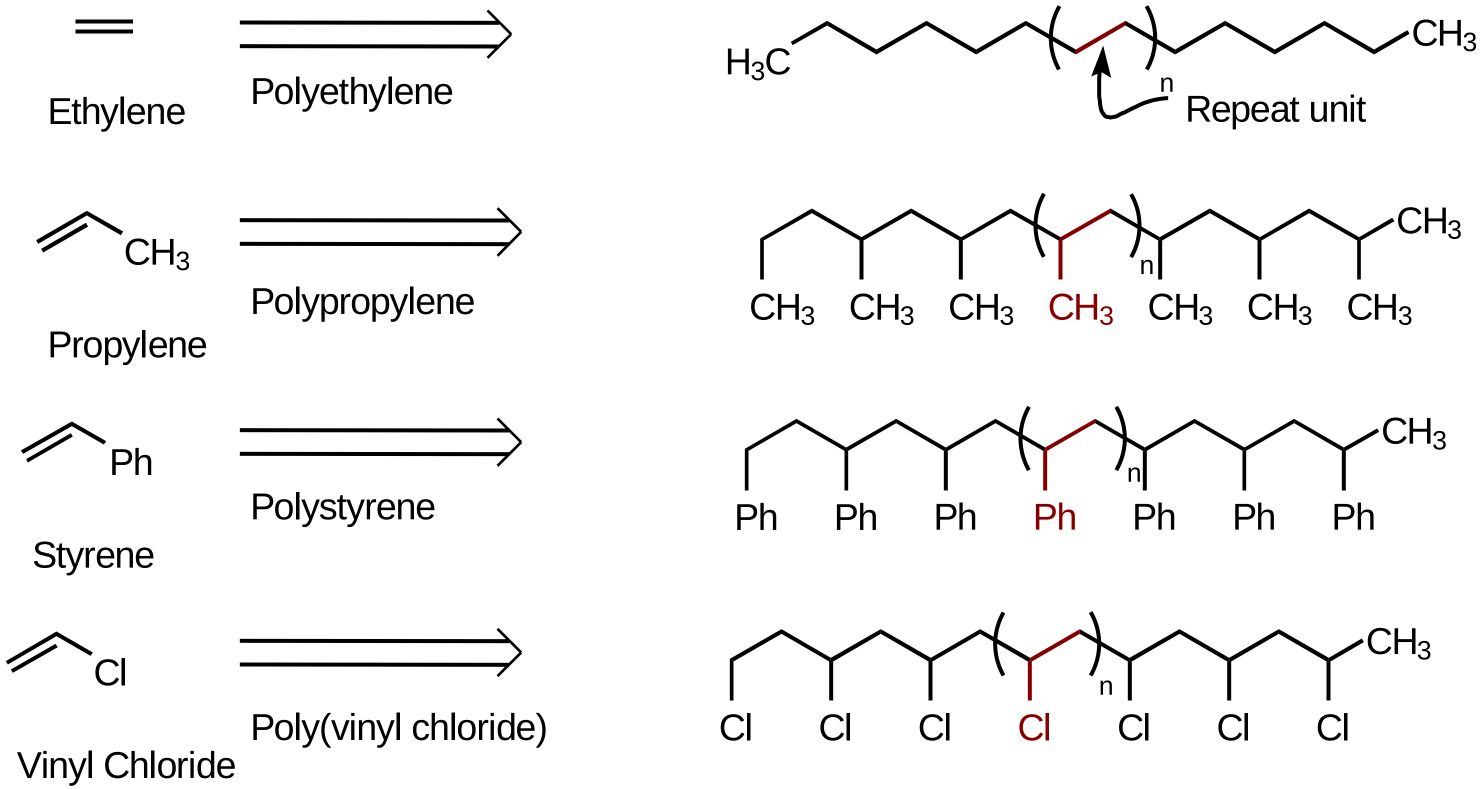
- **Polymer Classifications**
  - Thermoset: cross-linked polymer that cannot be melted (tires, rubber bands)
  - Thermoplastic: Meltable plastic
  - Elastomers: Polymers that stretch and then return to their original form: often thermoset polymers
  - Thermoplastic elastomers: Elastic polymers that can be melted (soles of tennis shoes)

- **Polymer Families**
  - Polyolefins: made from olefin (alkene) monomers
  - Polyesters, Polyamides, Polyurethanes, etc.: monomers linked by ester, amide, urethane or other functional groups
  - Natural Polymers: Polysaccharides, DNA, proteins

Polymers

Common Polyolefin's

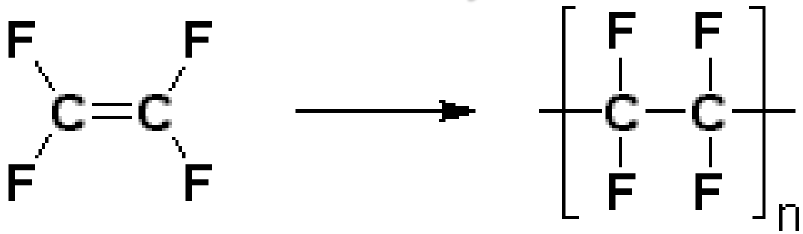
Monomer **Polymer**



Polymers

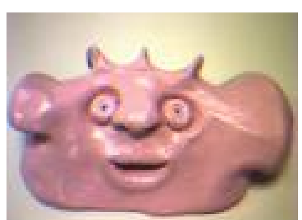
Introduction

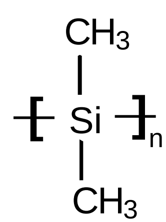
1938 – *TEFLON* Roy Plunkett



tetrafluoroethylene polytetrafluoroethylene

1943/1949 – *Silly Putty* James Wright / Peter Hodgson (viscoelastic material or dilatant fluid?)

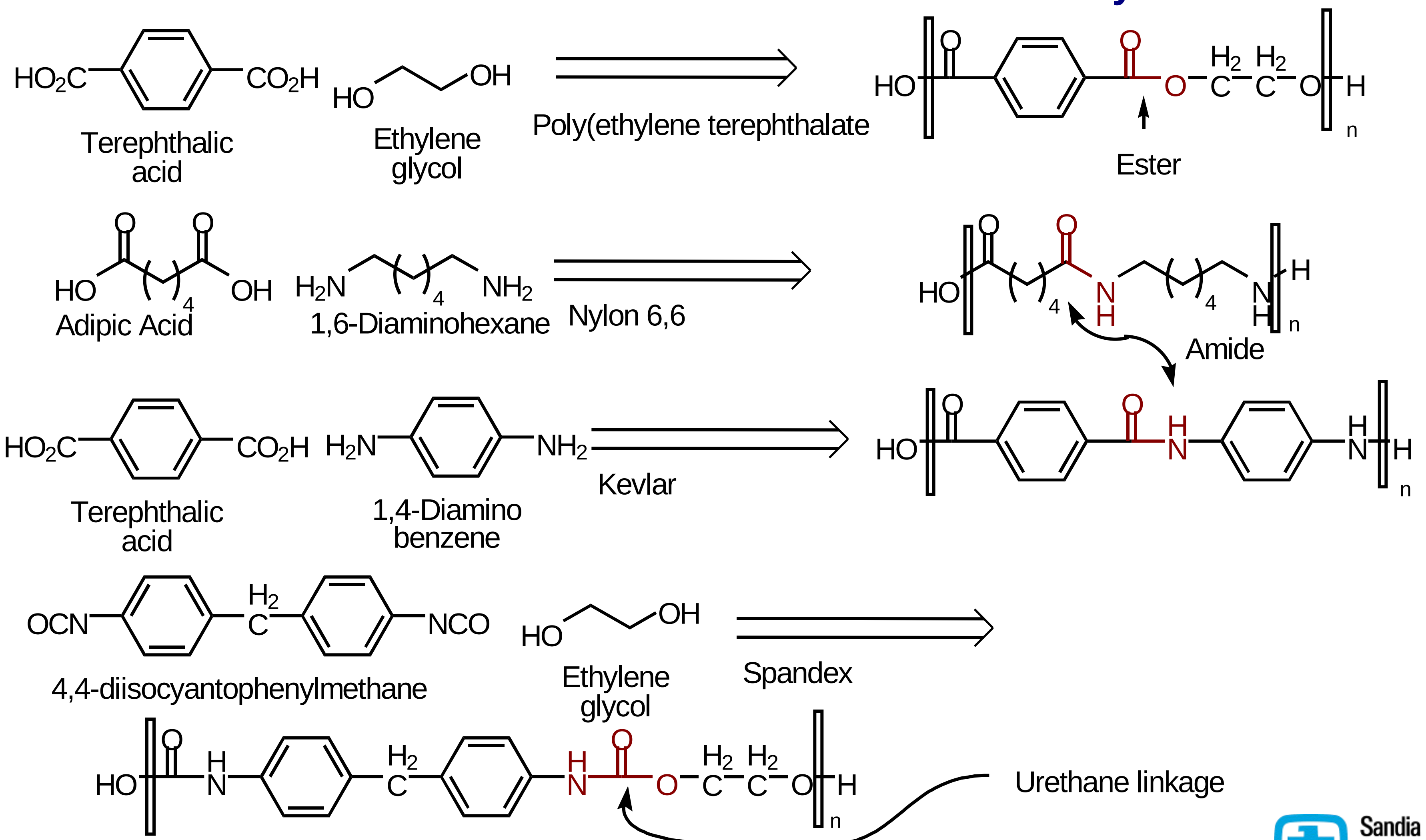




Polymers

Polyesters, Polyamides, and Polyurethanes

Monomer **Polymer**



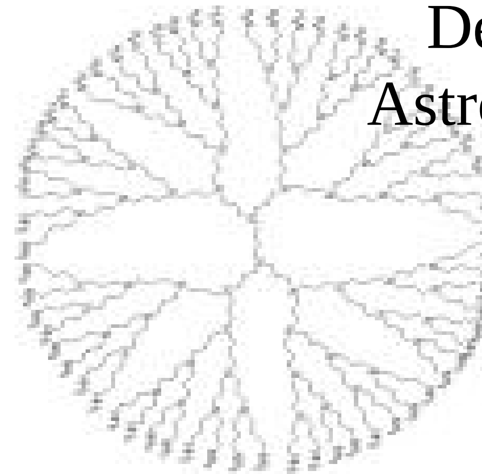
Polymers

Architectures

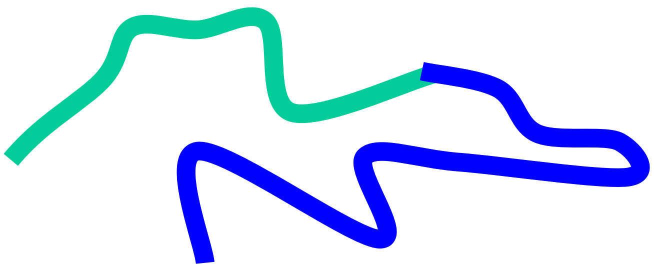
Linear random coil

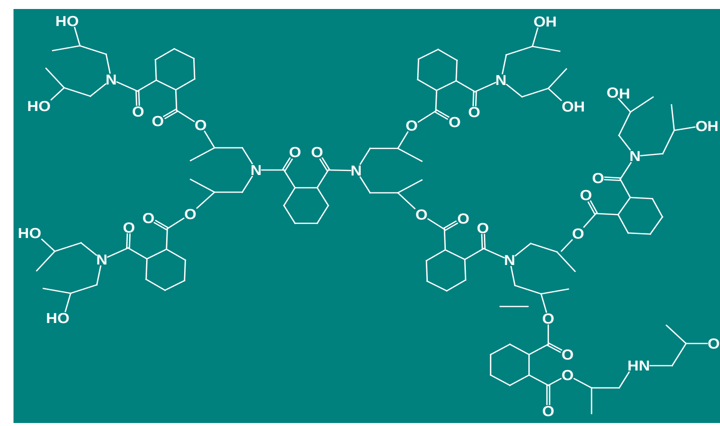
Star Shaped

Dendrimer
Astromol DSM

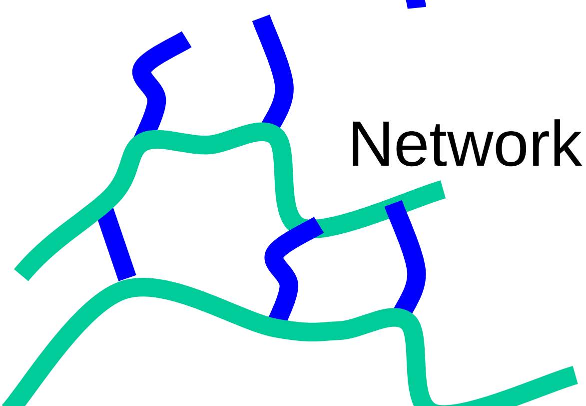


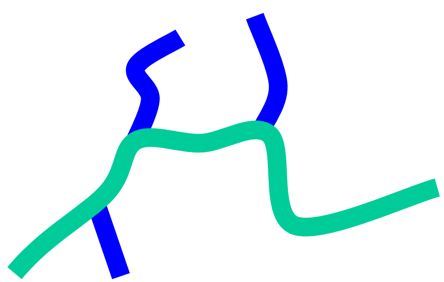
Linear AB
block-co-polymers





Network





Grafted

Hyper-branched
Hybrane DSM

Polymers

Polyvinylalcohol: Ionic Network

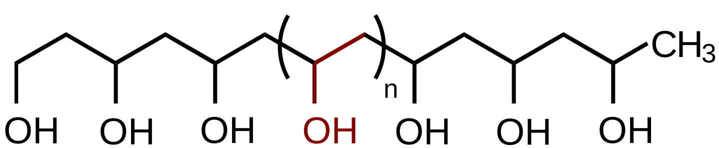
Materials Needed

- A 4% solution of polyvinylalcohol in water
  Fairly high MW (96,000 gm/mole)
- B 4% Borax Solution in water
  (40 gm of Borax dissolved in 1L of hot water)

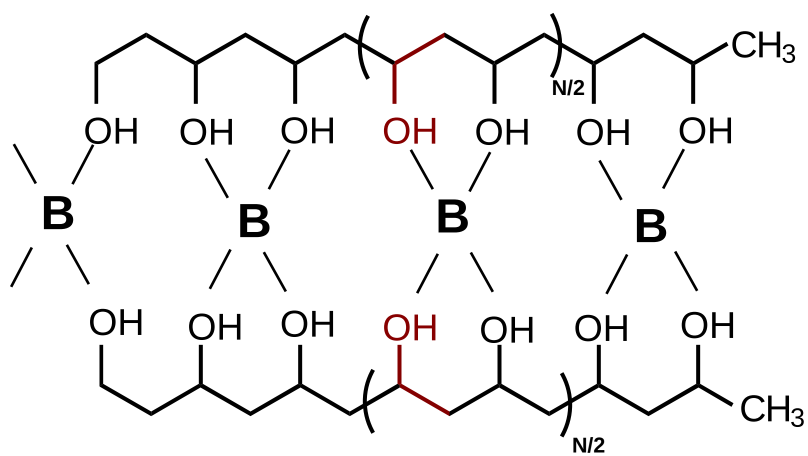
Procedure

- 1 part A to 5 parts B

$B(OH)_3 + 2\,H_2O \Longleftrightarrow B(OH)_4^- + H_3O^+$



$+\ B(OH)_4^-$



There are two major classes of polymer formation mechanisms

» **Chain growth polymerization**: *The polymer grows by sequential addition of monomers to a reactive site*

– Chain growth is linear

– Maximum molecular weight is obtained early in the reaction

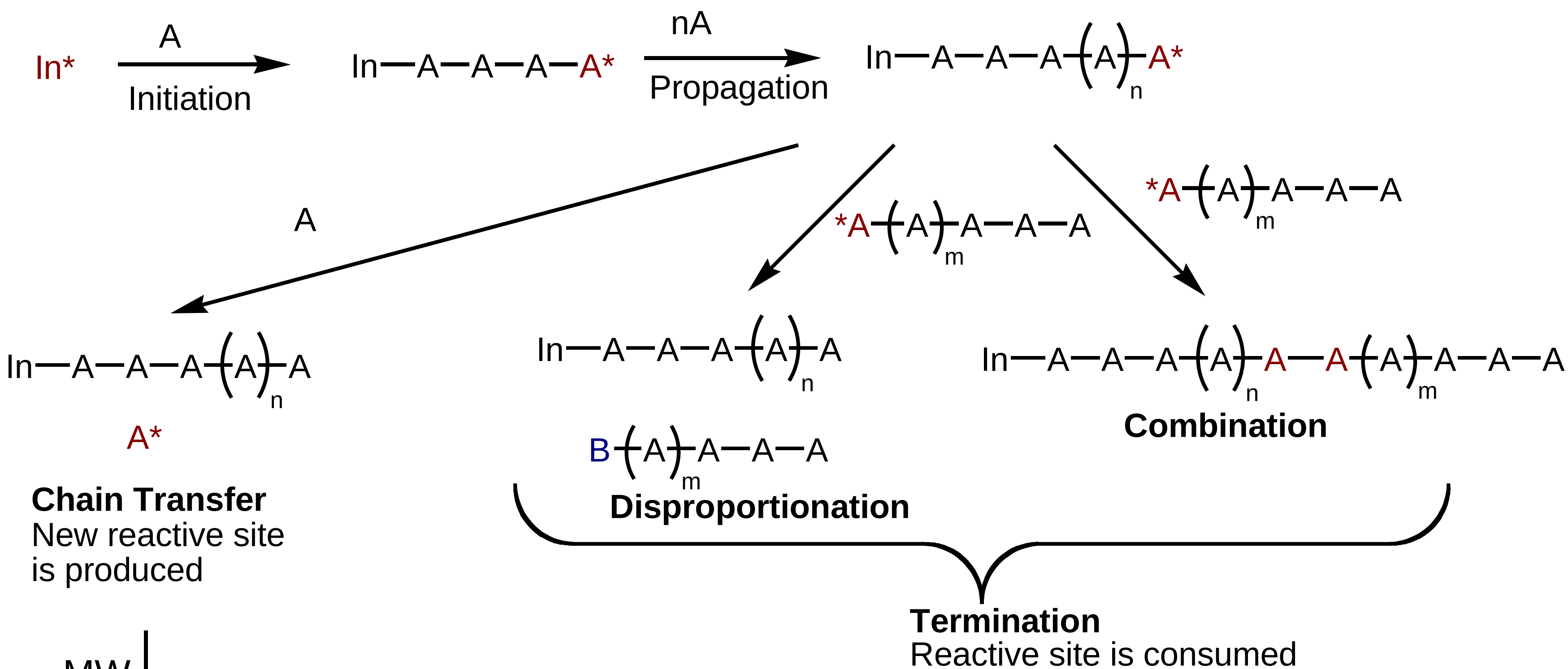
» **Step-Growth polymerization**: *Monomers react together to make small oligomers. Small oligomers make bigger ones, and big oligomers react to give polymers.*

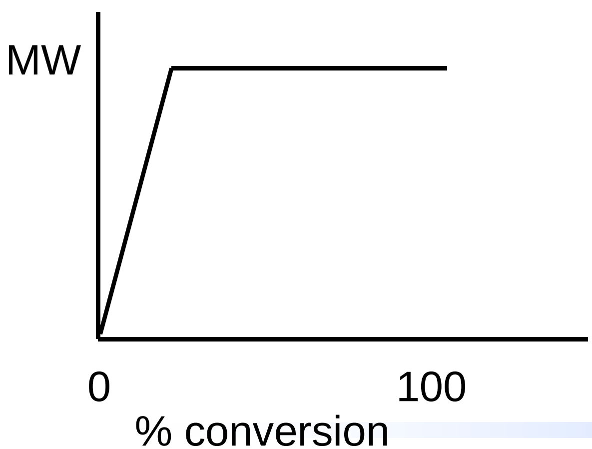
– Chain growth is exponential

– Maximum molecular weight is obtained late in the reaction

Polymers

Synthesis: Chain Growth Polymerization





$$MW \propto \frac{k_{propagation}}{k_{termination}}$$

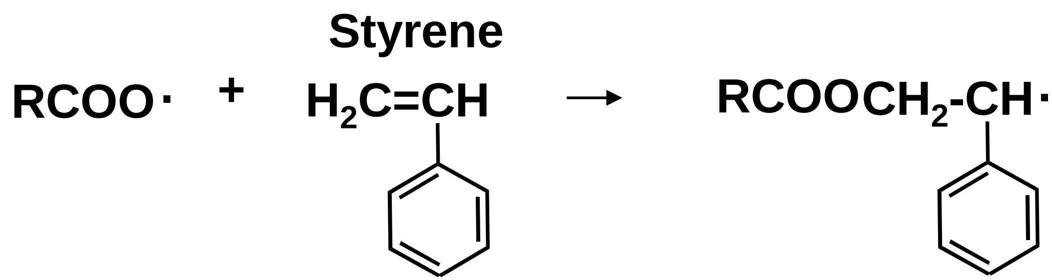
Cationic
Anionic
Radical

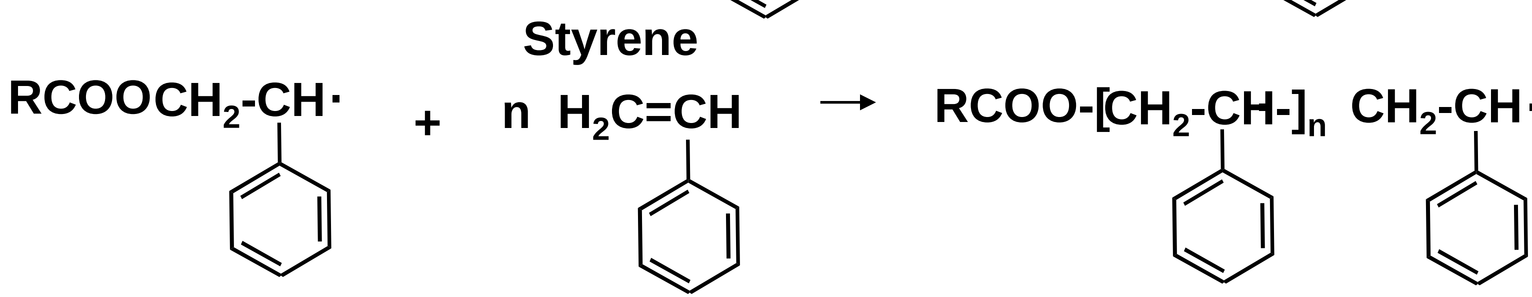
Polymers

Synthesis: Chain Growth Polymerization

Example Radical Initiation

$[RCOO]_2 \rightarrow 2\ RCOO$ **Benzoyl peroxide**





Polystyrene

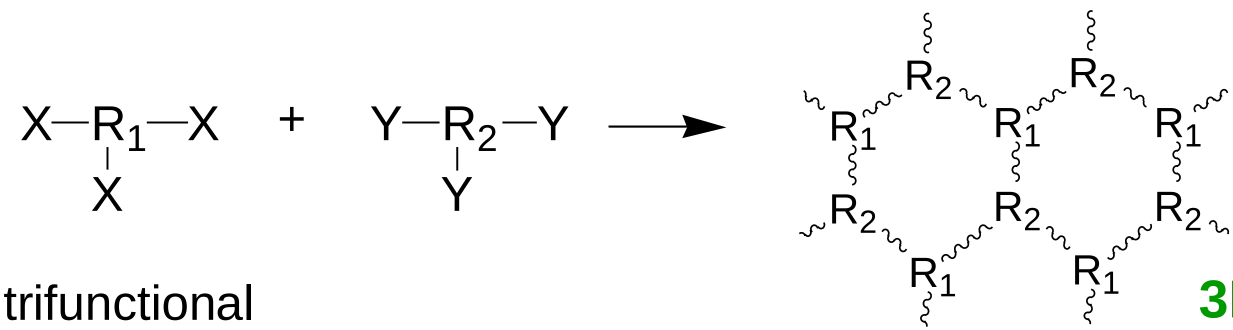
Reactive groups per molecule: Functionality

R_1-X monofunctional

$X-R_1-X \quad Y-R_2-Y \longrightarrow -Z-R_1-Z-R_2-Z-R_1-Z-$

difunctional

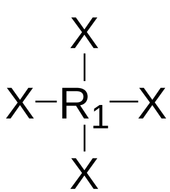
At minimum difunctional reagents are needed to form polymers



trifunctional

3D networks

trifunctional reagents **condense to** **complex polymer networks**



tetrafunctional

R_1-X_n

R_2-Y_n

multifunctional

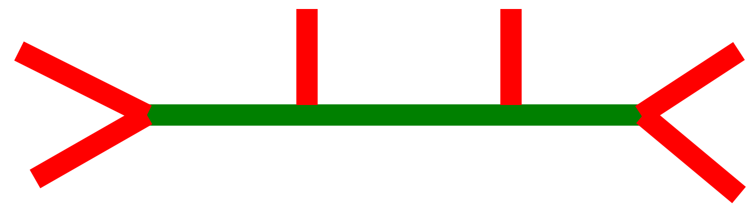
Controlled polymer architecture

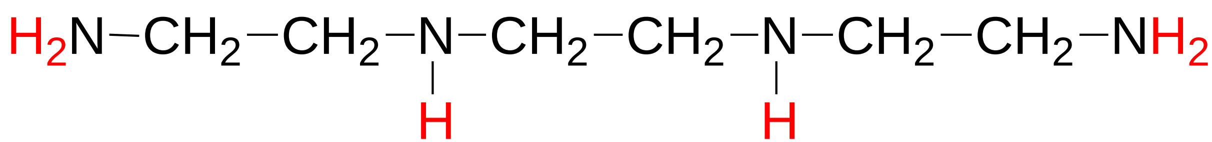
Remember: Number of reactive groups controls the physical aspects of network formation

Reactivity of resins and curatives

- **Example: A simple amine curing agent**
- **Triethylene tetra-amine TETA**
- **Six reactive hydrogens per molecule**
- **2 primary and 4 secondary hydrogens**
- **Strong crosslinker**

Functionality of 6





Molecular weight: 146.24 g/mol

Reactivity: 2 p-H per 146.24 gram or 73.12 g/ mol H
4 s-H per 146.24 gram or 36.56 g/ mol H

Can we buy this?

Total reactivity 6 H per 146.24 gram or 24.37 g/ mol H

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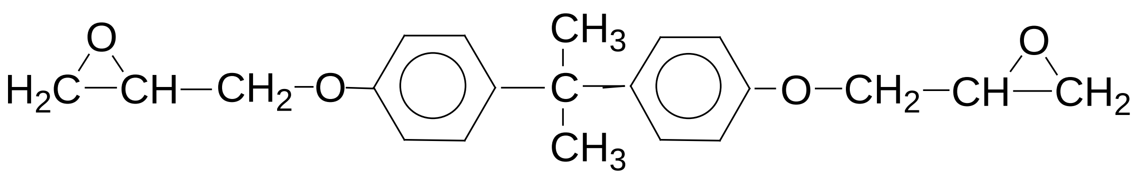
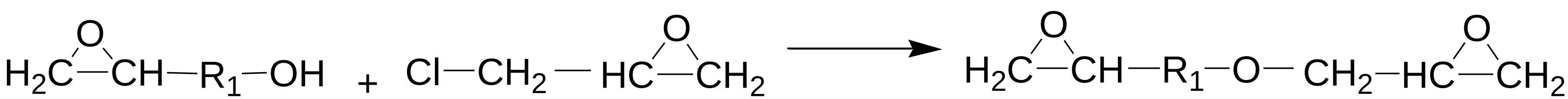
Examples of industrial resin types

Why do epoxies tend to condense?

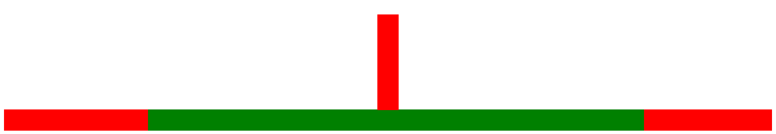


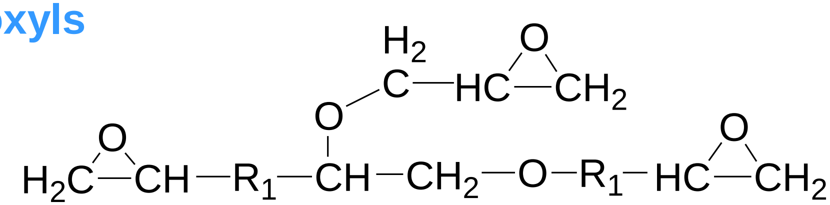
How do we make this?



Phenols plus epichlorohydrin

Epoxy groups will competitively react with hydroxyls





Higher functionalities are obtained as pre-condensed oligomers, sometimes called prepolymers

Examples of industrial resin types


Epon 828

Epon 161


Epon 154


Epon SU-8

Viscosity, functionality →

- Examples of epoxy pre-polymer resins
- From watery liquids to honey, syrup and solids
- Viscosity guides condensation grade and functionality
- Resins will require different processing temperatures
- Some may crosslink fast and are used only as additives

Sandia National Laboratories

Polymers

Step-Growth: Polyurethane Chemistry

Ingredients

- Polyol: $HO\text{-}(R)_x\text{-}OH$
- Polymeric diisocyanate: $O{=}C{=}N\text{-}(CH_2)_x\text{-}N{=}C{=}O$
- Water: H_2O

Reaction

$$HO\text{-}(R)_x\text{-}OH \;+\; O{=}C{=}N\text{-}(CH_2)_y\text{-}N{=}C{=}O$$

$$\downarrow$$

$$HO\text{-}(R)_x\text{-}O\text{-}\underset{\substack{\|\\ O}}{C}\text{-}NH\text{-}(CH_2)_y\text{-}N{=}C{=}O \;+\; H_2O$$

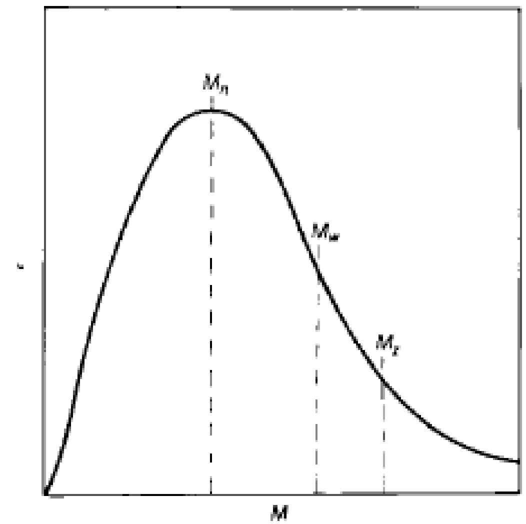
$$\downarrow \; \mathbf{-\,CO_2}$$

$$HO\text{-}(R)_x\text{-}O\text{-}\underset{\substack{\|\\ O}}{C}\text{-}NH\text{-}(CH_2)_y\text{-}NH_2$$

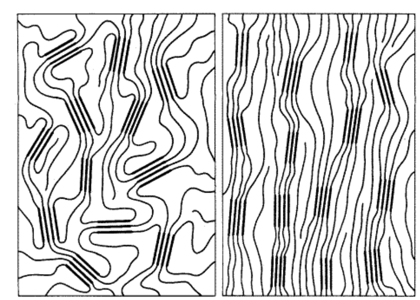
Polymers

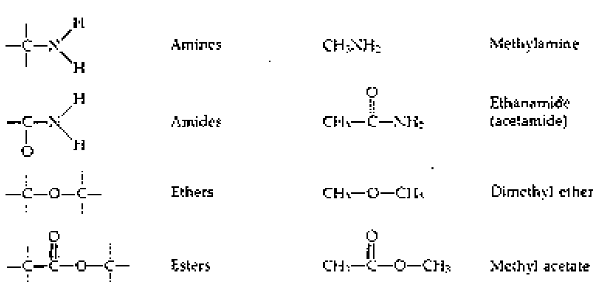
Properties of Polymers

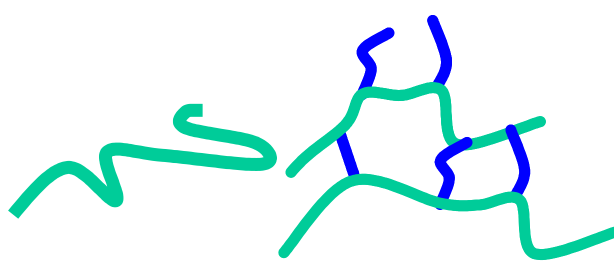
- **Uniquely different than small organic molecules due to the high molecular eights and architecture**
- **Viscosity - high viscosity, complex viscosity**
- **Molecular Weight Distribution**
  - » **High molecular weights**
  - » **Polydisperse**
- **Mechanical Properties, Physical features**
  - » **Viscous and elastic component**
  - » **Time-temperature superposition**
- **Topology – Linear, branched, or networks**
- **Thermal - partial crystallinity, glass transition temperature**
- **Chemical Composition – What's it made from?**



Polymer Morphology

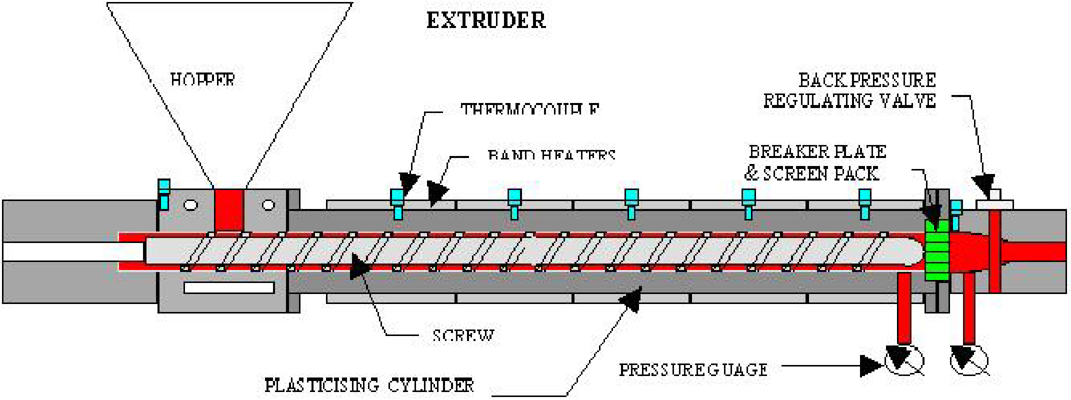






Polymers

Processing of Polymers



- **Modern polymer materials require interdisciplinary R&D**
- **Processing features are critical to every product we know**
- **Extrusion (parts-sheet-tube), blow molding, thermo forming, casting**
- **Cheap and variable processing implies polymer selection (i.e. PE, PP)**

PROPERTY

Polymer physics

STRUCTURE

Polymer chemistry

PROCESSING

Polymer rheology

OPTIMIZED PERFORMANCE

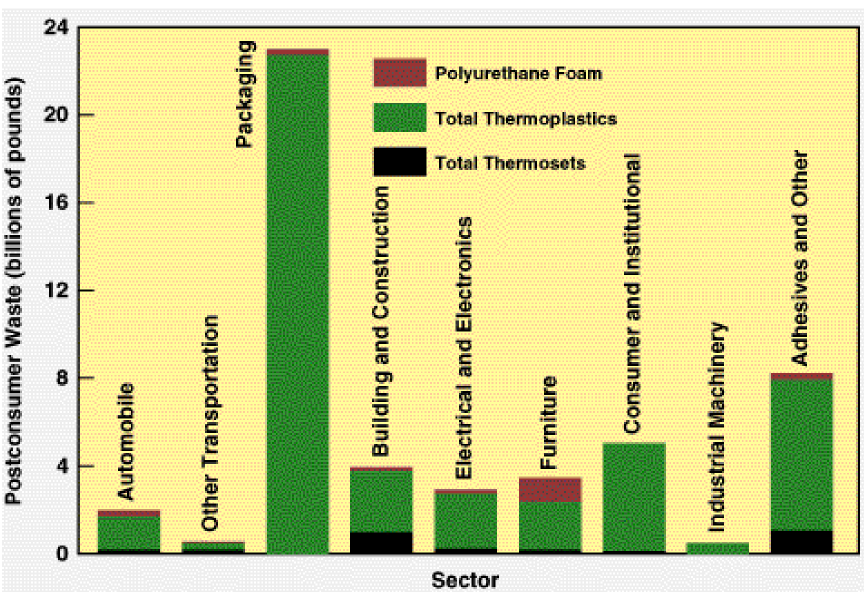
Aging, degradation

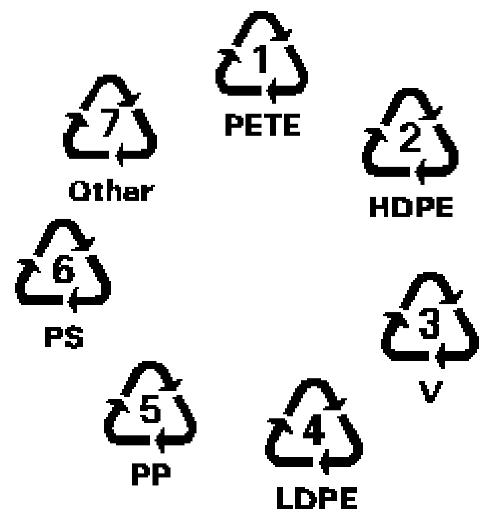
Environmental influence

Polymers

Recycling of Polymers

- Landfill – incinerators - recycling
- Key problem: Material incompatibility
- Materials separation is required
  - » Identification in mixed waste stream, spectroscopy
  - » Pre-sorting, commitment of users is critical
- Properties degrade with every processing step
- New biopolymers, polyesters, selective applications





Polymers

Recycling of Polymers

- Recycling - Major Issues
- Secondary products are often inferior, compare with glass
- But some products are attractive, plastic lumber, flower pots, insulation, invisible parts, or as chemical precursors
- Life-cycle environmental impact, washing, transportation, energy
- Currently only 3.5% is recycled, 34% paper, 22% glass, 30% metal
- One stray bottle PVC can ruin melt from 10000 PET bottles

- Main groups of recyclable polymers

- 1) PET soda bottles, sinks in water, good separation
- 2) HDPE, milk bottles, diary products, floats, non-food containers
- 3) PVC more demanding, due to sensitive processing
- 4) LDPE, plastic tubing, irrigation, plant holders
- 5) PP, containers, carpets etc, needs careful follow-up processing
- 6) PS, easy to recycle, but limited supply
- 7) i.e. tires, energy intensive shredding, crosslinked rubber crumbs, non-meltable, use as fillers?, glue pieces together

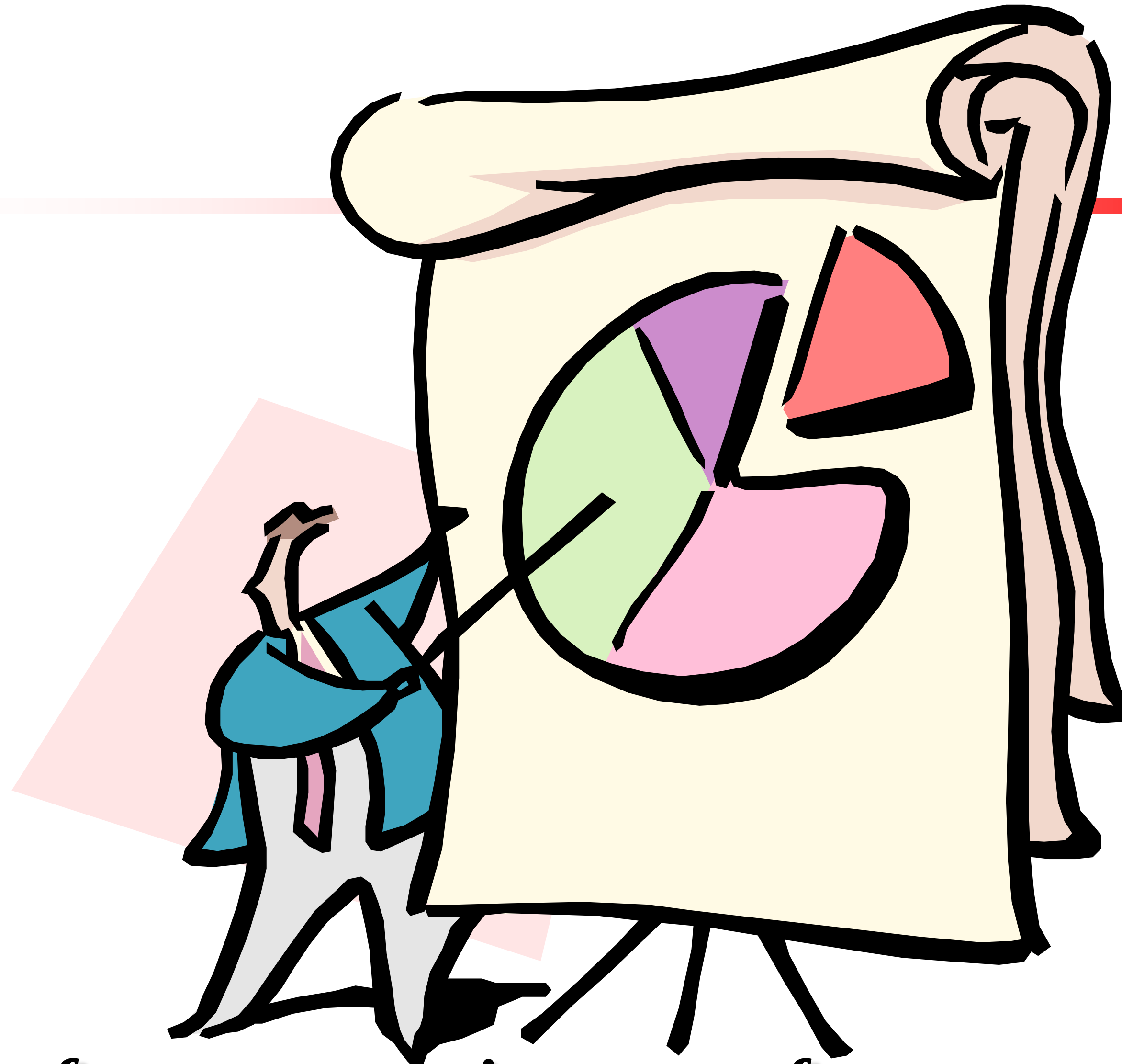
Only 1 planet to destroy

Polymers

Plastic Trash

- North Pacific garbage patch is twice the size of Texas
- UN – Environmental Program 6/9/2009
- 80% of all trash ending up in the oceans are plastics
- 46000 plastic pieces per km^2 in the oceans
- Per year 6.4×10^6 tons of plastic waste
- Animals, birds, turtles eat plastics

Need to prevent trash at the source, aim for sustainability



Thank you for your attention to our future: students, environment, population, peace

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.