Φασματοσκοπικός Χαρακτηρισμός Μακρομορίων Με Σκέδαση Ακτίνων Laser

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Syllabus

- Introduction
  - Polymers as Materials - Natural Polymers - Synthetic Polymers
- Types of Polymerization
  - Addition Polymerization (free radical or unpaired electron)
  - Condensation Polymerization
- Chemical Composition
  - Homopolymers
    - all the repeating units along the chain are the same
  - Copolymers
    - two or more different monomer units
      - Random-Alternating-Block-Graft
- Stereochemistry
  - Geometrical isomers-Configuration - atactic, isotactic, syndiotactic
- Topology
  - Chains - Branches - star, comb, random, Network
- Molecular Weight
  - Chain Dimensions - Measurement – Light Scattering
- Polymer Structure-Property Behavior
  - Chain Entanglement – Intermolecular forces – Time scale of motion
  - The Glass Transition
  - Relaxation in Polymers
- References

So what are polymers?

Tiny molecules strung in long repeating chains form polymers.

Why should you care?

- Well for one thing, your body is made of them.
- DNA, the genetic blueprint that defines people and other living things, is a polymer.
- So are the proteins and starches in the foods we eat, the wheels on our skateboards and in-line skates, and the tires on our bikes and cars.
- Understanding their chemistry can help us use them wisely.
- Once we're familiar with the varieties of polymers that people make, such as plastics, we can recycle many of them and use them again.
- That's good for the environment.

So what are polymers?

- Organic
  - Natural
    - Polysaccharides (Cellulose, starch, cotton)
    - Proteins (Biopolymers, wool)
    - Natural rubber (*cis*-1,4-polyisoprene)
  - Synthetic
    - Rubbers, Plastics, Fibres, Coatings, adhesives
- Inorganic
  - Natural
    - Clays, sand
  - Synthetic
    - Fibres (optical fibre)
    - Rubbers (silicones)

So what are polymers?

Silkworms

- People in China discovered more than 4,500 years ago that they could unravel silk, a polymer, from the worms' cocoons and weave it into soft fabrics.
- Incredibly, a single cocoon yields 300 to 900 meters of silk.
- For centuries, silk was so prized that exporting mulberry seeds or silkworm eggs from China was punished by death.

Latex

- South American Indians slash the bark of trees in the rain forest to obtain a milky white fluid called latex. They discovered that it could form a solid that was elastic; you could stretch it and it would snap back to its original shape.
- If you rubbed it on penciled words, the writing would disappear, so Europeans called it **rubber**.
- They pressed it between layers of fabric to produce a rain slicker called a mackintosh;
- They also molded it into tires for carriages and automobiles.
- The British smuggled rubber tree seeds from Brazil to England, where they produced seedlings for export to colonies in Ceylon, Malaysia, and Singapore. Descendants of those seeds now produce 90 percent of the world's natural rubber.

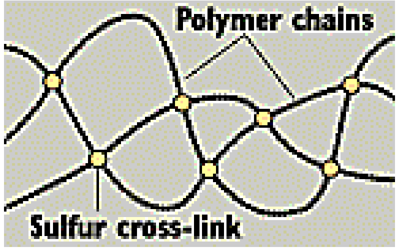
History of Rubber

- ~ 1500 Columbus Stumbles Across Haiti
- ~ 1600 Missionaries Observe Indians Making Crude Rubber Shoes (Caoutchouc)
- 1700 Joseph Priestly Invents a Name
- 1820 1st Rubber Shoes
- 1832 Charles Mackintosh (1766 – 1843)
- 1833 Goodyear Starts Work on Rubber
- 1844 Vulcanization
- 1942 Synthetic Rubber Project

Vulcanized rubber

- Natural rubber from latex, which comes from the sap of tropical trees, made nifty balls that you could bounce. But it became hard and brittle when it got too cold, a sticky mess when it got too warm.
- In 1839 Charles Goodyear discovered that latex heated with sulfur—or "vulcanized"—would remain elastic at a wide range of temperatures.
- Although Goodyear didn't know why his invention worked, we do today:
  - The sulfur made bridges between the long chain polymers in rubber to keep them from sliding past one another or contracting into knots.

Charles Goodyear



Biopolymers

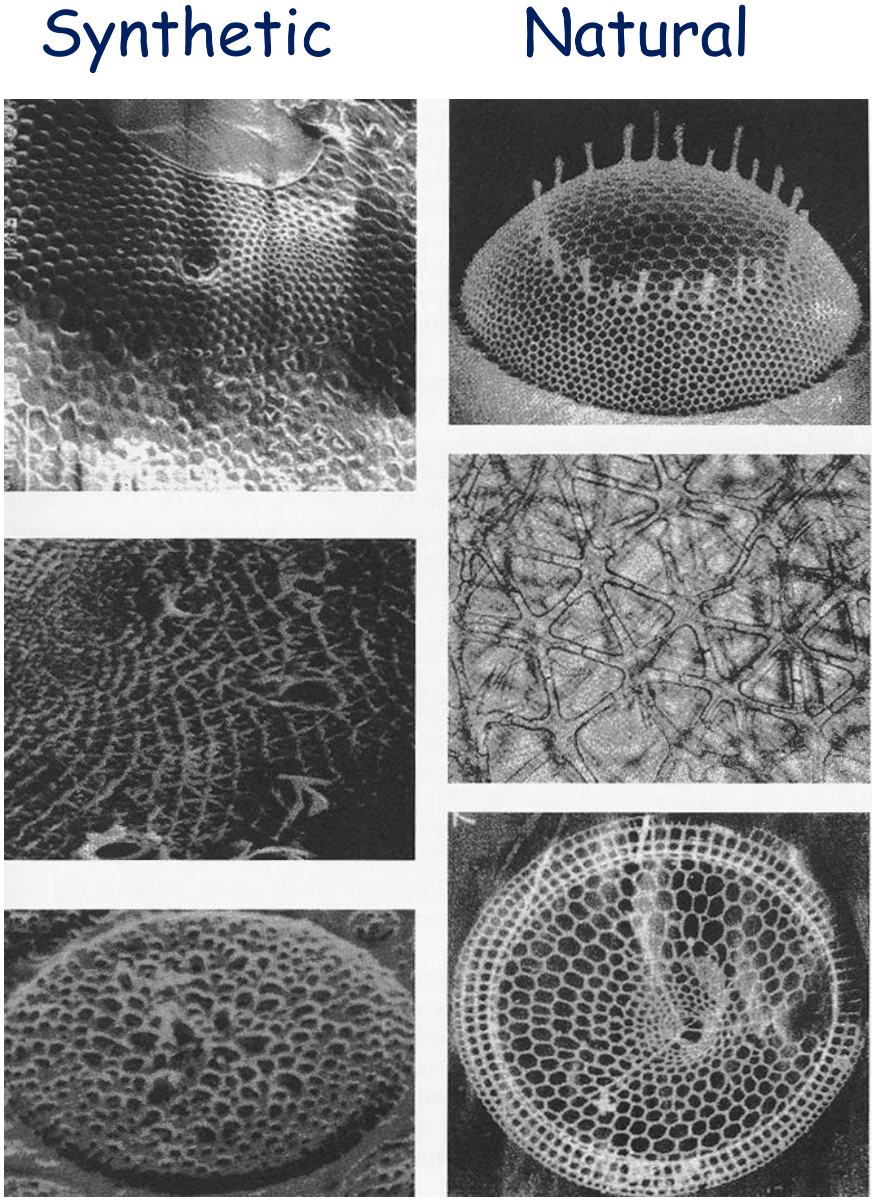
- Nearly unlimited resources
- More likely to be bio-compatible and biodegradable
- Good mechanical properties
- Already Designed and Optimized by nature to fulfill a certain task
- Easy to make derivatives with desired property profiles
- “Natural” name on ingredient lists

Biopolymers

- Single cell organisms
- Plants
- Animals
- And their by-products
    - Spider silk, etc.

Biopolymers

- Using nature as a template
- Synthetic structures can duplicate natural structure
- Marine organisms



Natural Macromolecules

Examples of how nature is better than most synthetic materials

- **Spider webs** - polymer fibers which take more energy to break than the same size steel
- **Eyes** - more sensitive than any photodetector we can make (in the visible region)
- **Nose** - more sensitive for most things than any chemical sensor we can make - faster too.
- **Bone** - tremendous strength/ weight.
- **Data storage (brain)** - one bit/ 3 molecules

Biomaterials Advantages

- Biological Materials
  - Self-generating
  - Self-healing

Imagine a bridge (steel)
which could detect internal flaws and could
send resources there to
"heal itself"

The facts of life...

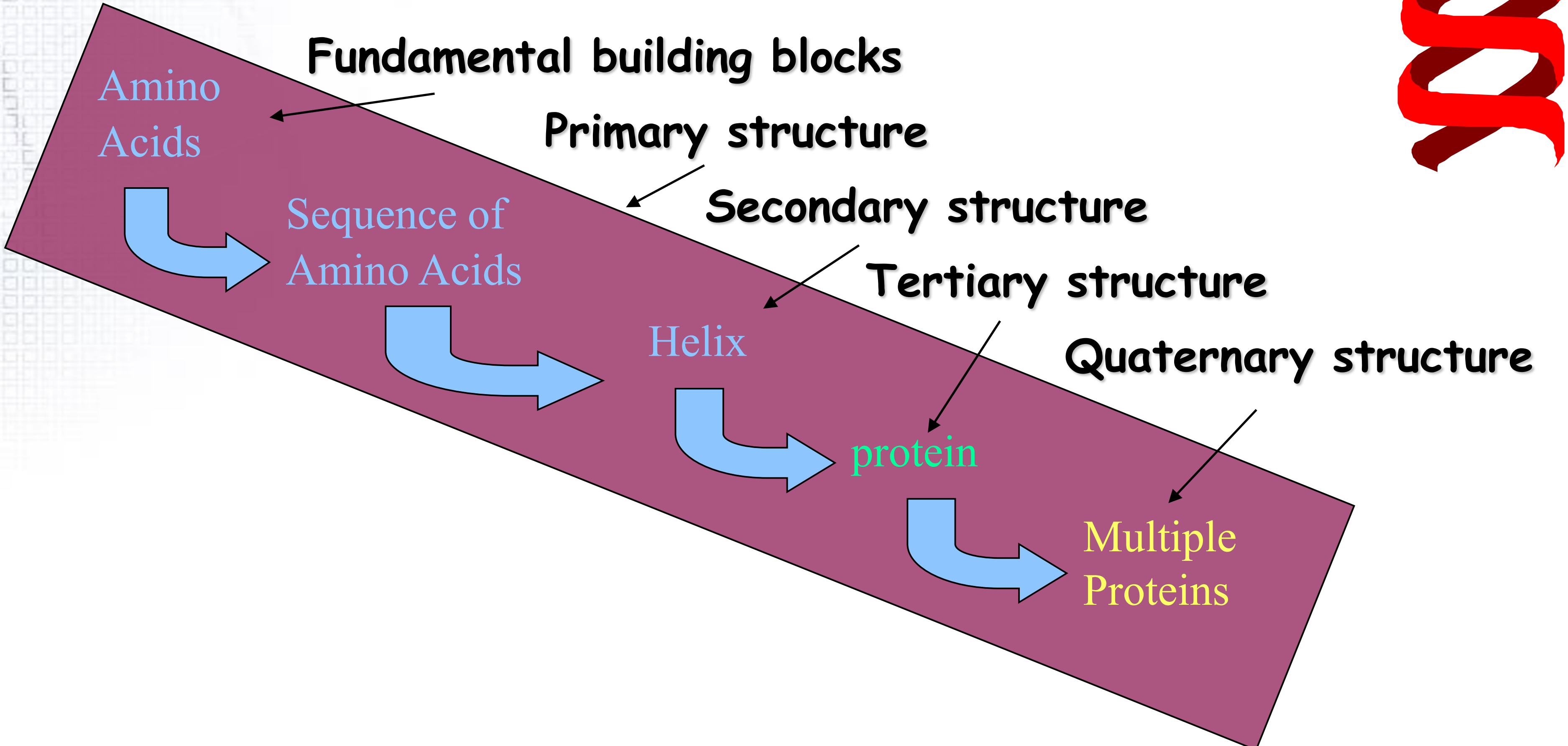
- **Life has an extremely simple tool kit:**
- Nearly all materials needed for an organism are made from:
  - Protein
  - Nucleic acids

} Called "functional polymers"

- **Compare to building blocks of synthetic polymers**
  - Nature has about 20 amino acids -- all proteins
  - Synthetic polymers have thousands of different types of "building blocks" - or monomers

The facts of Life… cont.

- Life accomplishes diversity with levels of structure:



Fundamental building blocks

Amino Acids

Primary structure

Sequence of Amino Acids

Secondary structure

Helix

Tertiary structure

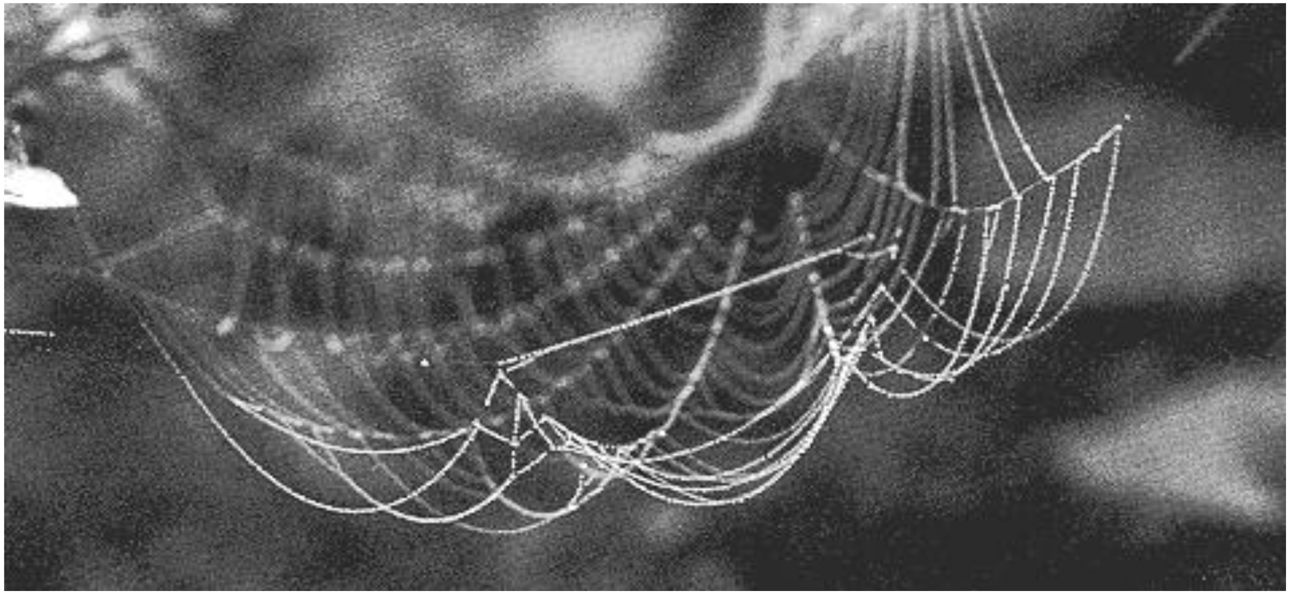
protein

Quaternary structure

Multiple Proteins

Amazing Biological Materials

- Question: How can a thread almost too small to see possess strength enough to stop a fly-sized projectile moving at 1 m/sec?



Mechanical Properties of Spider Silk

- Takes more energy to break than steel
- Stronger than the strongest synthetic polymer
  - e.g. Kevlar - used for anchoring oil rigs - bullet-resistant vests - VERY strong in tension –
  - Spider silk is stronger AND more resilient
  - Elongates 4 x before it breaks
  - Deformation isn't purely elastic - (otherwise bugs would "bounce off")
  - Almost 3/4 of the energy of the impact is dissipated as heat so little is left for recoil

Mechanical Properties of Spider Silk

- Fiber manufactures are most interested in capture silk, and especially dragline silk.
- **On an equal weight basis spider silk is stronger than steel and Kevlar.**
- Not only strong but elastic, capture silk can stretch up to 3 times original length.
- A thread of silk as thick as a pencil could stop a 747 in flight.

Spider Silk

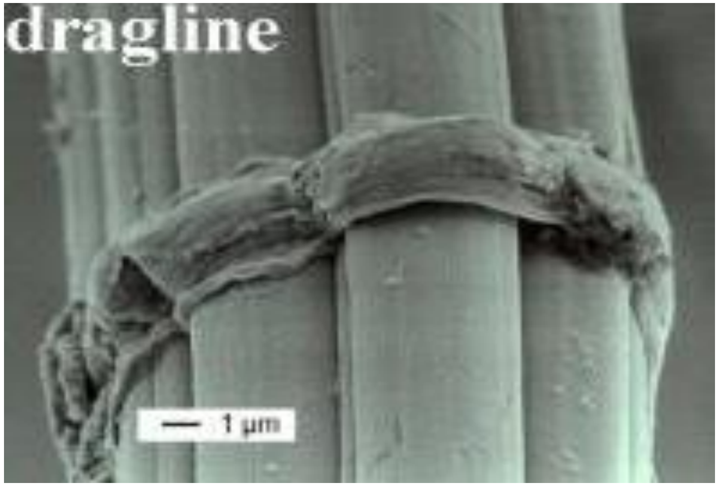
- Spiders make a variety of types of silk
  - Drag line - for making webs
  - Glue silk - to help attach webs
  - Attachment silk - strong thread to secure webs
  - Wrapping silk - (to bind prey)
- Each has a different amino acid composition

Chemical Make-Up

The silk is composed of seven amino acids.

– Two primary amino acids are:
  - Alanine
  - Glycine

The other five that appear in lesser amounts:
  - Glutamine
  - Leucine
  - Arginine
  - Tyrosine
  - Serine



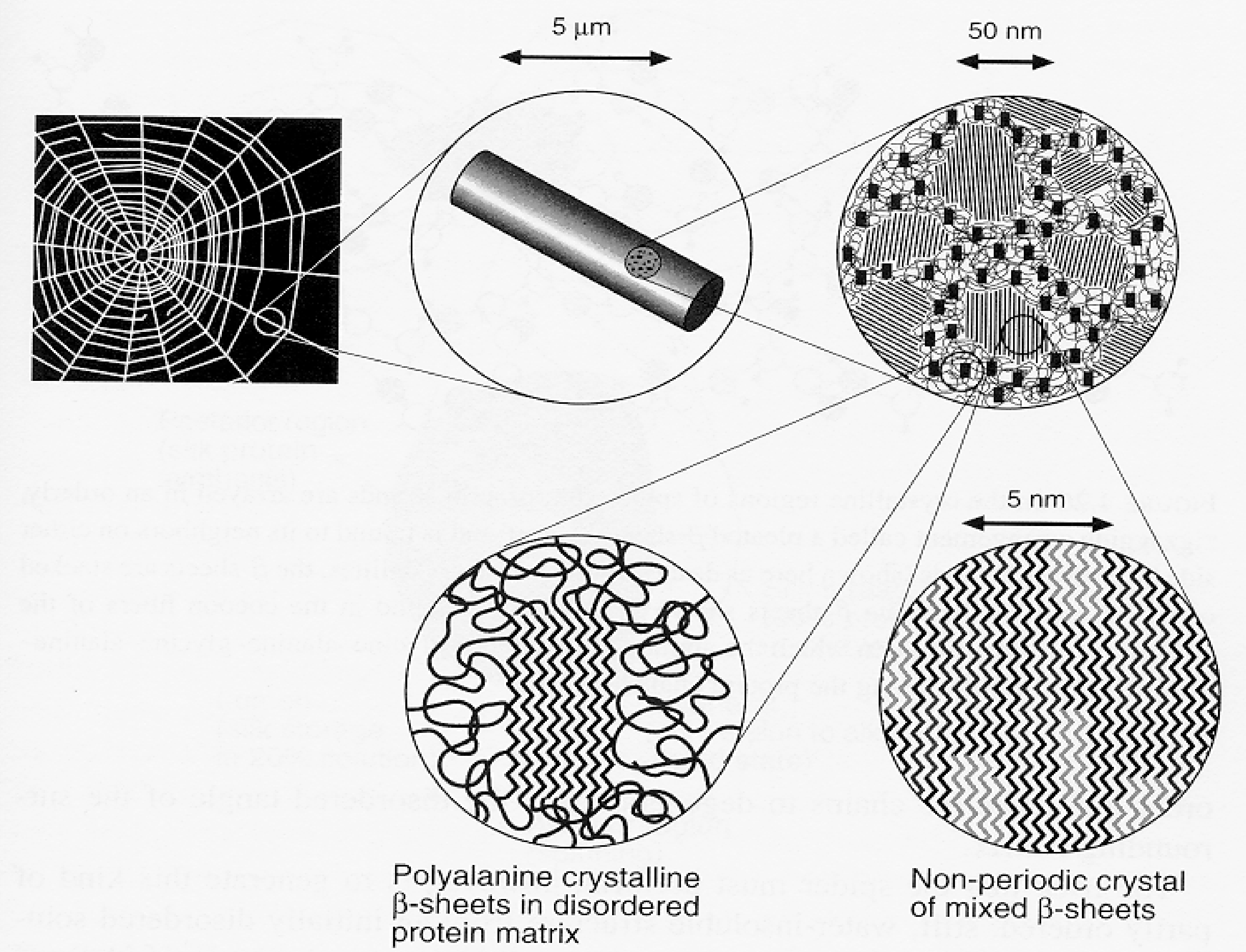
Spider Silk Structure

- Spider silk is a biopolymer, it has amorphous and crystalline structure.

- The seven amino acids repeat to form the protein that makes up the silk.

- Forms a spring like structure.

Spider Silk Structure



Spider Silk Structure

- Crystalline sections embedded in a disordered matrix
- Crystals provide strength
- Matrix provides flexibility

We copy this concept with many polymers

(e.g. polyethylene) - STILL not as strong as silk

Production of Synthetic Silk

- The entire genetic sequence of dragline silk has been found, it consists of over 22,000 base pairs.
  - researchers disagree on the amount of base pairs to be used in synthetic production.
- Differences in research methods.
  - DuPont is using only four short sequences.
  - Plant Cell Technologies are cloning the entire genetic sequence.
- Work being done to identify what each silk producing gene does.
  - Precise control of silk properties
    - Mechanical Properties
    - Color

Mass Production Methods

- It takes 500 spiders to make 1 m^2 of a spider silk cloth.
- Other organisms that would make production faster.
  - Bacteria
  - Fungi
  - Plants, soy beans
  - GOATS

Mass Production

- The Canadian company Nexia Biotechnologies developed a mass production method using goats milk.
  - The gene has been successfully spliced in to mice.
  - The transgenetic spider goats were born in early 2000.
- Concentrated product 2-15g/L of milk.
- Produced at or below cost of existing petrochemical base fibers.
- Environmentally friendly.
- Renewable resource.

technology

BioSteel®

BioSteel® is Nexia's recombinant dragline spider silk program and is based on using Nexia's transgenic goat technology. Spider silk has long been admired by material scientists for its unique combination of high-performance properties including toughness, strength, lightness and flexibility. Nexia has exclusive worldwide rights to broad patents covering spider silk genes and proteins and is in the process of developing a commercial spinning process for BioSteel®.

Nexia has decided to refocus fibre development towards biopolymer sales and specialized nano-scale fibre applications for spider silk and away from traditional fibres and yarns. This decision was prompted by the emerging interest in nanofibres and by the ongoing technical challenges of producing bulk, cost competitive spider silk fibres with superior mechanical properties, especially strength. Nexia has suspended it's outsourcing of spinning micron-sized fibres with Acordis SF and stopped its in-house spinning effort. Spinning of BioSteel® proteins into nanometer diameter fibres has been achieved and Nexia is now determining the product specifications for medical and micro-electronic applications.

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Fax: 514.371.7880

Contact Nexia

Important documents

Fiscal 2007 Annual

Use of Spider silk

- Safety
  - Ropes,seatbelts
- Medical
  - ligaments, tendons, and blood vessel support
- Public
  - wear resistant clothing
  - bridges
- Military
  - bullet resistant clothing

Polymer Science Basics

What is it ?

The Science of Large Molecules

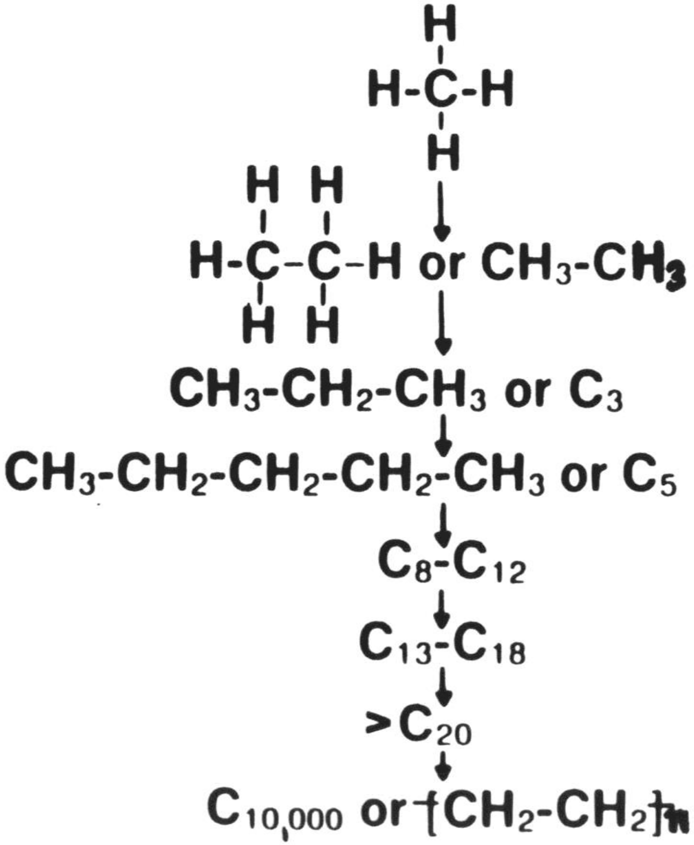
Poly.........mer **—M—M—M—M—M—M—**

This includes

- Synthesis
- Characterization
- Polymer Physics and Physical Chemistry
- Polymer Engineering
- Materials Science

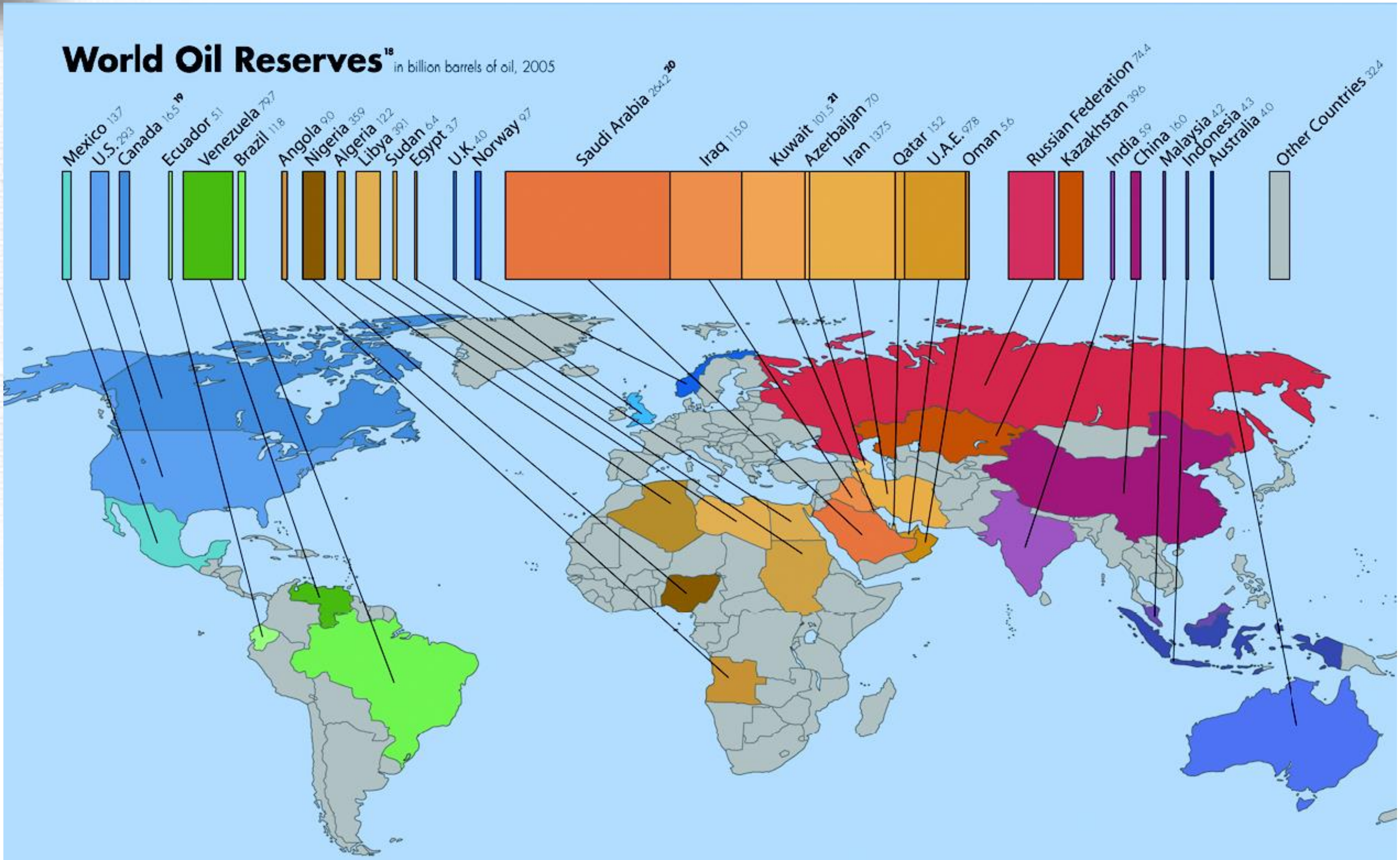
Some Basic Definitions

- **Polymer** — A large molecule made up of small building blocks
- **Monomers** — The building blocks
- **Homopolymer** — What you get if the building blocks are all the same
- **Copolymer** — A polymer composed of different monomers
- **Blend** — A mixture of different polymers

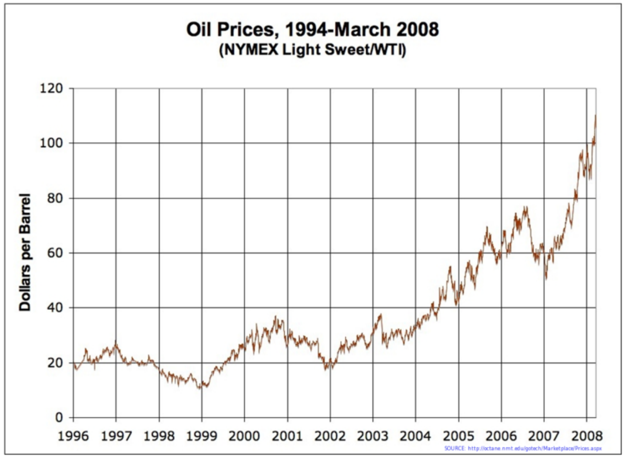


$\mathrm{H-\overset{H}{\underset{H}{C}}-H}$	Methane	[Gas]
$\mathrm{H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-H}$ or $CH_3\text{-}CH_3$	Ethane	[Gas]
$CH_3\text{-}CH_2\text{-}CH_3$ or C_3	Propane	[Gas]
$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$ or C_5	Pentane	[Liquid]
$C_8\text{-}C_{12}$	Gasoline	[Liquid]
$C_{13}\text{-}C_{18}$	Kerosene	[Liquid]
$>C_{20}$	Parafin Wax	[Solid]
$C_{10,000}$ or $\left[CH_2\text{-}CH_2\right]_n$	Polyethylene	[Solid]

World Oil Reserves

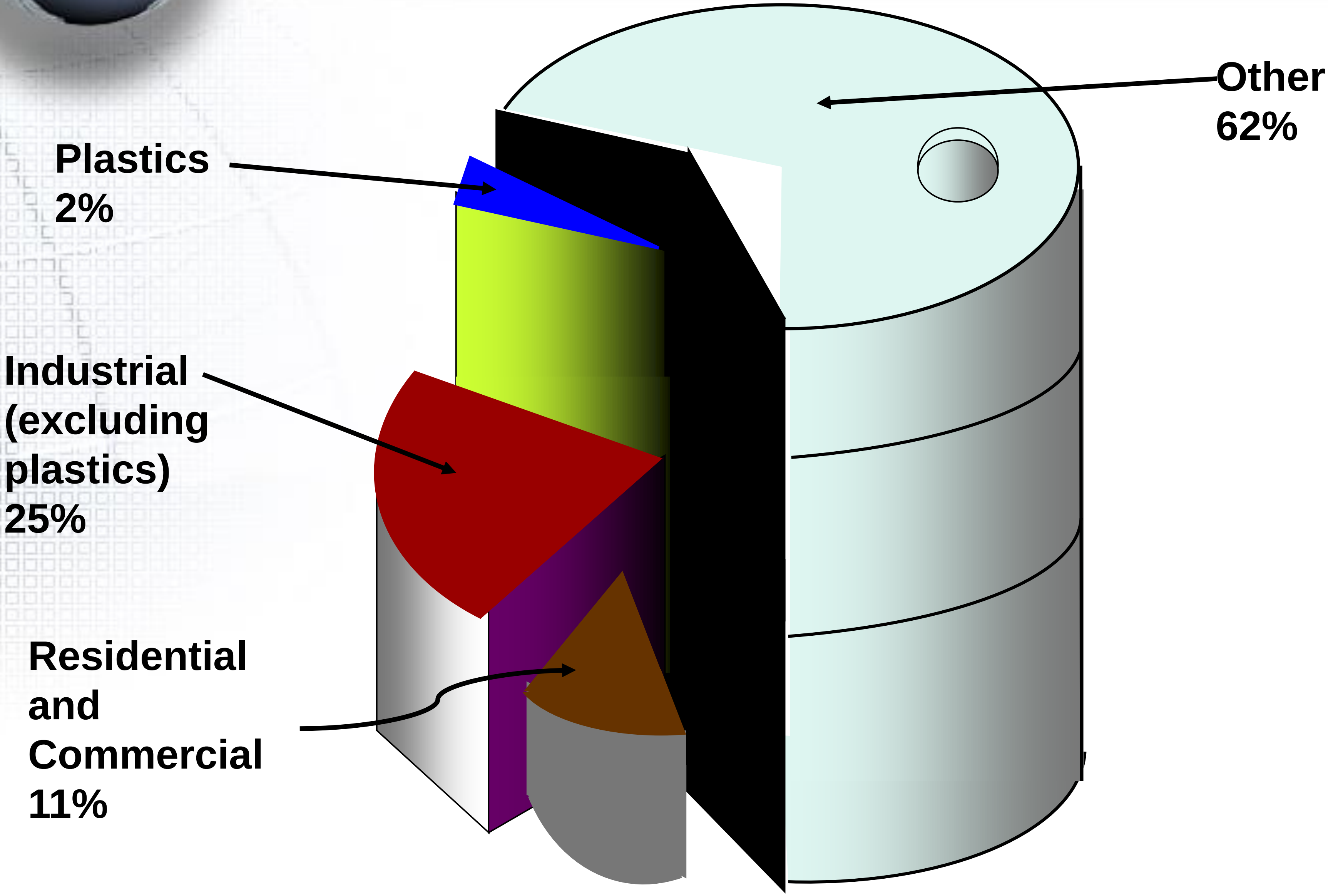


Spindletop-East Texas, 1901

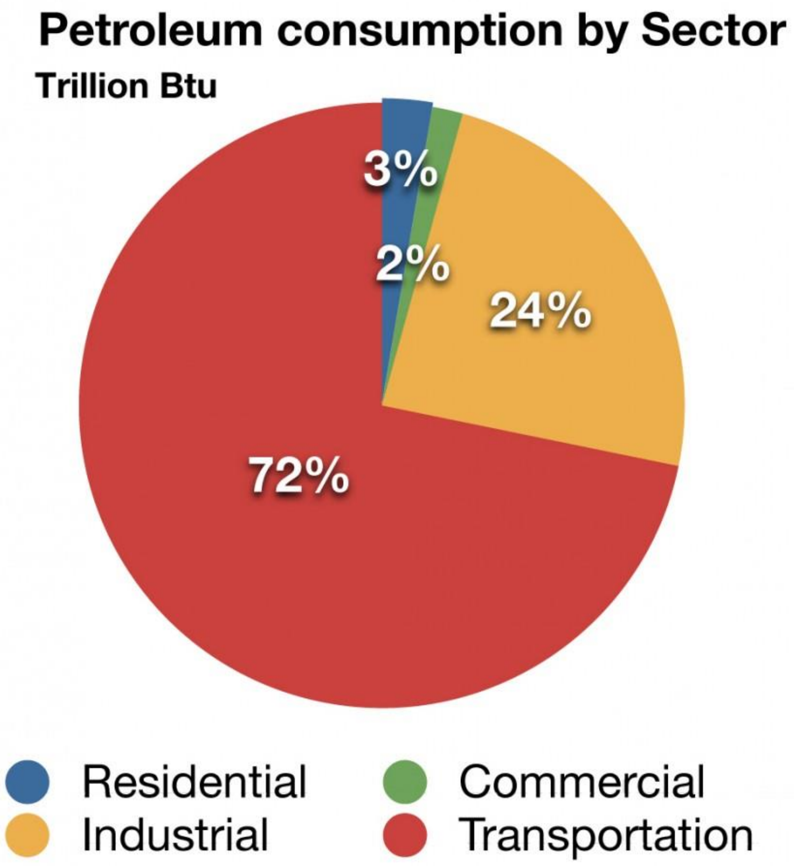


SOURCE: http://octane.nmt.edu/gotech/Marketplace/Prices.aspx

PETROLEUM CONSUMPTION



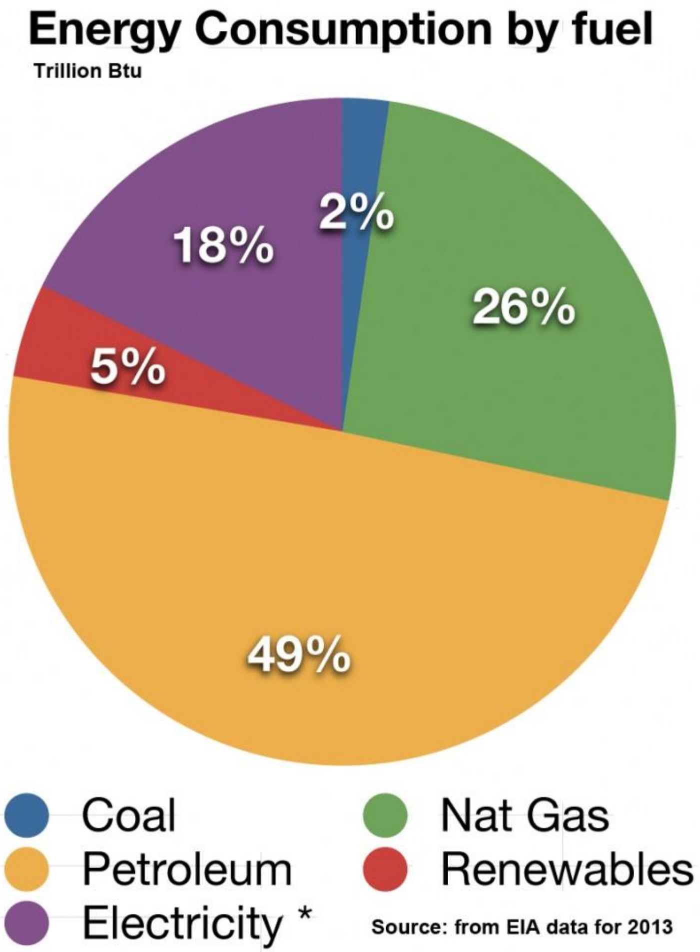
Crude Oil Consumption



Petroleum consumption by Sector

Trillion Btu

Source: EIA data 2013

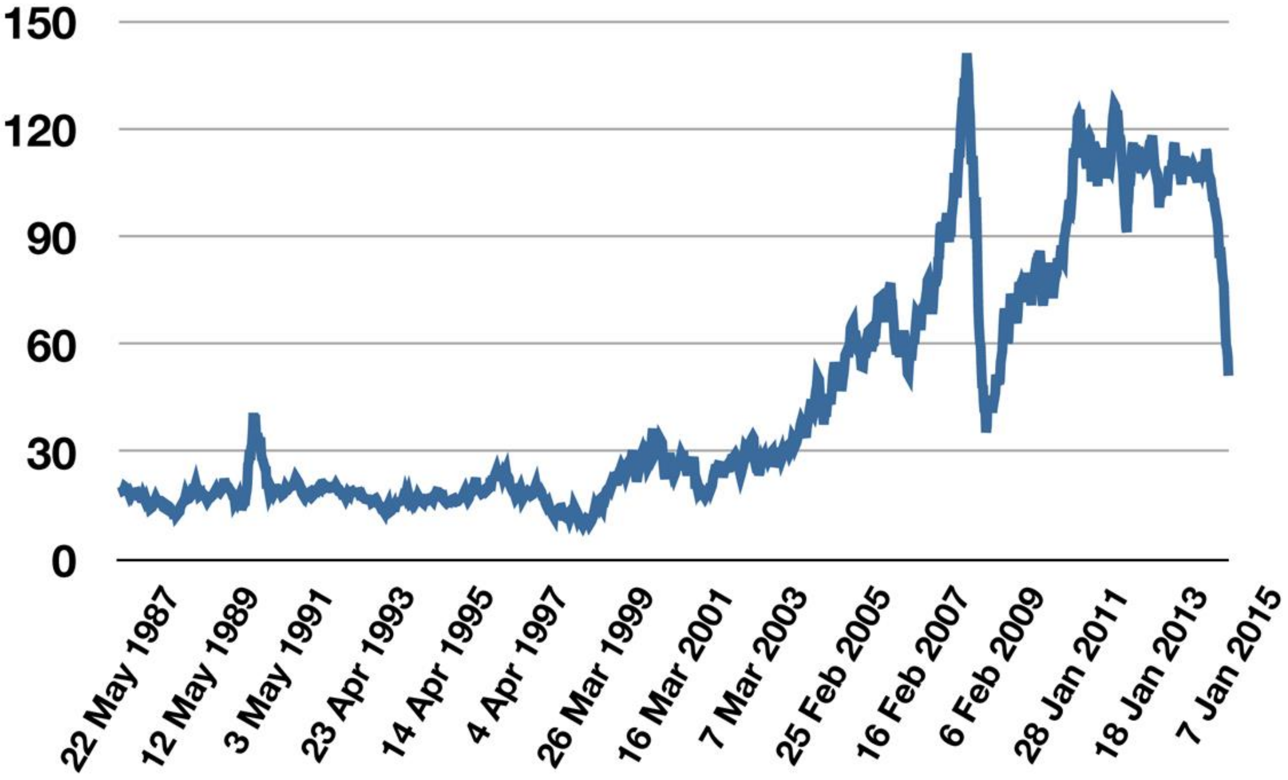


Energy Consumption by fuel

Trillion Btu

Source: from EIA data for 2013

Crude Oil Prices

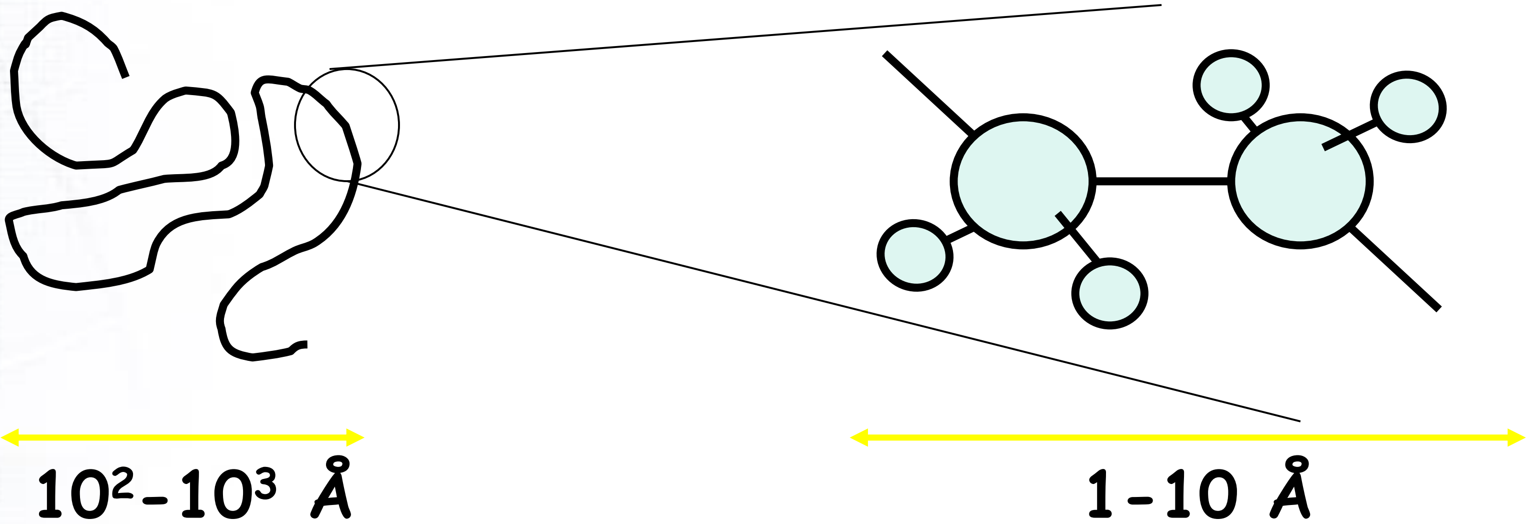


Brent Crude $ per barrel 1987 to 7 Jan 2015

Sources: EIA and Jan daily spot prices

BASIC NOTIONS & DEFINITIONS

Polymer: High MW ($\geq 10^4$) Organic Molecule Comprised Of Covalently Attached Repeat Units.



Synthetic Polymer: Product Of Chemical Synthesis Controlled By Humans.

Biopolymer: Product Of Biological Process (eg. Proteins)

The Past of Polymers

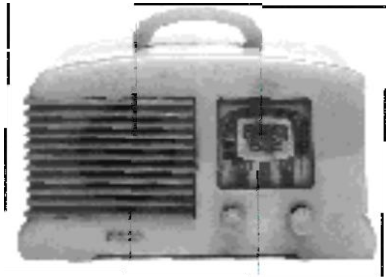
- Limited to specialized service in products such as,
  - Fibers.
  - Films.
  - Coatings.
  - Light-Duty, inexpensive plastic.

Bakelite molded products

Baekeland
1863-1944

Form 9 Novalac fixtures made of Bakelite

Rocket launcher Mounted under P-47 Thunderbolt Wing, made of BAKELITE composite materials



Bakelite radio (1930s)

The Today of Polymers

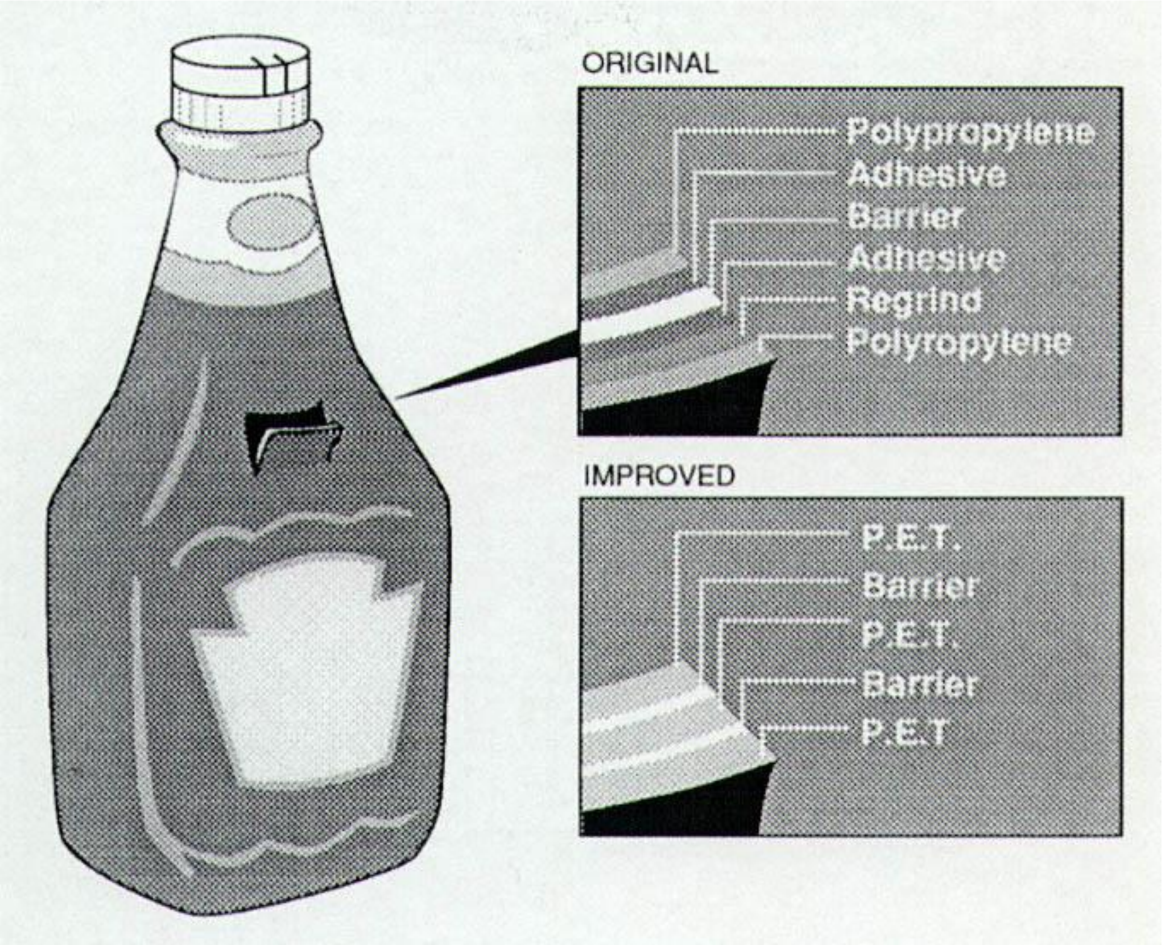
- In the advancing environment of technology traditional materials are changing.

Polymers

- Replacing or already replaced aluminum and other structural metals exposing to high temperatures and mechanical stress.
- Replaced materials used in electronic and optical communication and computation, substitute for further materials.
- New usage areas occured such as Medicine and Biology.

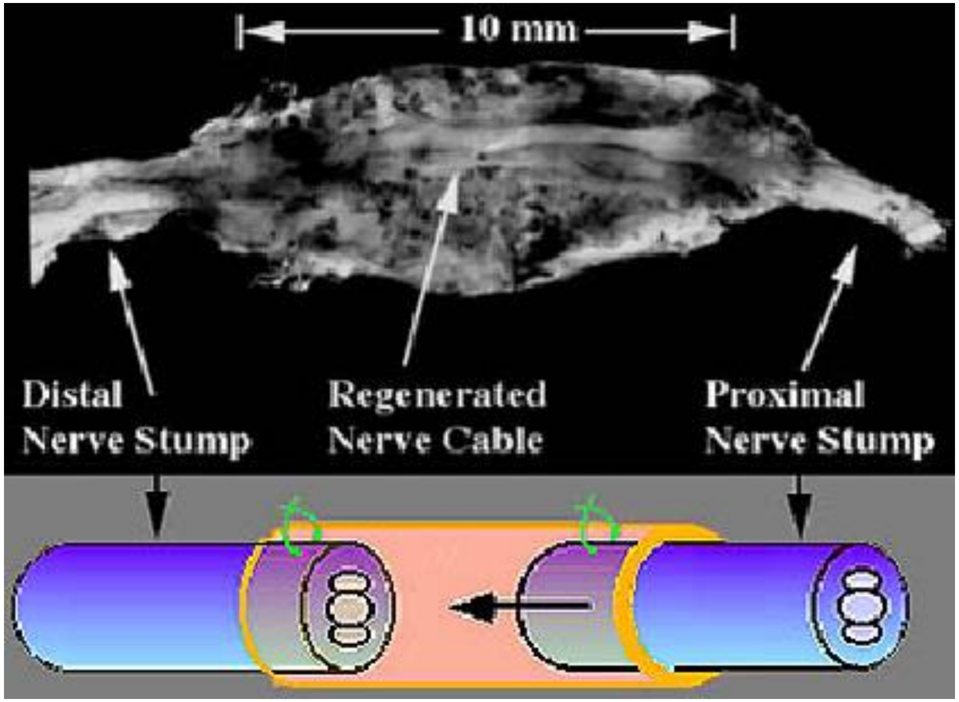
Polymers and Plastics

Multi-layered Bottle

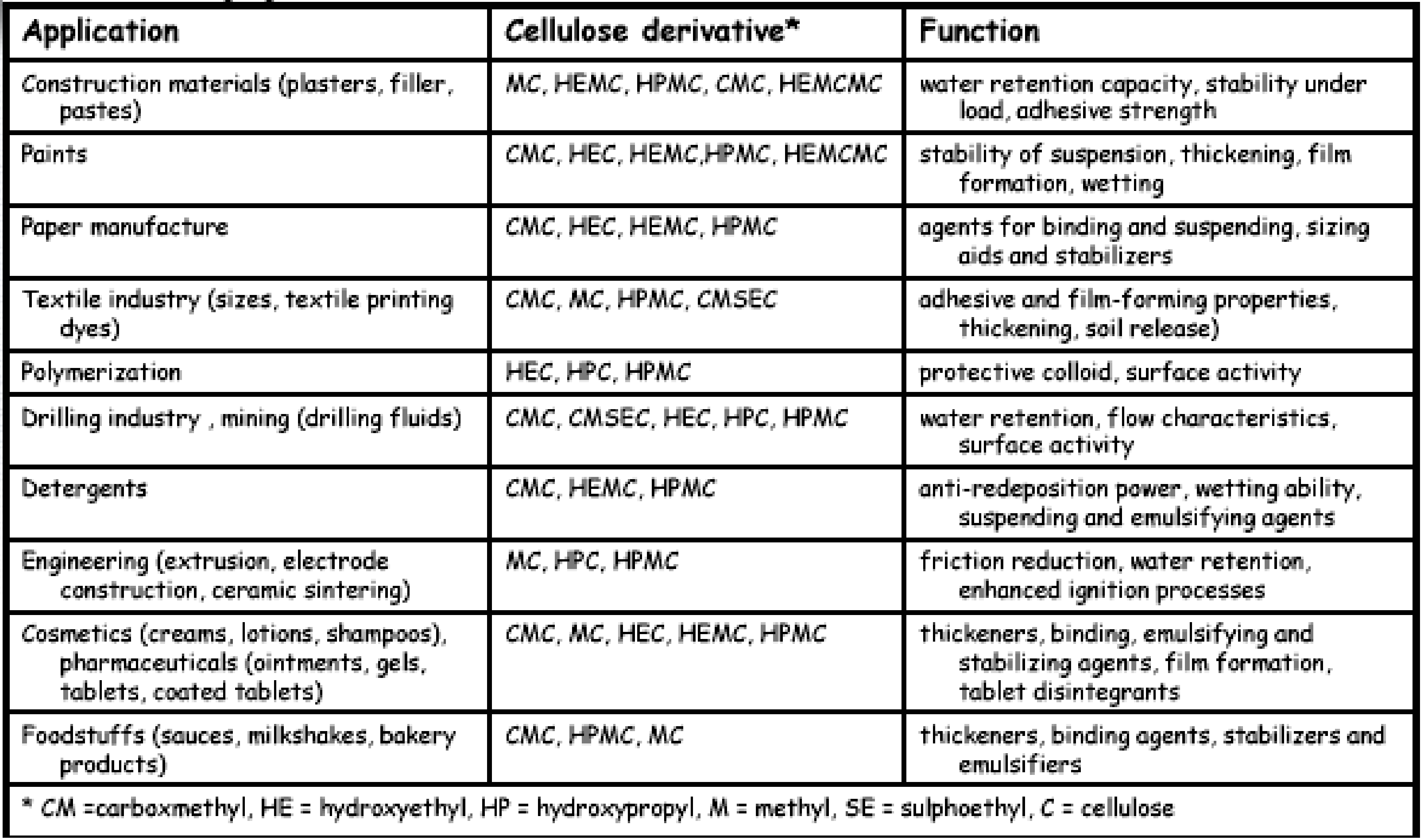


Therapeutic Plastics

- **Electricity-conducting polymer** that can stimulate new **growth** in **damaged nerves**.
- **The Tube** brigdes gaps in a damaged nerve with tubes made from the **plastic and sugar**.
- The sugar slowly breaks down, forming **angiogenetic byproducts**--substances that encourage the **growth** of blood vessels.
- These new vessels help the **nerve** begin to **regrow** within the tube, which **degrades** over a period of two to six weeks.



Examples of Biopolymers



Application	Cellulose derivative*	Function
Construction materials (plasters, filler, pastes)	MC, HEMC, HPMC, CMC, HEMCMC	water retention capacity, stability under load, adhesive strength
Paints	CMC, HEC, HEMC,HPMC, HEMCMC	stability of suspension, thickening, film formation, wetting
Paper manufacture	CMC, HEC, HEMC, HPMC	agents for binding and suspending, sizing aids and stabilizers
Textile industry (sizes, textile printing dyes)	CMC, MC, HPMC, CMSEC	adhesive and film-forming properties, thickening, soil release)
Polymerization	HEC, HPC, HPMC	protective colloid, surface activity
Drilling industry , mining (drilling fluids)	CMC, CMSEC, HEC, HPC, HPMC	water retention, flow characteristics, surface activity
Detergents	CMC, HEMC, HPMC	anti-redeposition power, wetting ability, suspending and emulsifying agents
Engineering (extrusion, electrode construction, ceramic sintering)	MC, HPC, HPMC	friction reduction, water retention, enhanced ignition processes
Cosmetics (creams, lotions, shampoos), pharmaceuticals (ointments, gels, tablets, coated tablets)	CMC, MC, HEC, HEMC, HPMC	thickeners, binding, emulsifying and stabilizing agents, film formation, tablet disintegrants
Foodstuffs (sauces, milkshakes, bakery products)	CMC, HPMC, MC	thickeners, binding agents, stabilizers and emulsifiers

* CM =carboxmethyl, HE = hydroxyethyl, HP = hydroxypropyl, M = methyl, SE = sulphoethyl, C = cellulose

Historical Context

- **1920 - STAUDINGER;** The macromolecular hypothesis
  - "*Drop the idea of large molecules. Organic molecules with a molecular weight higher than 5000 do not exist*."

  — Advice given to Hermann Staudinger*

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

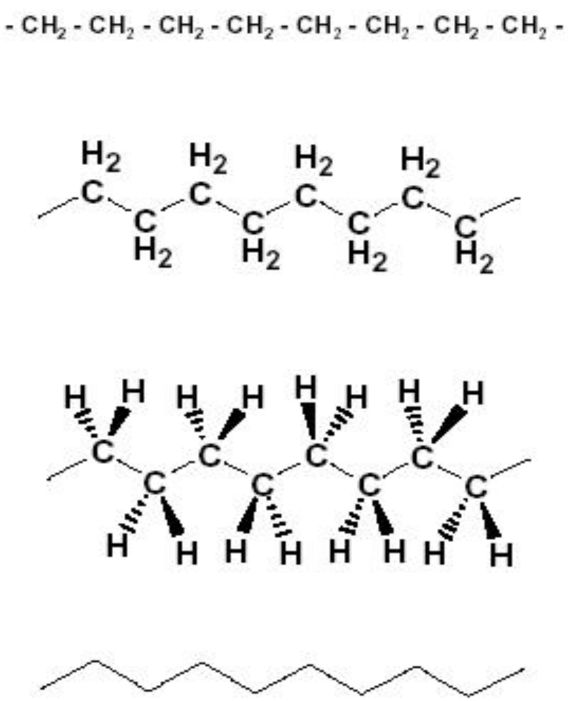
- **LATE 1920's - CAROTHERS;** Set out to prove the existence of macromolecules by systematically building them from small molecules using well known chemistry

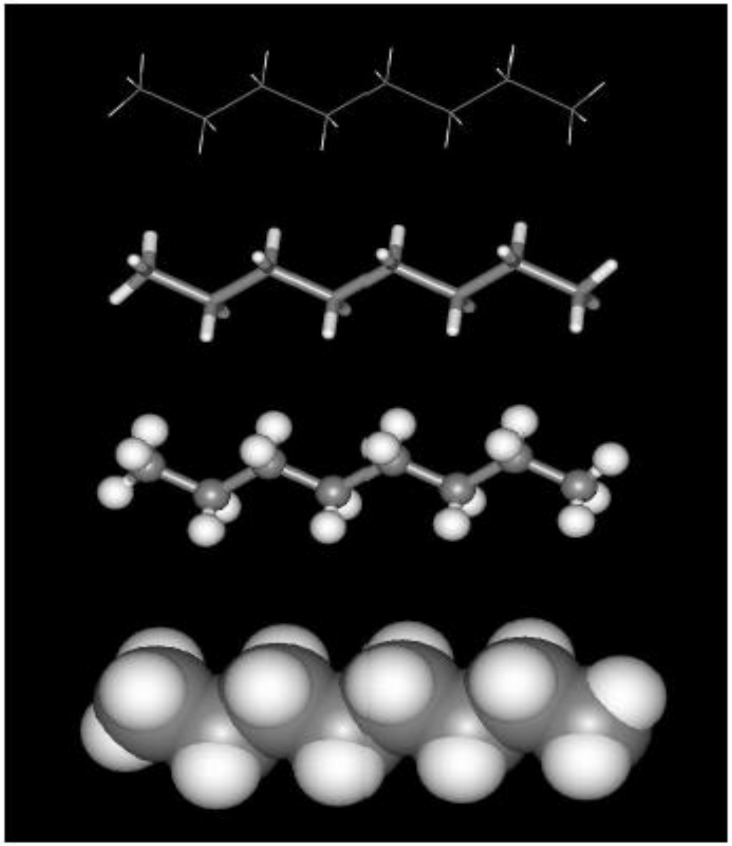
Wallace Carothers
Nylon and Synthetic Rubber

Wallace Carothers (1896-1937), *depressed by the death of his sister and convinced that his life's work was a failure committed suicide at the age of 41 at Du Pont.*

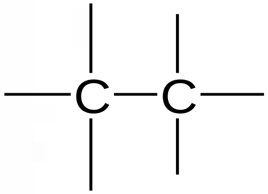
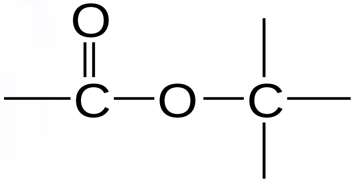
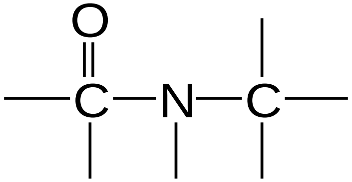
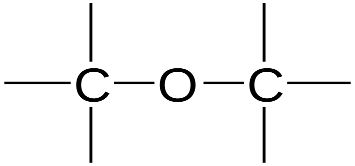
Polymer Science

- The simple, repeating chemical structure of polyethylene—a chain of carbon atoms, each bonded to a pair of hydrogen atoms—typifies the building-block nature of polymers.





Chemical Linkages of Primary Molecules in Macromolecules

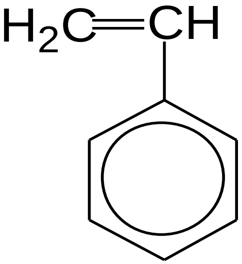
Bond Type	Type of linking of the primary molecule symbol	Examples: Synthetic macromolecules	Natural macromolecules
Carbon bond	 $-\overset{\vert}{\underset{\vert}{C}}-\overset{\vert}{\underset{\vert}{C}}-$	Polyethylene, vinyl and acrylic polymerizates	Caoutchouc, gutta-percha
Ester bond	 $-\overset{\overset{O}{\Vert}}{C}-O-\overset{\vert}{\underset{\vert}{C}}-$	Polyesters	Nucleic acids (phosphoric acid Esters of substituted saccharides)
Amide bond	 $-\overset{\overset{O}{\Vert}}{\underset{\vert}{C}}-\underset{\vert}{N}-\overset{\vert}{\underset{\vert}{C}}-$	Polyamides (Nylon, Perlon)	Albumin, wool, silk
Ether bond	 $-\overset{\vert}{\underset{\vert}{C}}-O-\overset{\vert}{\underset{\vert}{C}}-$	Polyoxymethylene, poly(ethylene oxide)	Polysaccharides, cellulose, starch

MONOMER FUNCTIONALITY, f:

Number Of Potential Bonds With Other Monomers

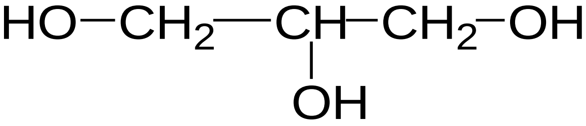
Examples:

Styrene



f = 2

Glycerol

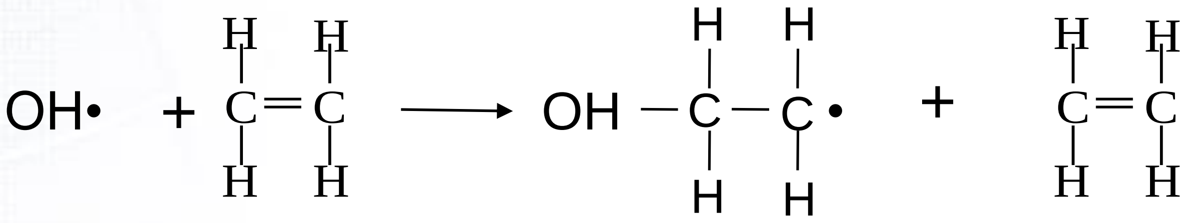


$$\mathrm{HO-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-OH}$$

f = 3

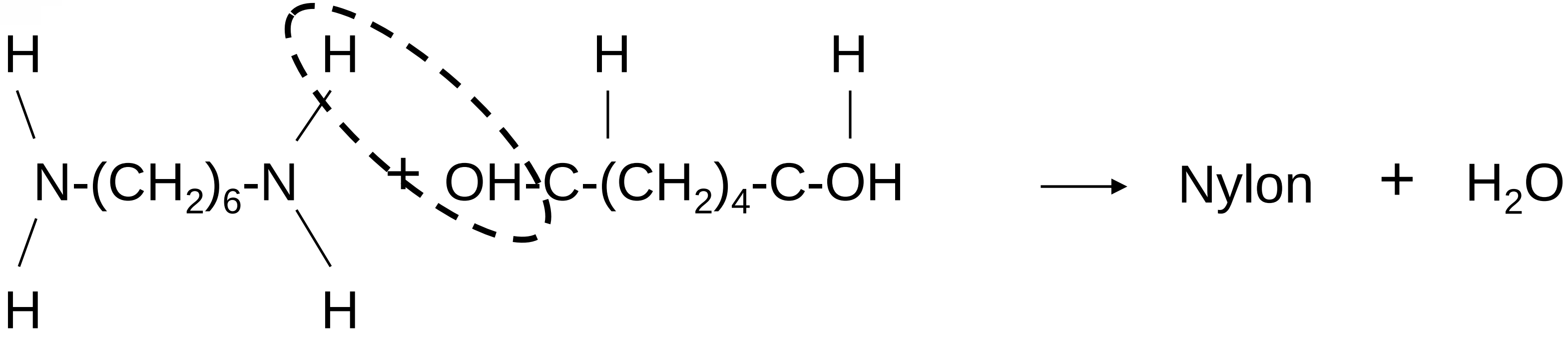
Types of Polymerization

- Addition Polymerization (free radical or unpaired electron)



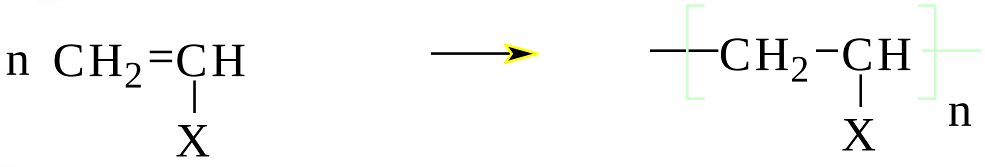
$$\mathrm{OH}\bullet + \underset{H}{\overset{H}{C}}{=}\underset{H}{\overset{H}{C}} \longrightarrow \mathrm{OH}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\bullet + \underset{H}{\overset{H}{C}}{=}\underset{H}{\overset{H}{C}}$$

- Condensation Polymerization

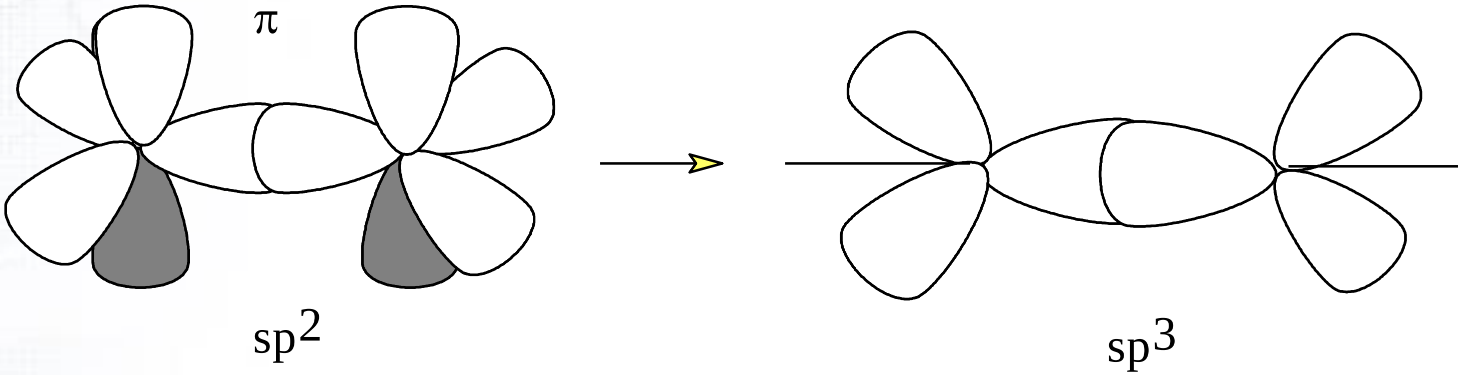


$$\underset{H}{\overset{H}{N}}\text{-}(\mathrm{CH_2})_6\text{-}\underset{H}{\overset{H}{N}} + \mathrm{OH}\text{-}\overset{H}{C}\text{-}(\mathrm{CH_2})_4\text{-}\overset{H}{C}\text{-}\mathrm{OH} \longrightarrow \text{Nylon} + \mathrm{H_2O}$$

Chain Polymerization



$$n\ CH_2{=}\underset{X}{\underset{|}{CH}} \longrightarrow \left[CH_2-\underset{X}{\underset{|}{CH}} \right]_n$$



- Must be activated
- Basic individual steps
  - Initiation
  - Propagation
  - Termination

Polymerization Energy

Bond energies (kcal/mol)	Heat of polymerization ΔH (kcal/mol)
C=C to C – C	- 20
C=O to C – O	- 5
C=N to C – N	- 1.4
C≡N to C = N	- 7.2
C=S to C – S	- 2
S=O to S – O	- 7

General Polymerization Mechanism

Initiation

$$X-X \longrightarrow 2\ X^*$$

$$X^* + CH_2{=}CH_2 \longrightarrow X-CH_2-CH_2^*$$

Propagation

$$X-CH_2-CH_2^* + CH_2{=}CH_2 \longrightarrow X-(CH_2CH_2)_n-CH_2CH_2^*$$

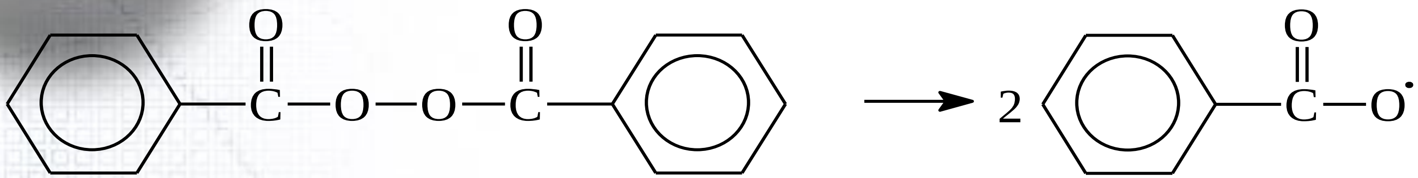
Termination

$$X-(CH_2CH_2)_n-CH_2CH_2^* \longrightarrow X-(CH_2CH_2)_n-CH_2CH_2-Y$$

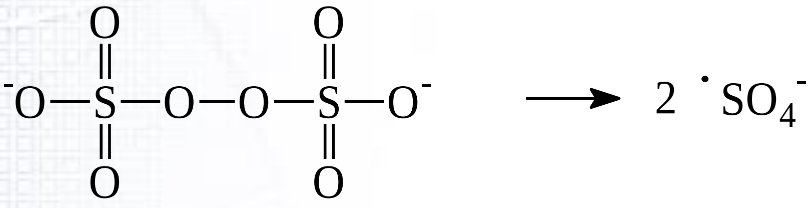
Generation of Free Radicals

- Thermal
  - Rate constant 10^{-5} - 10^{-8} sec^{-1}
  - Decompose at 50-150 ^{o}C
- Photochemical
  - Short wavelength for direct initiation
  - Longer wavelength uses photochemical initiator such as benzoin or AIBN
- High Energy Radiation
  - Electrons, gamma rays, x-rays, slow neutrons
  - Relatively uncontrolled because of high energy
- Redox
  - Aqueous media
  - Often used for emulsion polymerization
- Electrochemical

Sources of Free Radicals



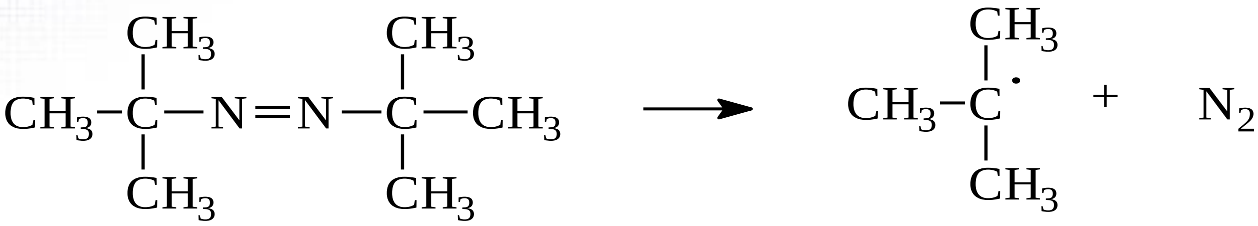
Benzoyl peroxide



$${}^{-}O-\overset{O}{\underset{O}{S}}-O-O-\overset{O}{\underset{O}{S}}-O^{-} \longrightarrow 2\ {}^{\cdot}SO_4^{-}$$

Persulfate

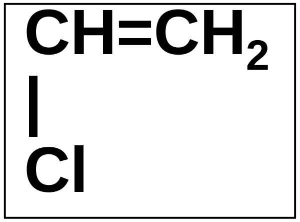
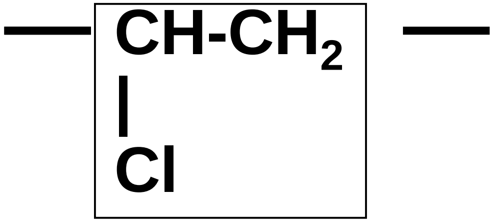
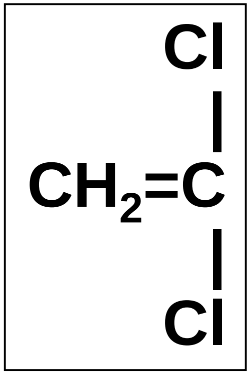
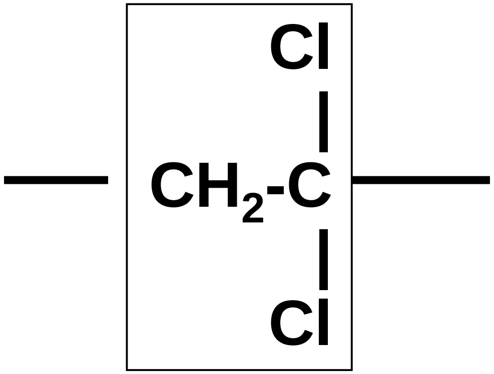
$$2\ {}^{\cdot}SO_4^{-} + 2\ H_2O \longrightarrow 2\ HSO_4^{-} + 2\ HO^{\cdot}$$



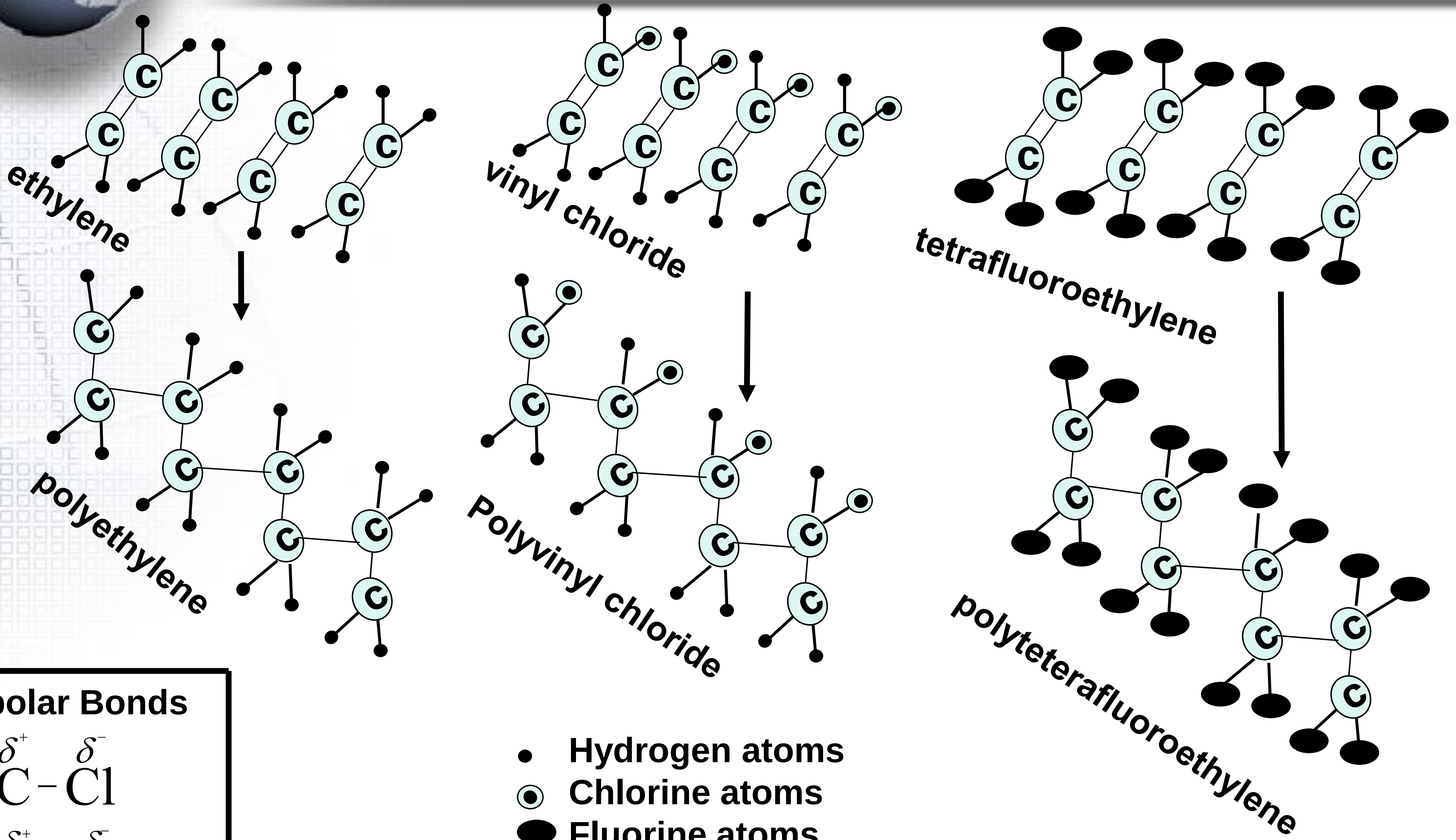
$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-N=N-\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C^{\cdot}}} + N_2$$

AIBN – Azo-bis-IsoButyroNitrile

Chain Growth Polymerization

	Monomer	Repeating Unit	Unit weight
Polyethylene (PE)	$\boxed{CH_2{=}CH_2}$	$—\boxed{CH_2\text{-}CH_2}—$	**28**
Polyvinyl chloride (PVC)	 $\boxed{\underset{\underset{Cl}{\vert}}{CH}{=}CH_2}$	 $—\boxed{\underset{\underset{Cl}{\vert}}{CH}\text{-}CH_2}—$	**82.5**
Polyvinylidene Chloride (PVDC)	 $\boxed{CH_2{=}\overset{\overset{Cl}{\vert}}{\underset{\underset{Cl}{\vert}}{C}}}$	 $—\boxed{CH_2\text{-}\overset{\overset{Cl}{\vert}}{\underset{\underset{Cl}{\vert}}{C}}}—$	**97**

Chain Growth Polymerization



- ● Hydrogen atoms
- ◉ Chlorine atoms
- ⬬ Fluorine atoms

Dipolar Bonds

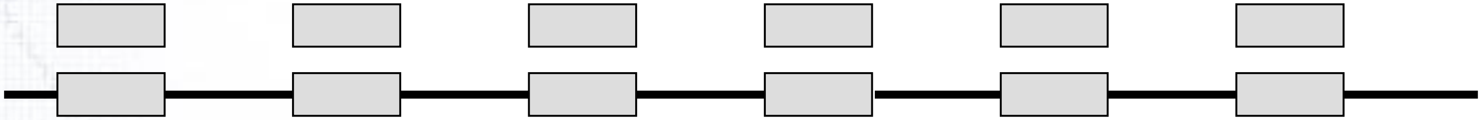
$$\overset{\delta^+}{\mathrm{C}}-\overset{\delta^-}{\mathrm{Cl}}$$

$$\overset{\delta^+}{\mathrm{H}}-\overset{\delta^-}{\mathrm{Cl}}$$

Homopolymers

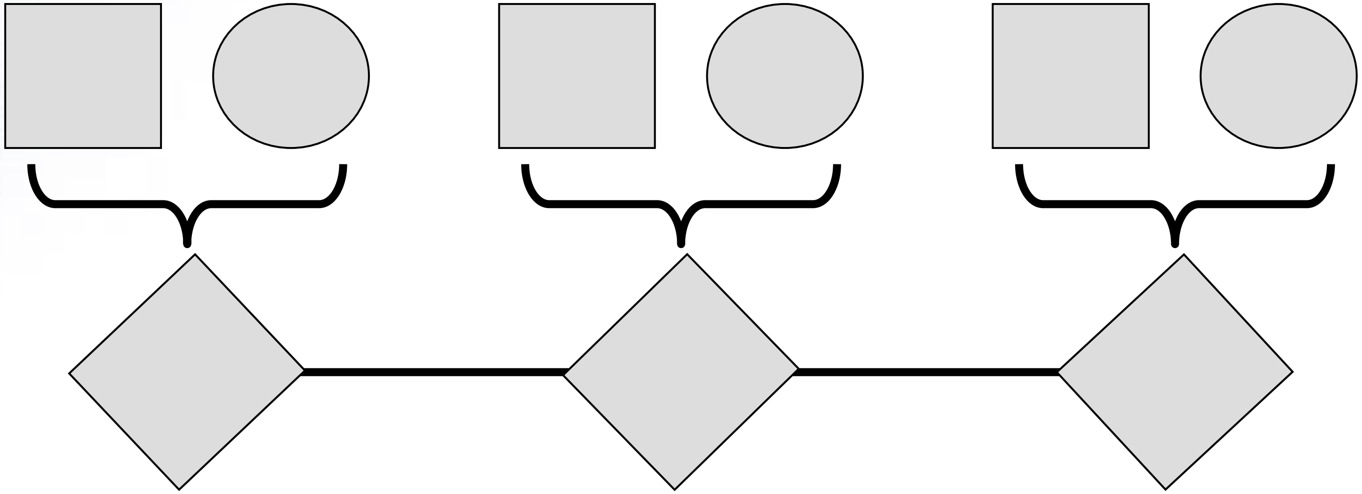
High Density polyethylene (HDPE)

Monomer Units are The same

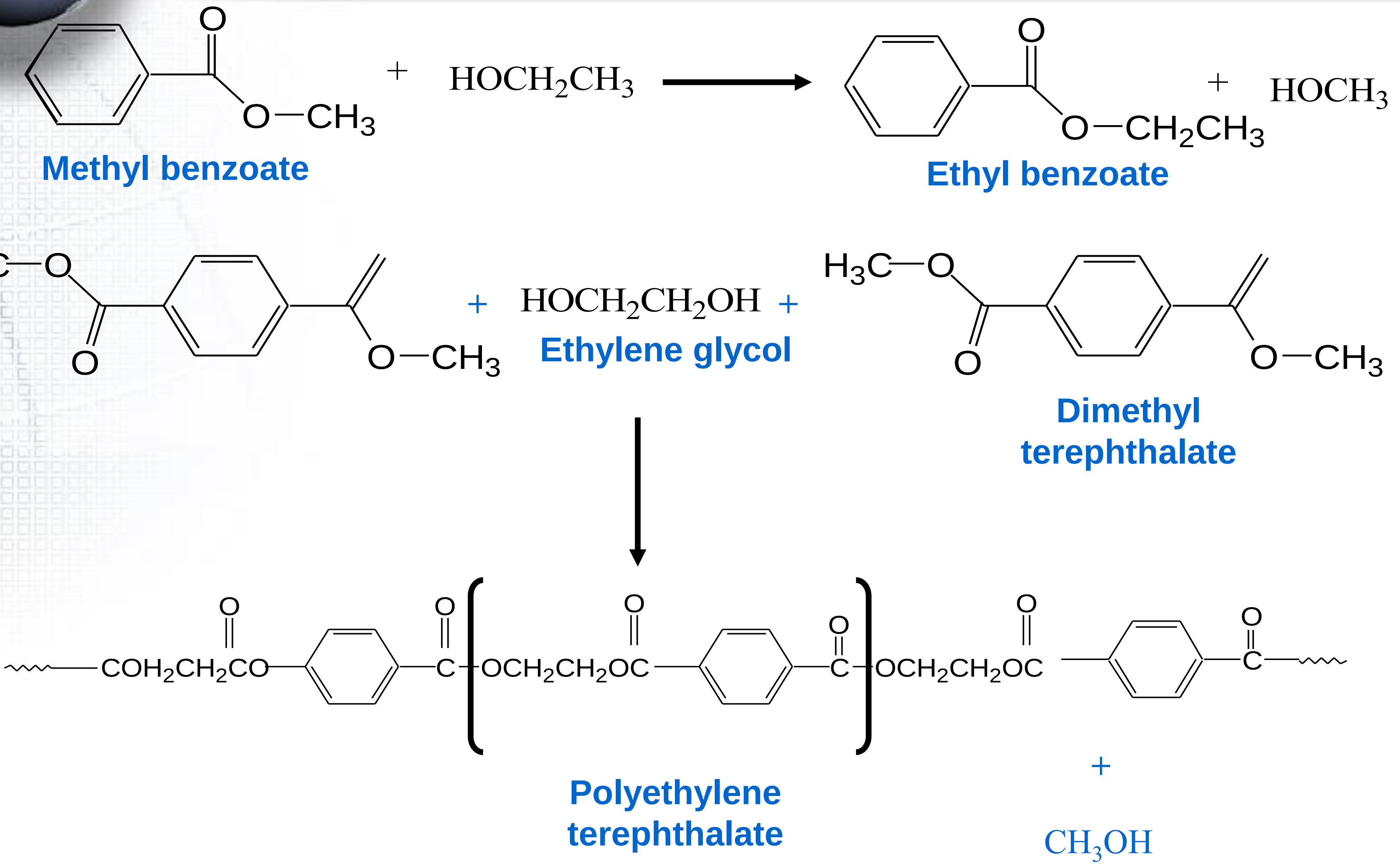


Repeating units in the polymer are all the same

Polyethylene terephthalate (PET)

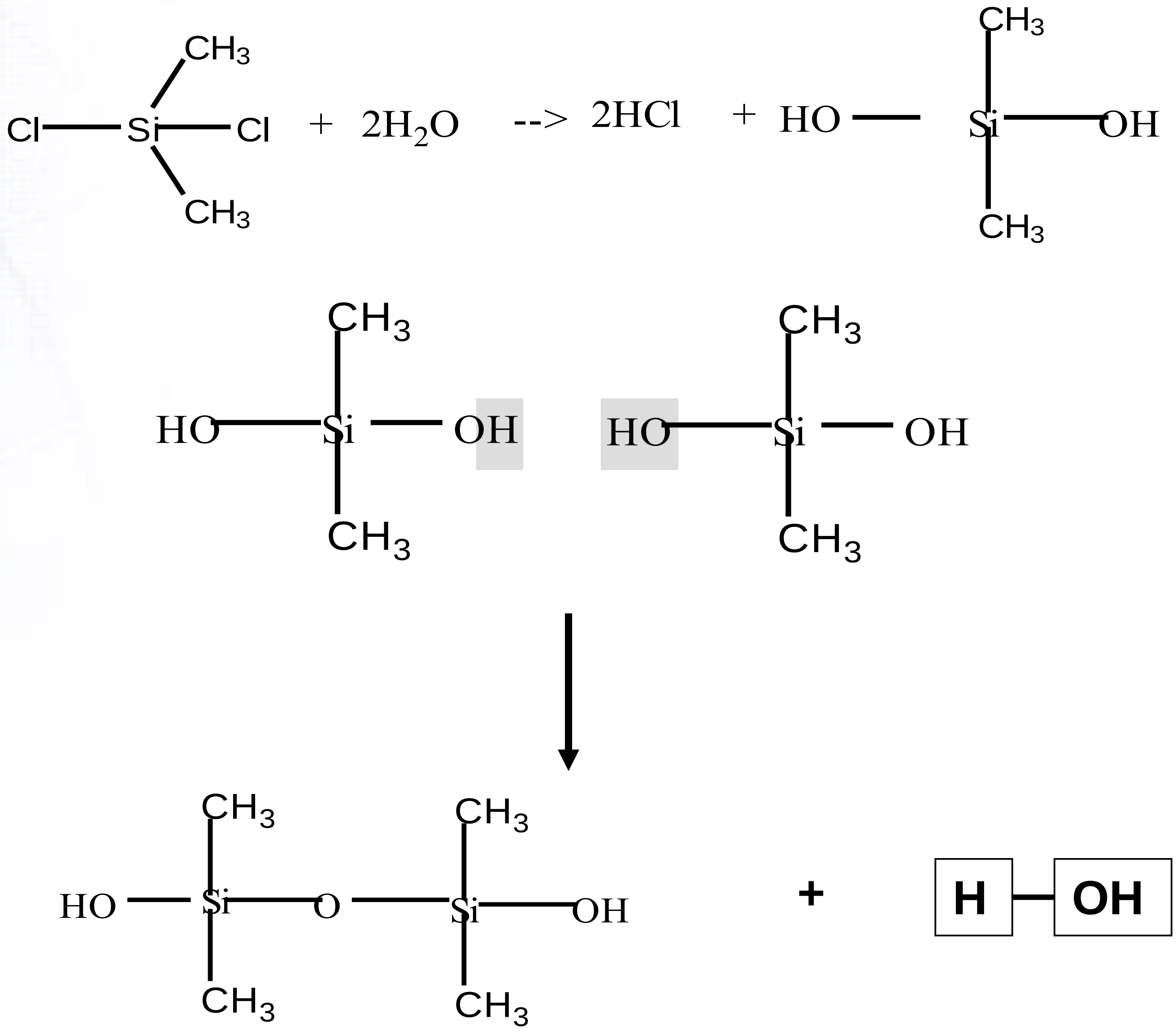


Polyethylene terephthalate (PET)



Eugene Rochow - Silicones

Eugene Rochow - Silicones



The Polymer Parameters

Chemical Composition

- Homopolymers
  - all the repeating units along the chain are the same
- Copolymers
  - two or more different monomer units
    - Random – Alternating – Block - Graft

Molecular Weight

Stereochemistry

- Geometrical isomers
- Configuration - atactic, isotactic, syndiotactic

Topology

- Chains
- Branches - star, comb, random
- Network

Chemical Composition

Homopolymers

~AAAAAAAAAAAAAAAAAAAAAAAAAAA~

Copolymers

Random

~AAABBBBAABBBBBBABABBBAAABBBBB~

Block

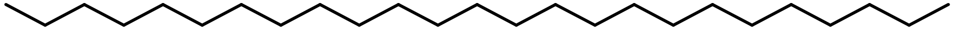
~AAA~~~~~~AAABBB~~~~~~BBB~

Graft

```
~AAAAAAAAAAAAAAAAAAAAAAAAAAAAA~
               B
               B
               BBBBBBBBBB~
```

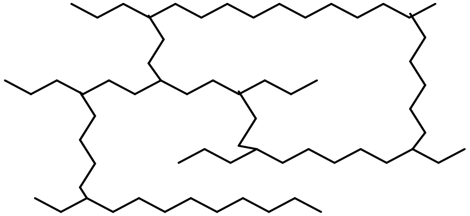
Topology

Chains



Branches - star, comb, random

Network



Properties of Polymers

- Physical properties of polymers depend on;
  - shape
  - molecular structure
  - molecular weight

- Why,
  - because these factors influence intra-molecular forces

Shape of Molecules

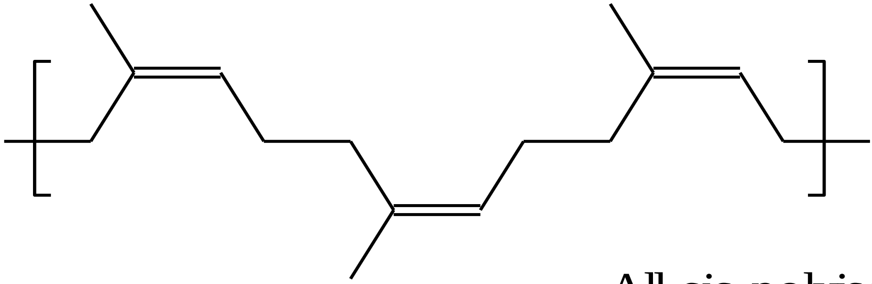
- Influences the **properties** of polymers
- The pendant groups attached to the backbone can vary in **position**.
- The arangement of position of pendant groups is called **tacticity**.

Tacticity

- If the position of the pendant groups are in order the molecule is called **isotactic**.
- If positions are **not** in order the molecule is called **atactic**.
- Syndiotactic.

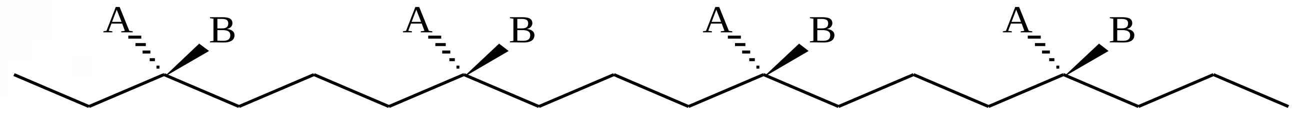
Stereochemistry

Geometrical isomers

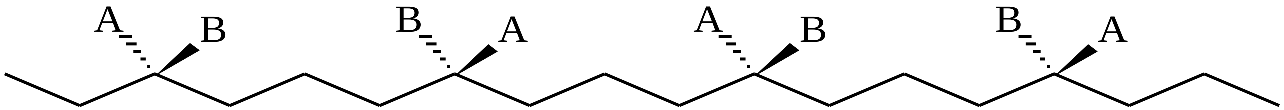


All *cis*-polyisoprene

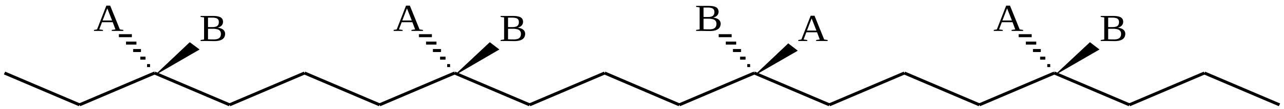
Configuration - atactic, isotactic, syndiotactic



isotactic



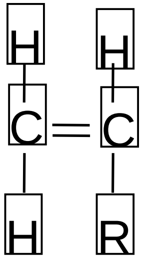
syndiotactic



atactic

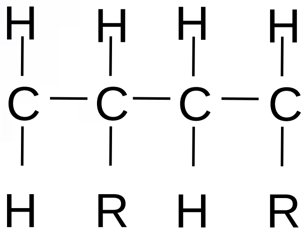
Molecular Structure Stereoisomerism

Consider monomer

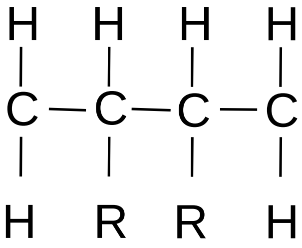


$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & R \end{array}$$

Possible polymer forms



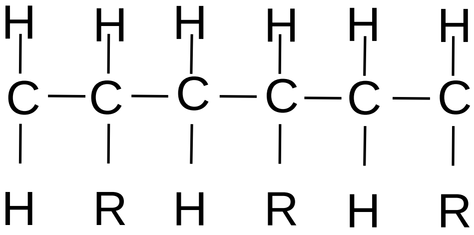
$$\begin{array}{ccccccc} H & & H & & H & & H \\ | & & | & & | & & | \\ C & - & C & - & C & - & C \\ | & & | & & | & & | \\ H & & R & & H & & R \end{array}$$



$$\begin{array}{ccccccc} H & & H & & H & & H \\ | & & | & & | & & | \\ C & - & C & - & C & - & C \\ | & & | & & | & & | \\ H & & R & & R & & H \end{array}$$

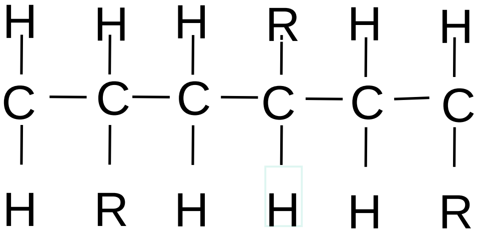
repulsion between R groups
makes this configuration unlikely

<u>isotactic</u>



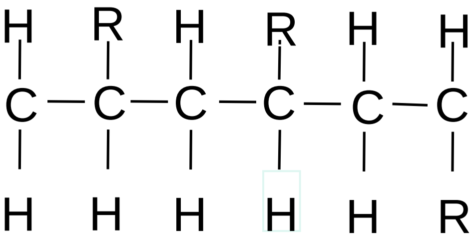
$$\begin{array}{ccccccccccc} H & & H & & H & & H & & H & & H \\ | & & | & & | & & | & & | & & | \\ C & - & C & - & C & - & C & - & C & - & C \\ | & & | & & | & & | & & | & & | \\ H & & R & & H & & R & & H & & R \end{array}$$

<u>syndiotactic</u>



$$\begin{array}{ccccccccccc} H & & H & & H & & R & & H & & H \\ | & & | & & | & & | & & | & & | \\ C & - & C & - & C & - & C & - & C & - & C \\ | & & | & & | & & | & & | & & | \\ H & & R & & H & & H & & H & & R \end{array}$$

<u>atactic</u>



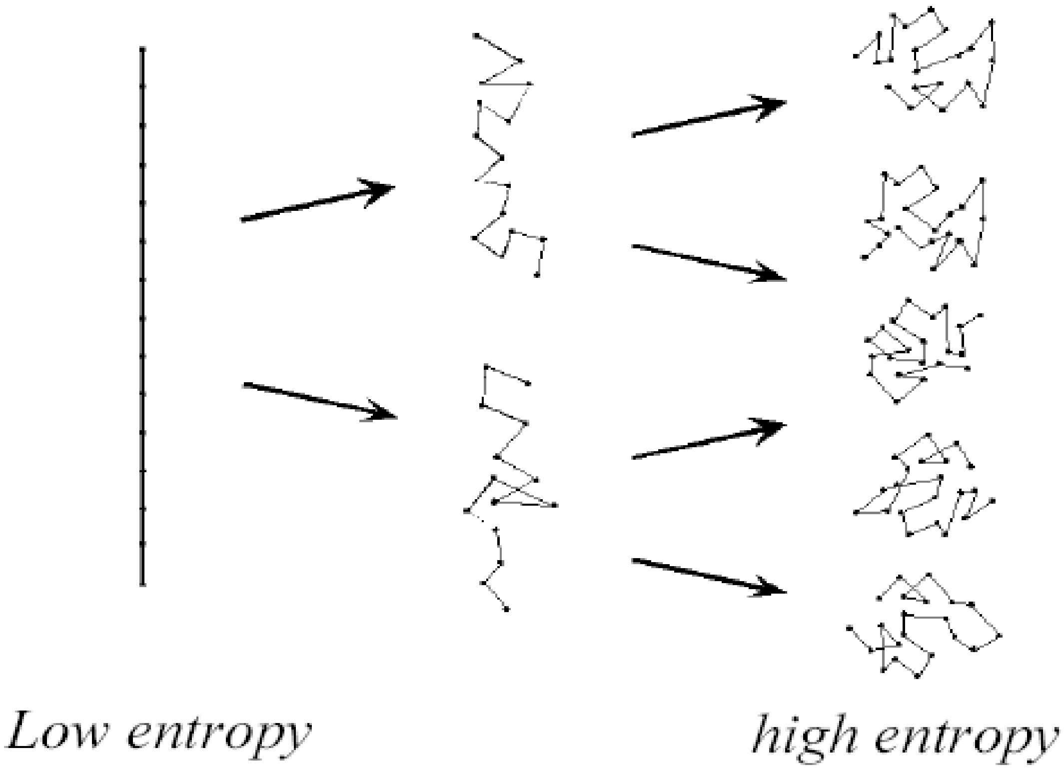
$$\begin{array}{ccccccccccc} H & & R & & H & & R & & H & & H \\ | & & | & & | & & | & & | & & | \\ C & - & C & - & C & - & C & - & C & - & C \\ | & & | & & | & & | & & | & & | \\ H & & H & & H & & H & & H & & R \end{array}$$

Thermodynamics

Polymers like to coil up!

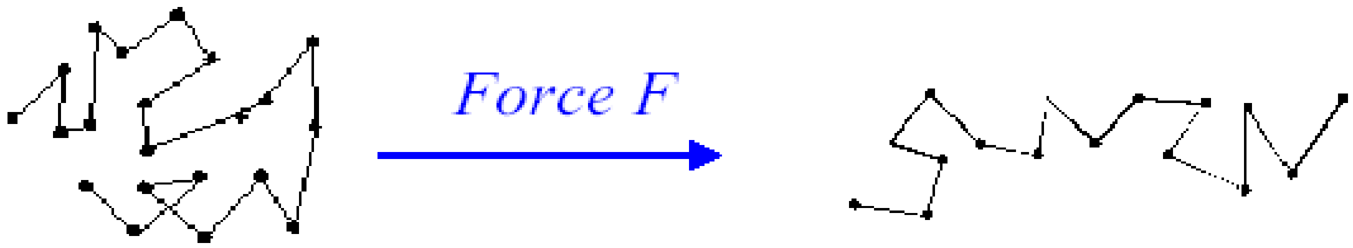
Gibbs free energy *G*: $G = H - TS$

Entropy *S*: $S = k_B \ln W$



Thermodynamics

A force is needed to stretch the polymer



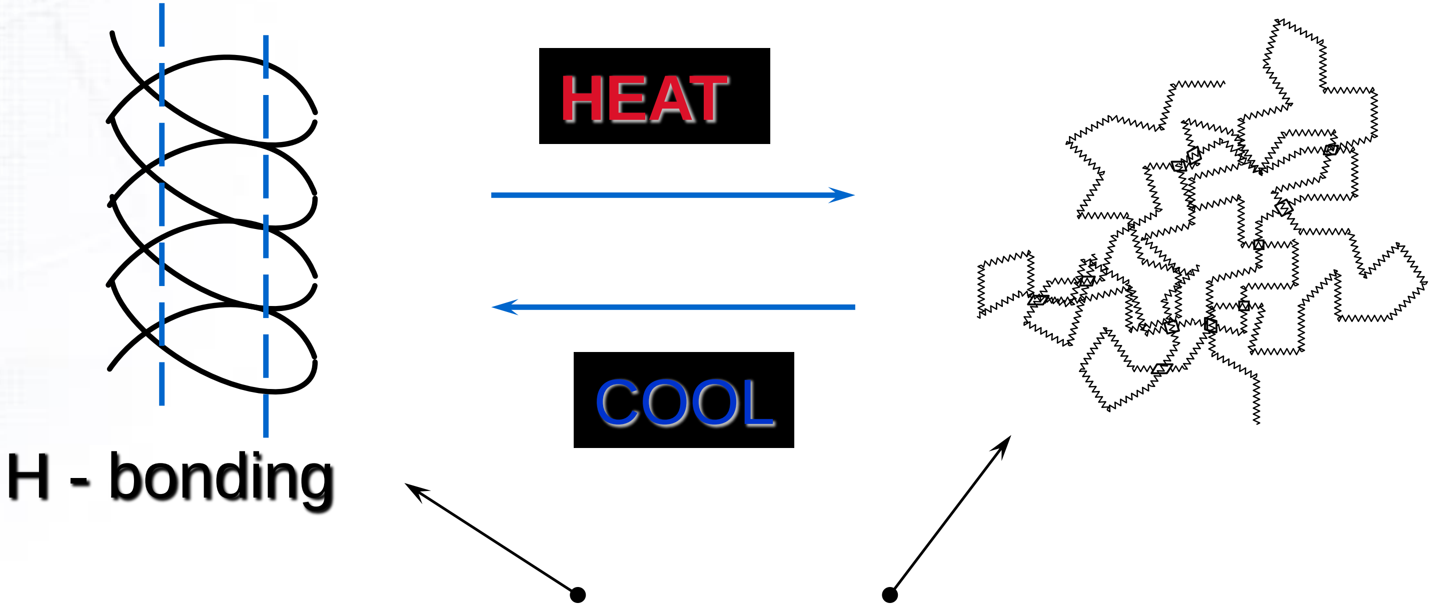
Higher S
Lower G

Lower S
Higher G

$$F = +\frac{\partial G}{\partial R} = -T\frac{\partial S}{\partial R}$$

for freely joint chain

Chain Energy (Thermodynamics)



HEAT

COOL

H - bonding

$$\Delta G = \Delta H - T\Delta S$$

Chain Dimensions

Conformation

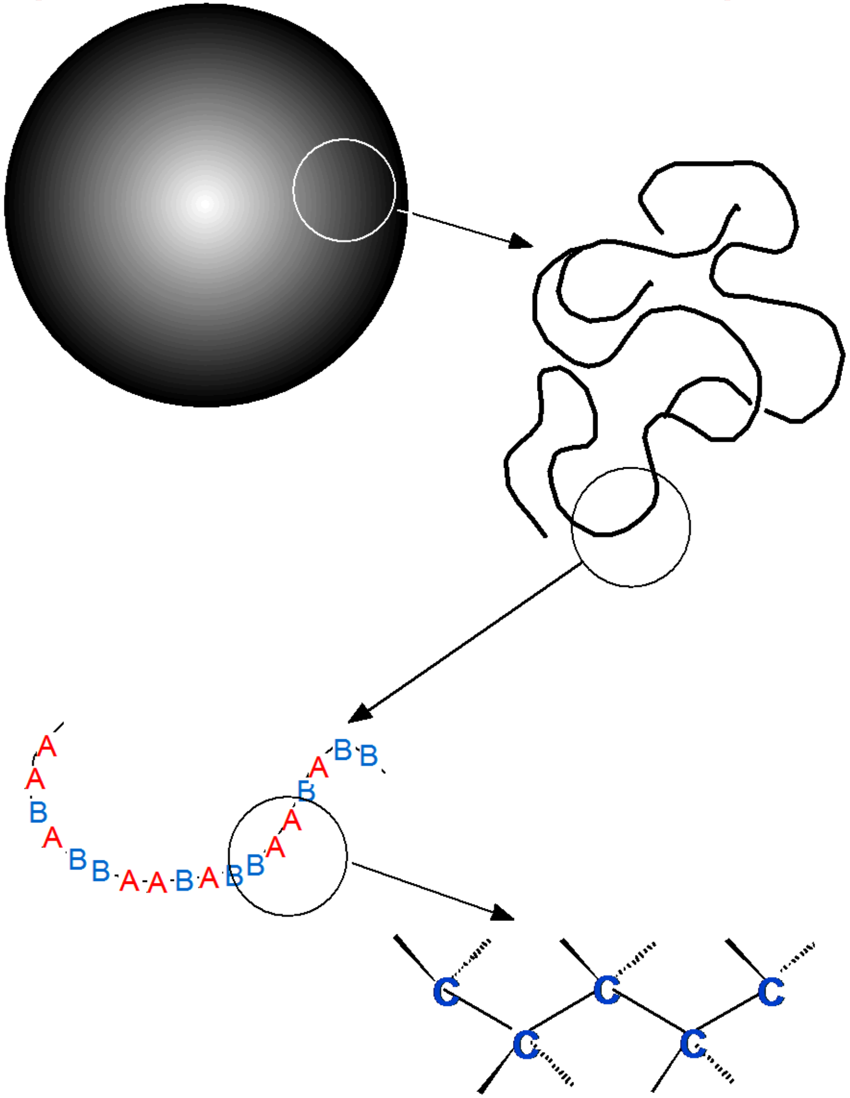
- spatial arrangement
- changes with rotation around bonds

Configuration

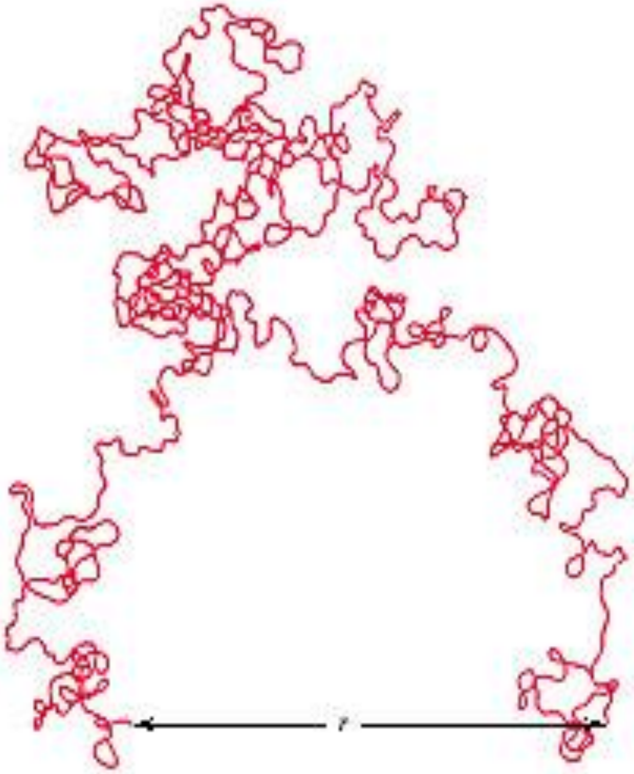
- bonding arrangement
- changes only through bond breakage

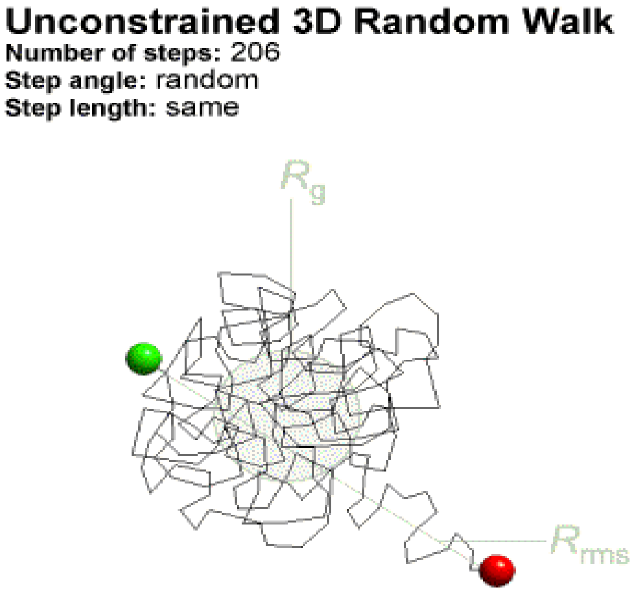
Characterization

Microscopic Characterization Needed at Many Resolutions:



Molecular Shape Zig-Zag & “Spaghetti”





r : *end-to-end distance*, much smaller than chain length, but is proportional to chain length

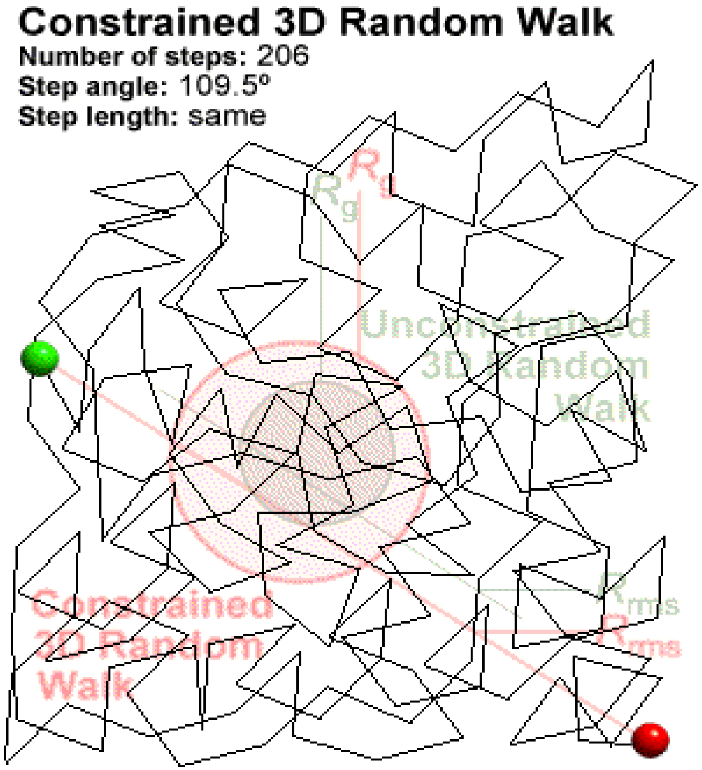
Chain Dimensions

End to End Distance

$$\langle r^2 \rangle = \frac{\sum_{i=1}^{n} m_i \bar{r}_i^{\,2}}{\sum_{i=1}^{n} m_i}$$

Radius of Gyration

$$\langle s^2 \rangle = \frac{\langle r^2 \rangle}{6}$$



Constrained 3D Random Walk

Number of steps: 206

Step angle: 109.5º

Step length: same

m - mass of repeat unit (segment)

r - vector from center of gravity to atom i

Chain Dimensions
Characteristic Dimensions

$$\langle r^2 \rangle_0 = Cnl^2$$

where:

$<r^2>_o$ - chain dimensions at Θ-conditions

C - Characteristic Chain Ratio

n - number of segments

l - segment dimension (length)

Chain Dimensions - Measurement

- Absolute Methods
  - Mn
    - Membrane Osmometry
    - Freezing Pt depression
    - Boiling Pt. elevation
  - Mw
    - Solution light scattering
  - Mz
    - ultracentrifugation

- Relative Methods
  - GPC
  - Viscosity
  - Vapor phase osmometry
  - Fractionation
  - End group titration

Chain Dimensions

Experimental Methods

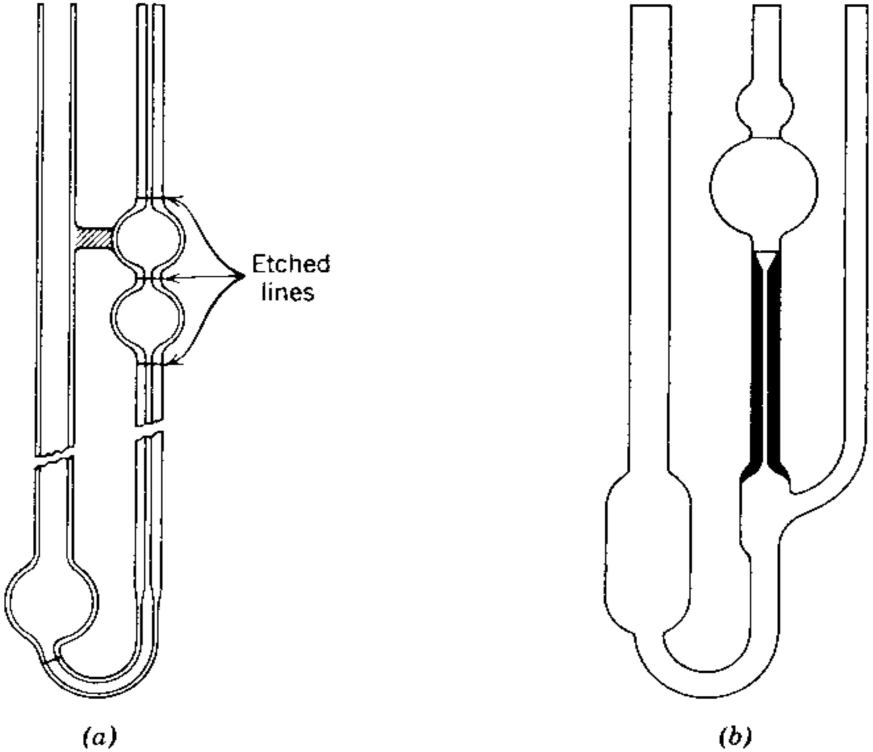
- Scattering
  - Absolute method (Mw)
  - Light
  - X-Ray
  - Neutron
- Viscosity
  - Relative method (Mv)
  - Mark-Houwink

Measurement of MW

- End group analysis
  - Measure concentration of end-groups (from initiator or terminator)
  - Chemical or spectroscopic analysis
  - Only for $M_n < 10,000$ g mol^{-1}
- Colligative properties
  - freezing point depression, boiling point elevation, osmotic pressure, vapour pressure
  - gives concentration in mol dm^{-3}, so if we know the mass we can calculate M_n
- Viscosity
- GPC

Measurement of MW

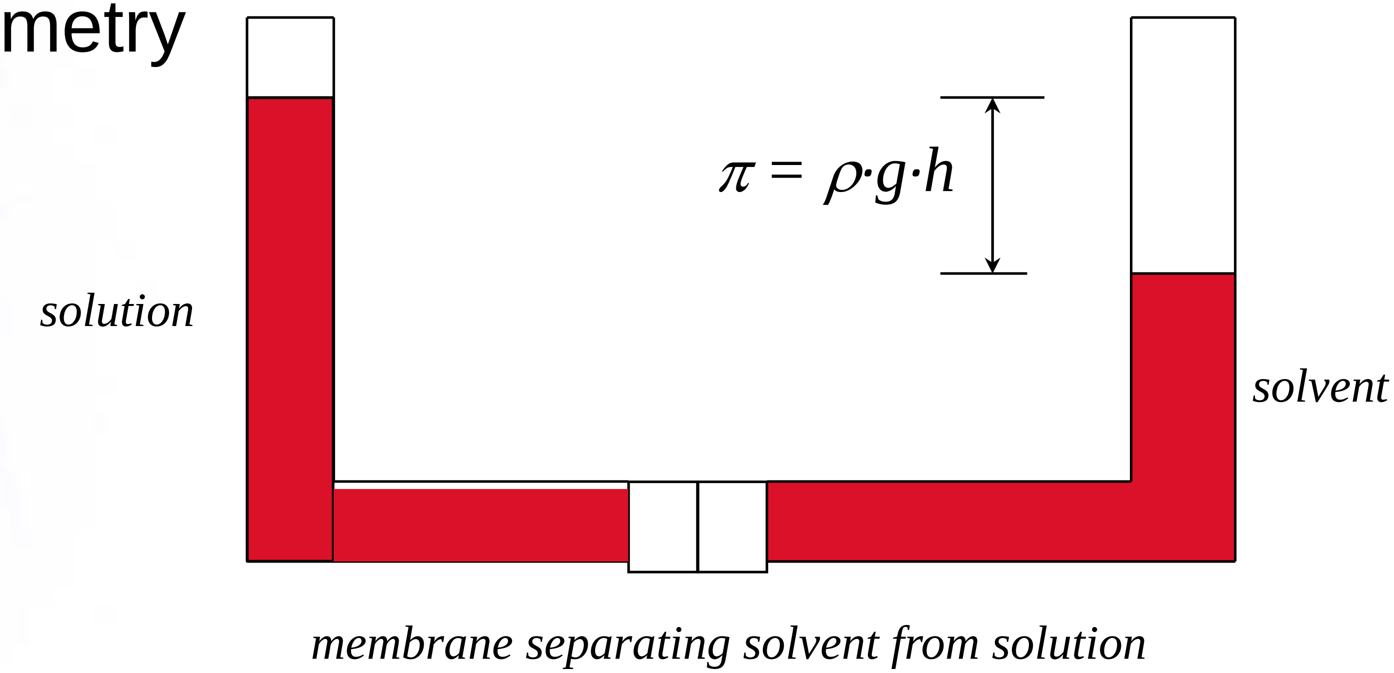
- Solution viscometry
  - time taken to flow through a capillary
  - viscosity increases with MW



Capillary viscometers commonly used for measurement of polymer solution viscosities: (a) Ostwald–Fenske and (b) Ubbelohde.

Measurement of MW

- Osmometry



Polymer cannot penetrate the membrane so solvent passes through until there is sufficient pressure to equalize the chemical potentials on each side

$$\pi = \frac{c}{M}RT \qquad \pi = \frac{c}{M}RT + Ac^2 + Bc^3 + \dots..$$

Measurement of MW

Osmometry

- plot of π/c *vs*. c has an intercept of RT/M gives M
- polymer must be in solution
- A is a measure of solvent-solute interaction.
  - Good solvent gives high A
- colligative effect decreases as M increases - only useful up to 50,000
- absolute method - no need to calibrate against standards

$$\pi = \frac{c}{M}RT \qquad \pi = \frac{c}{M}RT + Ac^2 + Bc^3 + ...$$

Measurement of MW - comparisons

Polymer, M_n = 20,000 g mol^{-1}, c = 0.01 g cm^{3}

Property	Size of effect
V.P. Lowering	4×10^{-3} mm Hg
B.P. Elevation	1.3×10^{-3} ^{o}C
F.P. Depression	2.5×10^{-3} ^{o}C
Osmotic pressure	15 cm solvent

Osmotic pressure is most sensitive

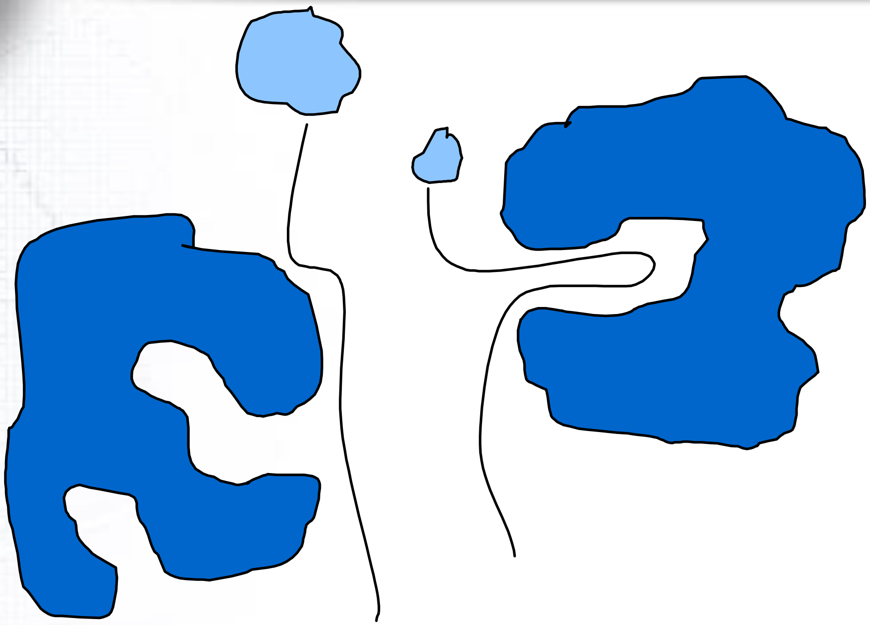
Measurement of MW - ranges

Technique	Upper limit
End group analysis	10,000
BP elevation	50,000
FP lowering	50,000
Solution Viscometry	50,000
VP Lowering	50,000
Membrane Osmometry	1,000,000

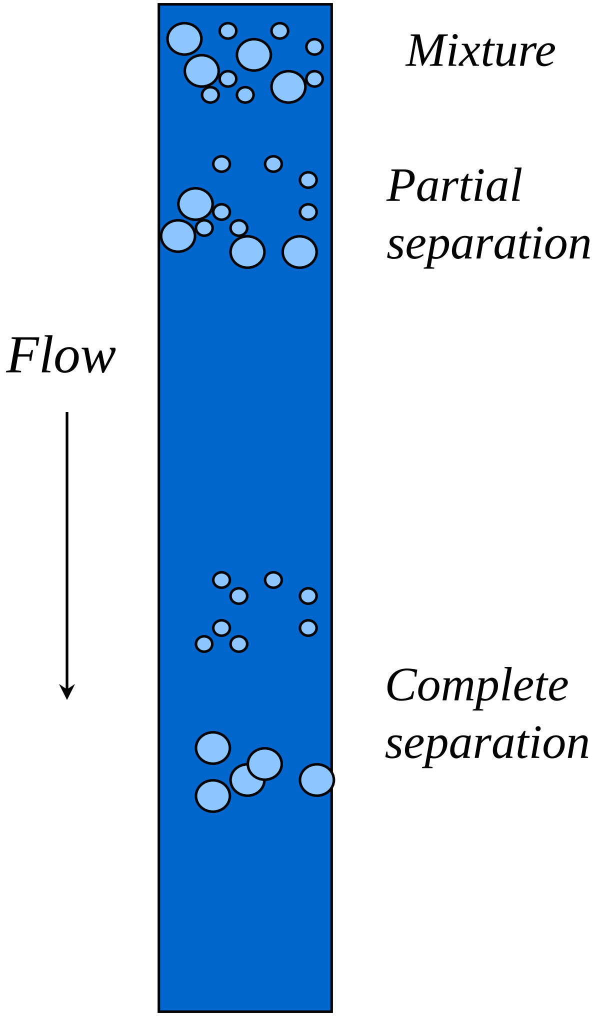
Gel Permeation Chromatography (GPC)

- Very quick and fairly accurate
- Gives molecular weight distributions
- Needs standards
  - not necessarily of the specific polymer
- Polymer must be soluble
  - temperature can be increased to improve solubility
  - wide range of solvents may be used

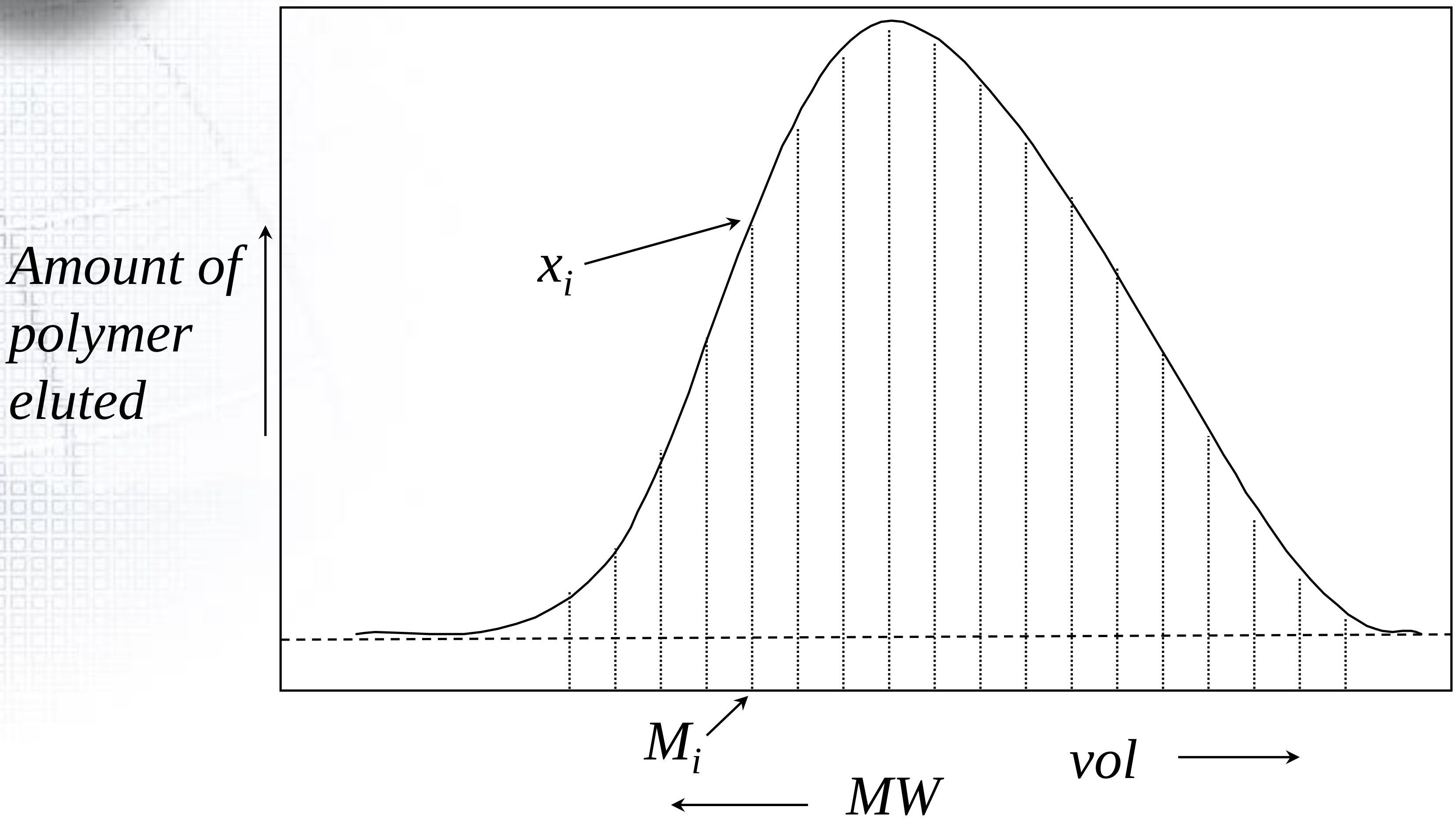
Gel Permeation Chromatography



Gel Permeation (Size Exclusion) Chromatography



Typical GPC trace

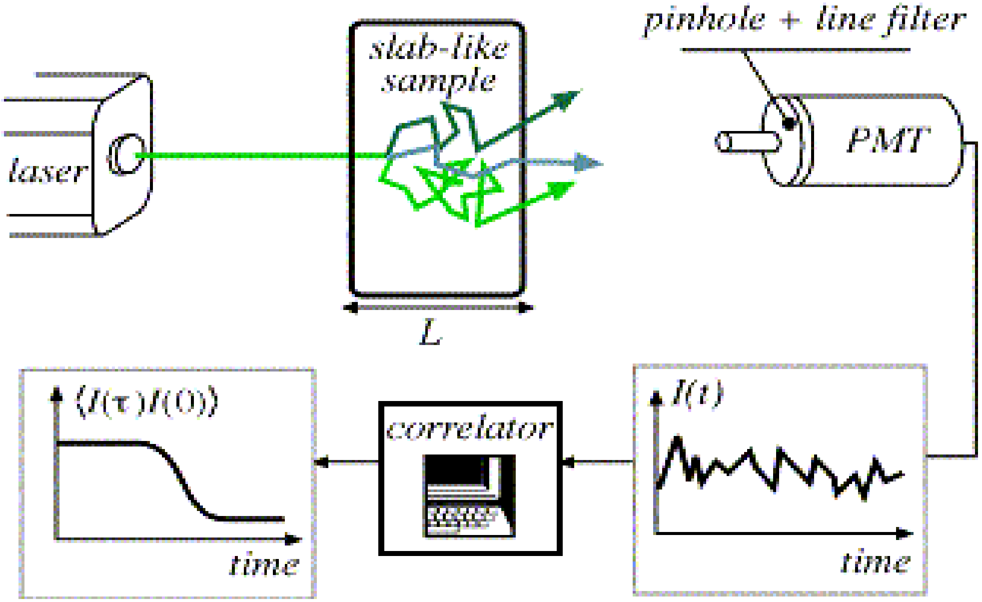


$$M_n = \frac{\sum x_i M_i}{\sum x_i} \qquad M_w = \frac{\sum x_i M_i^2}{\sum x_i M_i}$$

Structure and Dynamics

- In order to provide a comprehensive characterization of the dynamics of polymeric materials one has to study not only local motional processes but the global ones, too.

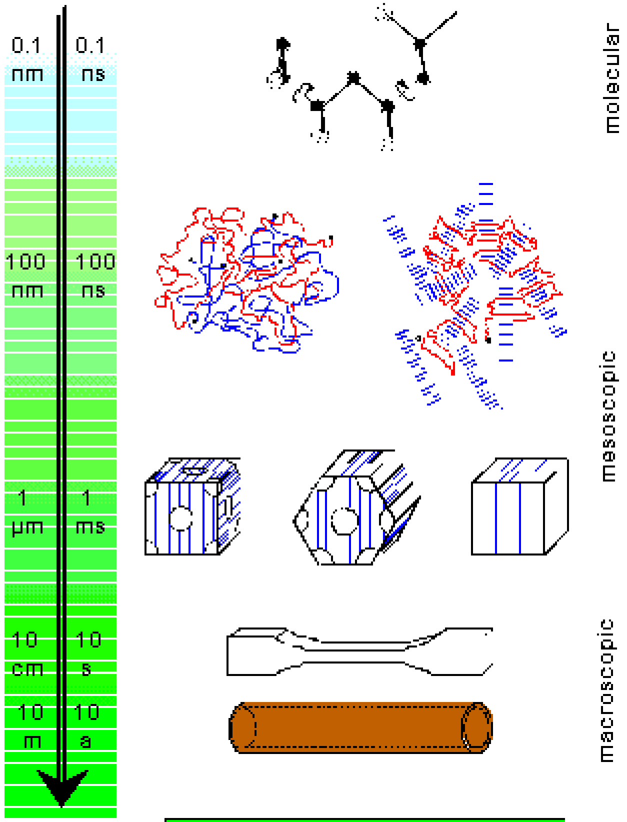
- With Photon Correlation Spectroscopy (PCS), a broad time window from 10^{-7} to 10^{5} sec can be probed.



Characteristic Time and Length Scales

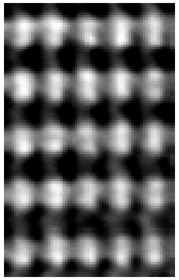
- The relationships between the macroscopic properties of macromolecules and their molecular structure, dynamics as well as supramolecular organization are complex.
  - They involve enormous length and timescales from the molecular, via mesoscopic to macroscopic dimensions and from picoseconds to years

- These properties do not only depend:
  - on the chemical nature of the repeat units (monomers), but also
  - on the manner how these monomers are linked together by covalent bonds.



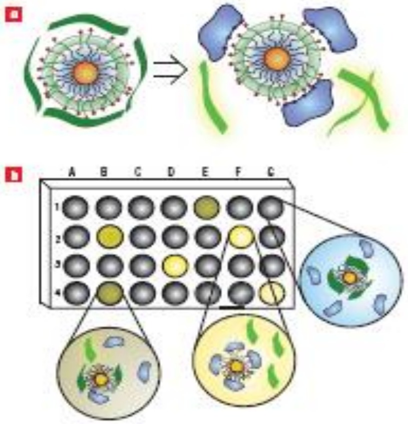
Length - and Timescales of Polymer Materials

Νανοκλίμακα (Nanoscale)



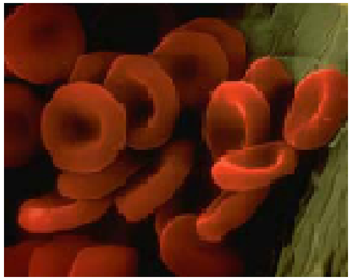
Atoms of silicon
spacing 0.078 nm

DNA
~2-1/2 nm diameter



5 nm

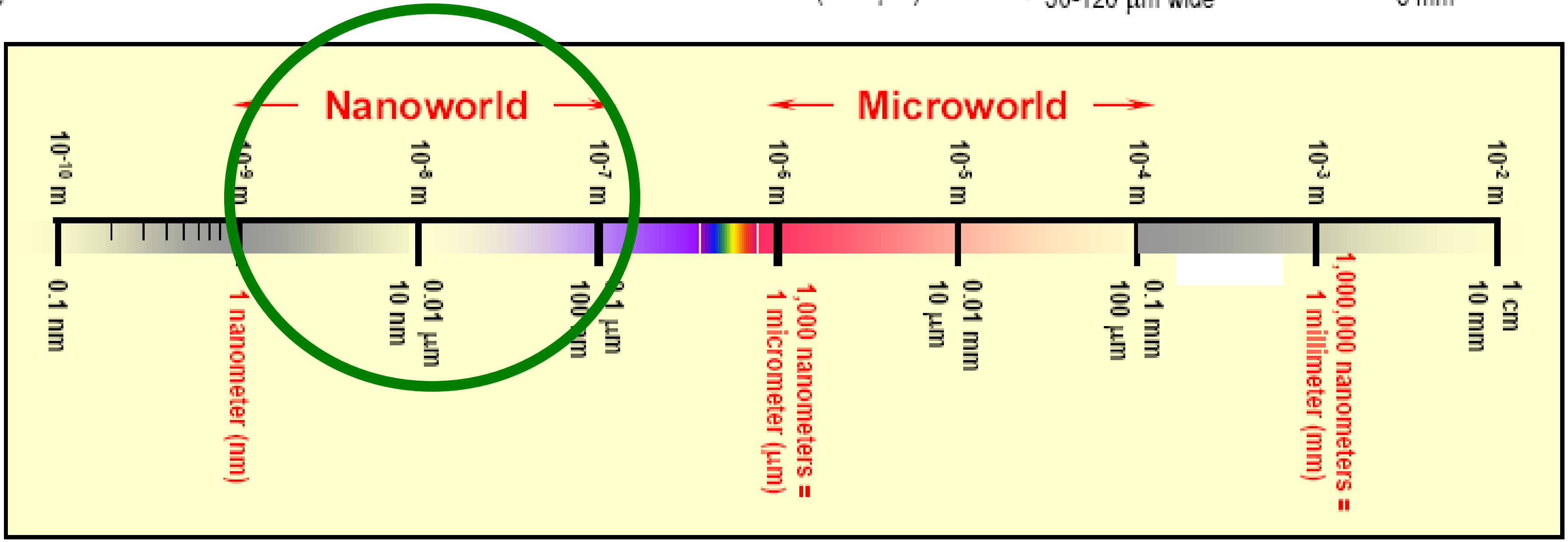
500 nm



Red blood cells
(~7-8 µm)

Human hair
~ 50-120 µm wide

Ant
~ 5 mm



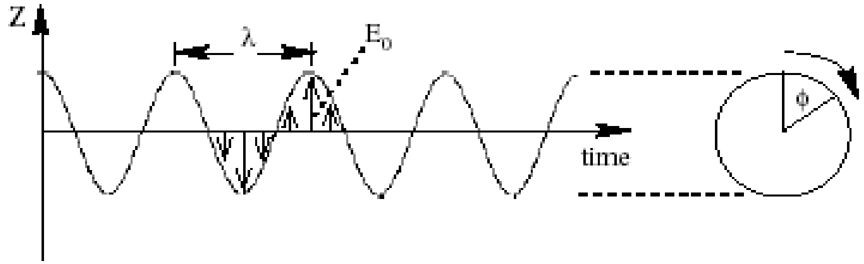
Images adapted from http://www.er.doe.gov/bes/scale_of_things.html

The Origin of Light Scattering

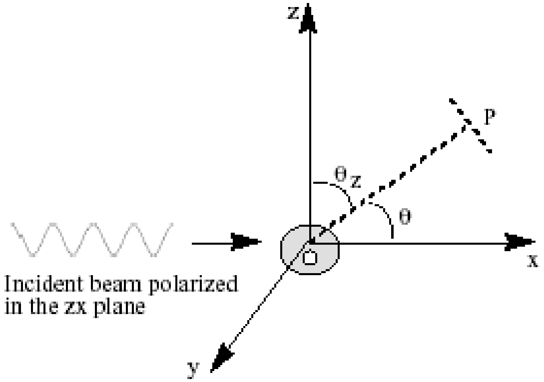
- Occurs when the bound electron cloud in the material removes energy from the light beam, then re-emits the energy without otherwise altering it.
- 1869 – First quantitative experiments in by Tyndall (scattering of small particles in the air –Tyndall effect).
- 1871 – Lord Rayleigh started a quantitative study and theory
  - Basic idea: incident monochromatic linearly polarized light beam incident on a sample.

Assume:

- No absorption
- Randomly oriented and positioned scatterers
- Independently scattering particles (dilute)
- Particles small compared to wavelength of light



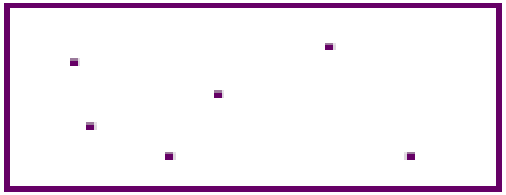
LIGHT AS AN OSCILLATING ELECTRIC FIELD



Classical description - The electric field of The incident light induces Oscillations of the Electrons in the molecule, So that the molecule now Emits light in all directions

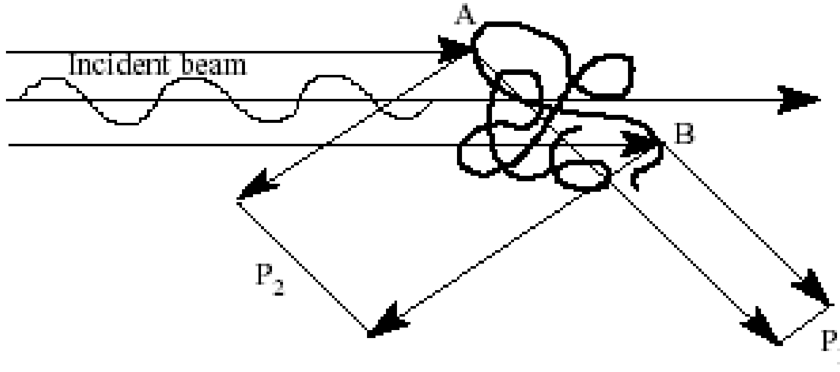
The Origin of Light Scattering - Fluctuations

Pure liquids - density
Solutions - concentration

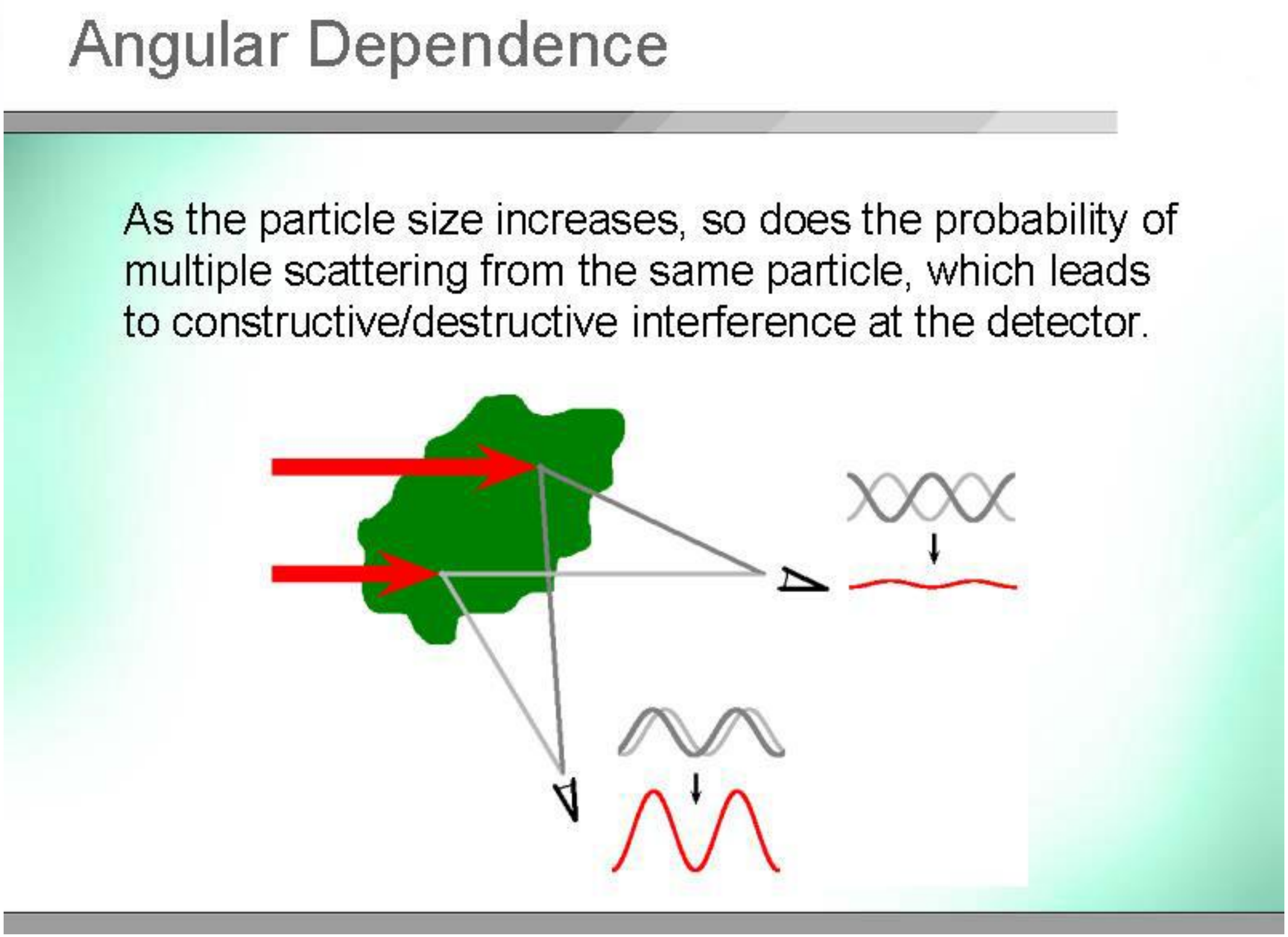


$$\frac{K\,(1+\cos^2\theta)\,c}{R_\theta^0} = \frac{1}{\overline{M}_w}\left(1+2\Gamma_2 c + \text{------}\right)$$

But a polymer is too large to Be considered a single oscillator (ie a point source of radiation). Must consider interference effects



Light Scattering



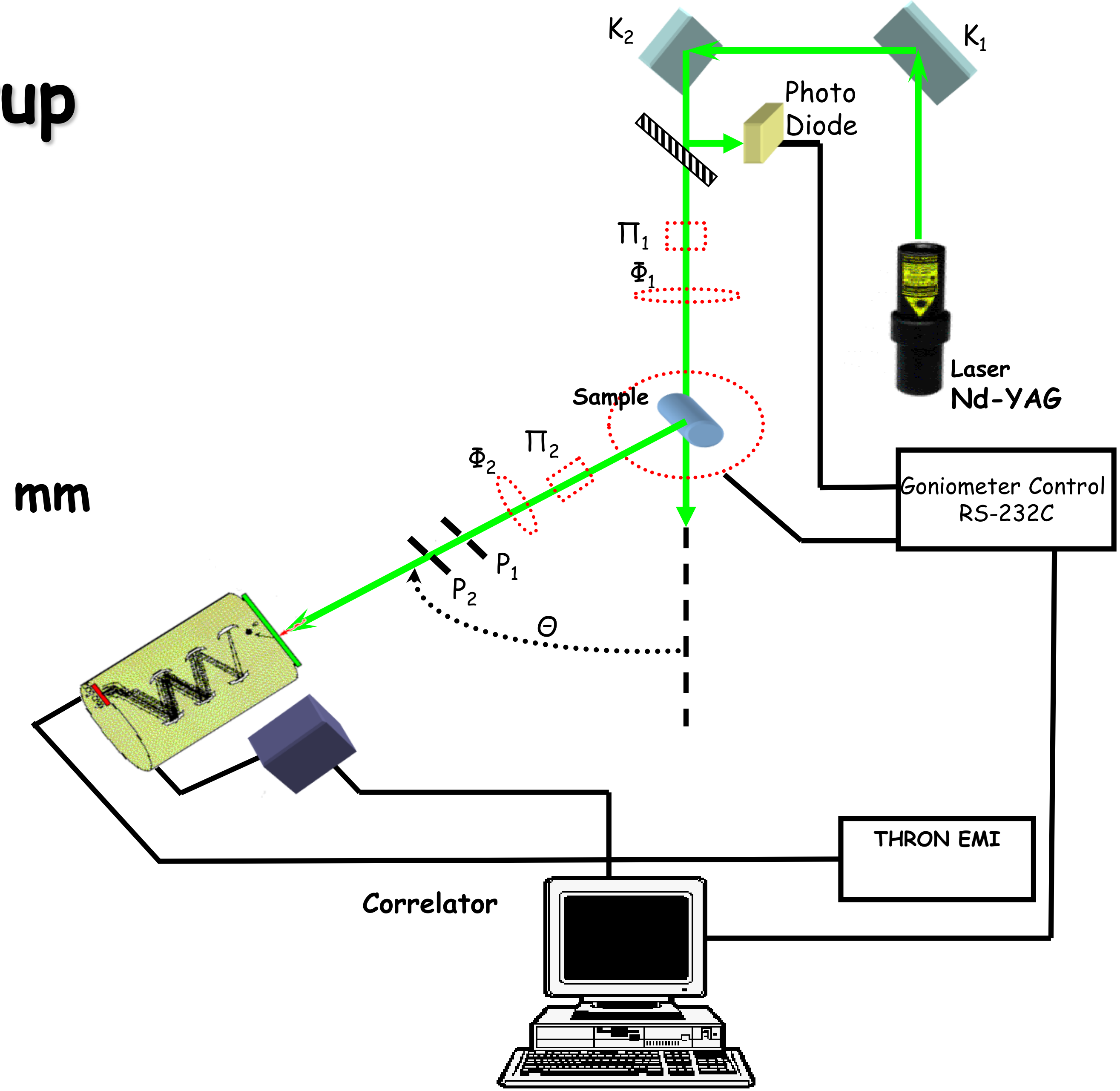
Angular Dependence

As the particle size increases, so does the probability of multiple scattering from the same particle, which leads to constructive/destructive interference at the detector.

A test to determine multiple scattering:
double c and see if the scattered light intensity doubles

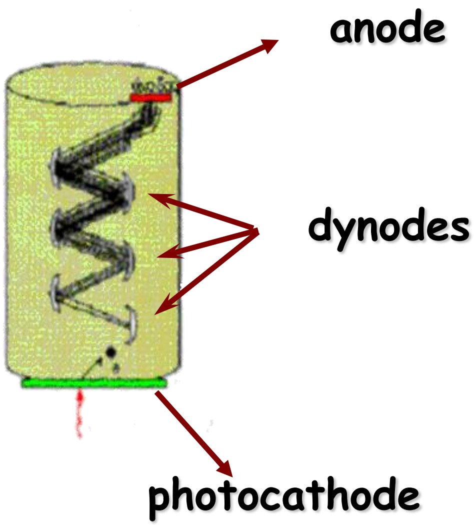
Experimental Setup

- Nd-YAG Laser
- λ = 532 nm
- at 100 mW
- beam diameter = 0,32 mm



Experimental Setup

Photomultiplier Tube:



- For every **6-10 photons 1 e is emitted.**
- The dynode stage increases the number of electrons.
- Can Detect radiation of extremely low intensity.

Correlator:

- **ALV 5000/E**
- **288 channels**
- **Time window 10^{-7} έως 10^{5} sec**

Static and Dynamic Light Scattering

- The overall scattering intensity as detected by **static light scattering** contains contributions from different particles (scatterers) or **dynamic modes** in the system.

- These contributions can be separated by means of dynamic light scattering, supposed their time autocorrelation functions decay on different time scales.

- Having the range of accessible scattering vectors (the so-called *q*-window) and the time window defined, different things can be seen by light scattering in these windows, depending on experimental conditions.

Why Laser Light Scattering…

- The suitability of the technique is based on the fact that

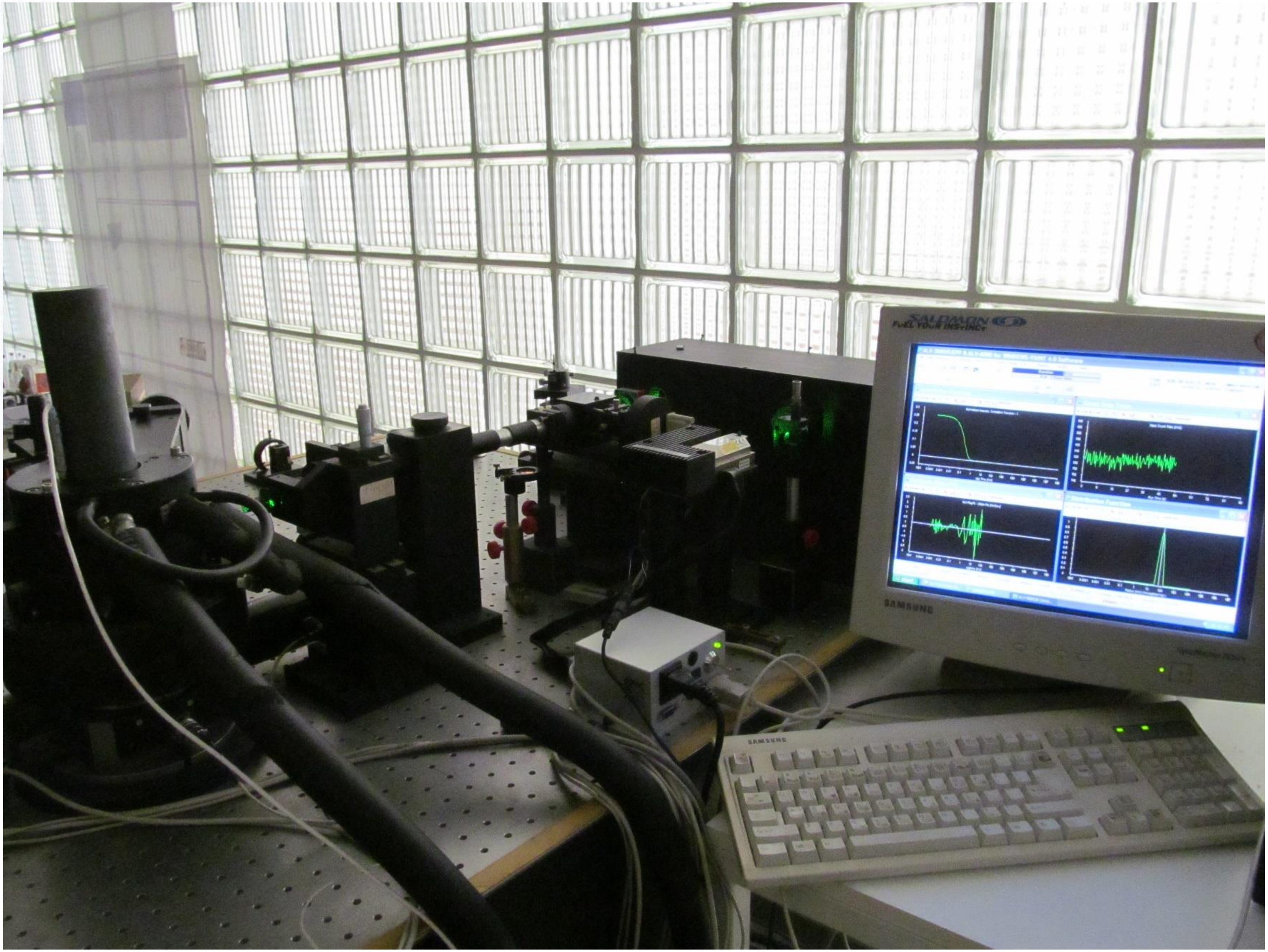
  (i) the values of scattering vectors accessible by light scattering are on the order of the size of (bio)macromolecular chains, interchain separation distances, etc.,

  (ii) the range of relaxation times accessible by dynamic light scattering covers a substantial portion of (bio) macromolecular dynamics, and

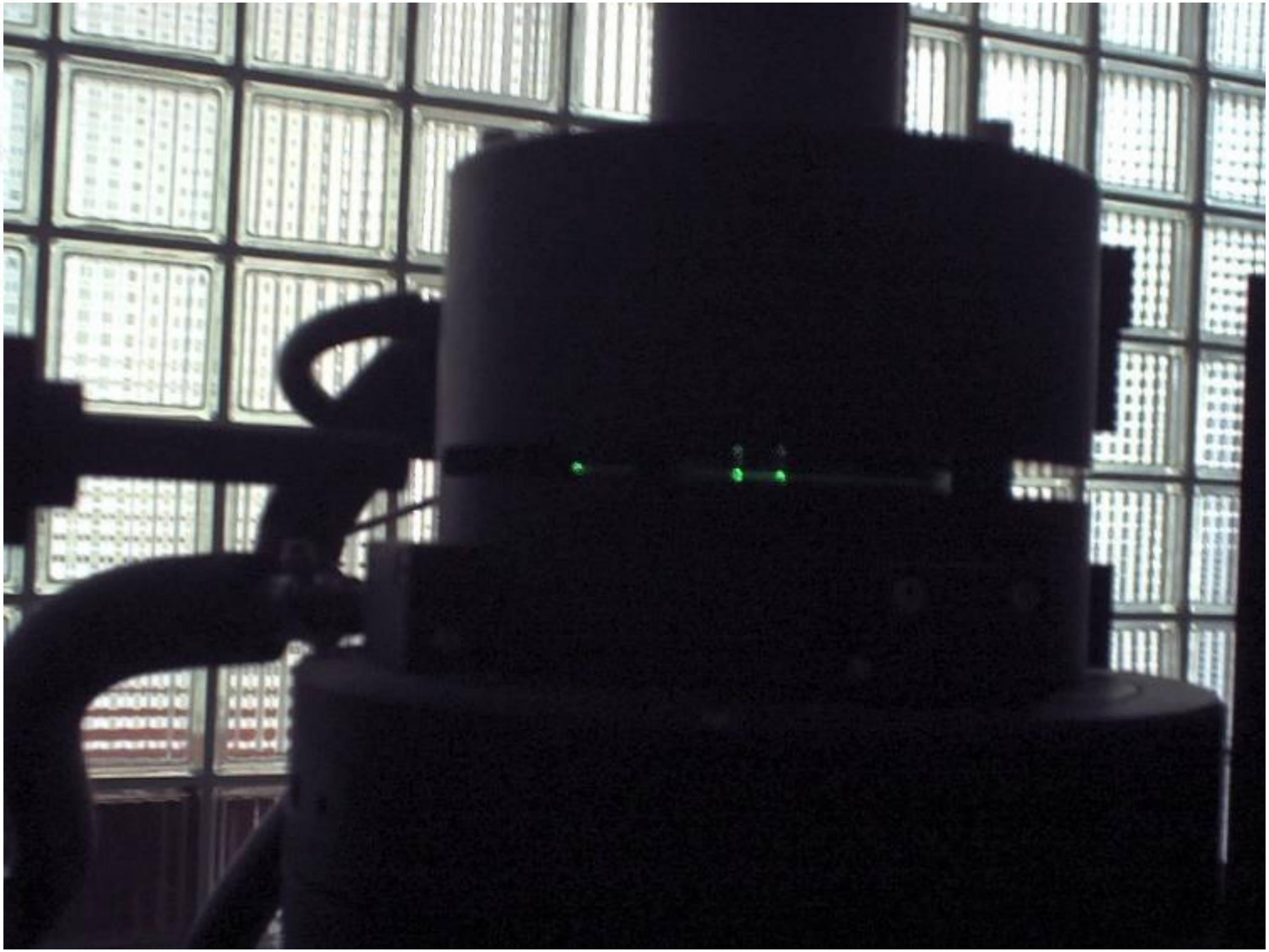
  (iii) absolute values of scattering intensities are thermodynamic quantities which enable at certain circumstances to calculate such important parameters as

    - (bio) macromolecule molecular weight or
    - the second virial coefficient in the virial expansion of osmotic pressure.

Static and Dynamic Light Scattering



Static and Dynamic Light Scattering



Light Scattering Pro and Cons

- *Advantages*

- **Probes all motion**
- **Non-perturbing**
- **Fast**
- **Study complex systems**
- **Little sample needed**
- **Everything scatters**
- **High molar mass molecules scatter relatively good**
- **Apart from a clean sample no special conditions needed for a good experiment**

- *Disadvantages*

- Everything scatters
- Cleaning a sample can be problematic
- as protein solutions often contain aggregates it is difficult to study single proteins.

Laser Light Scattering

Dynamic Light Scattering
Typical Applications

- Particle size distributions
- Particle aggregation phenomena
- Micellar systems
- Micro-emulsion technology
- Colloid behavior
- Vessicles & Liposomes
- Plasmid DNA's
- Particle size growth
- Nucleation processes & Protein crystallization

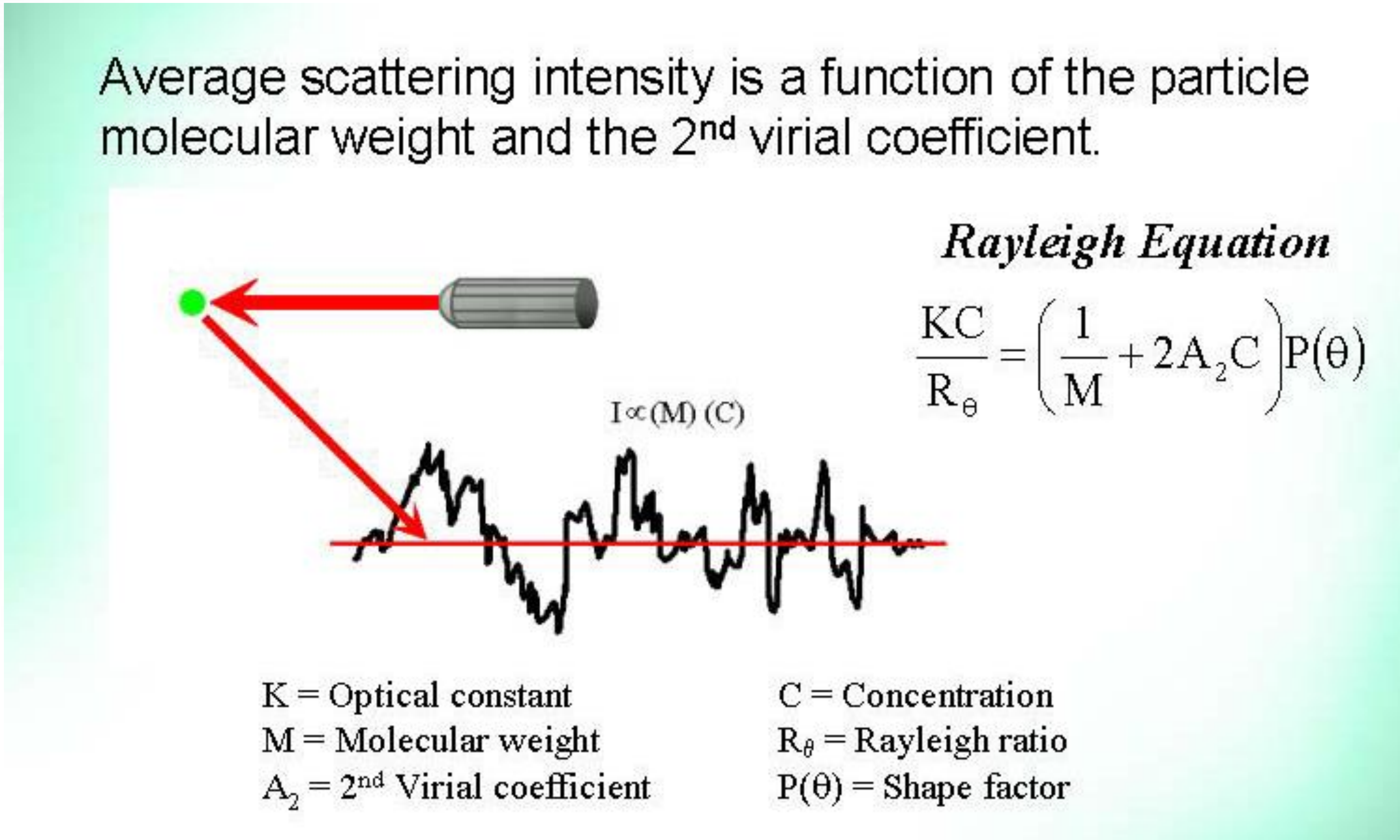
Laser Light Scattering

Static Light Scattering

Typical Applications

- M_w Molecular weight determinations
- R_g Radius of gyration
- A_2 Determination of second virial coefficient
- Micro-emulsion technology
- Colloid behavior
- Complex fluid characterization
- Emulsion polymerization
- Particle size growth
- Nucleation processes

Static Light Scattering



Average scattering intensity is a function of the particle molecular weight and the 2nd virial coefficient.

Rayleigh Equation

$$\frac{KC}{R_\theta} = \left(\frac{1}{M} + 2A_2C\right)P(\theta)$$

K = Optical constant

M = Molecular weight

A_2 = 2nd Virial coefficient

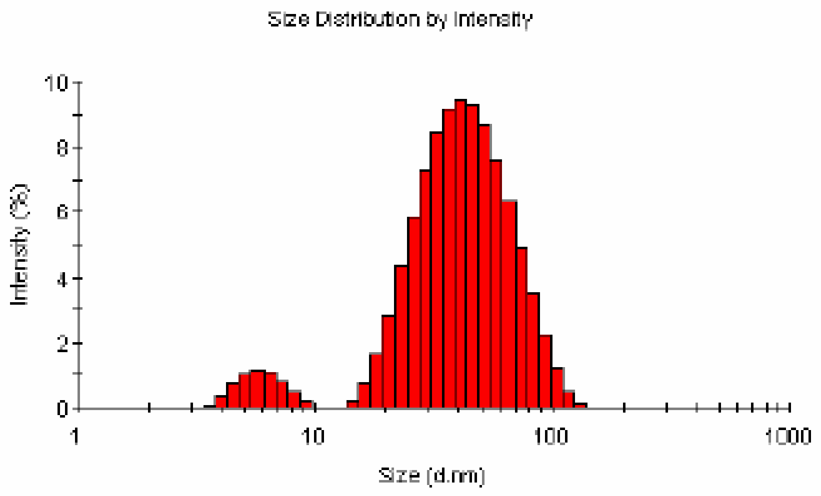
C = Concentration

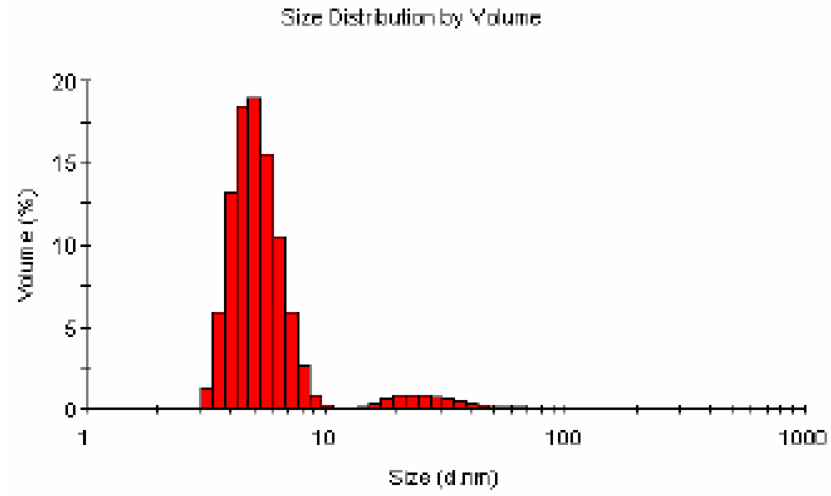
R_θ = Rayleigh ratio

$P(\theta)$ = Shape factor

The scattering intensity:

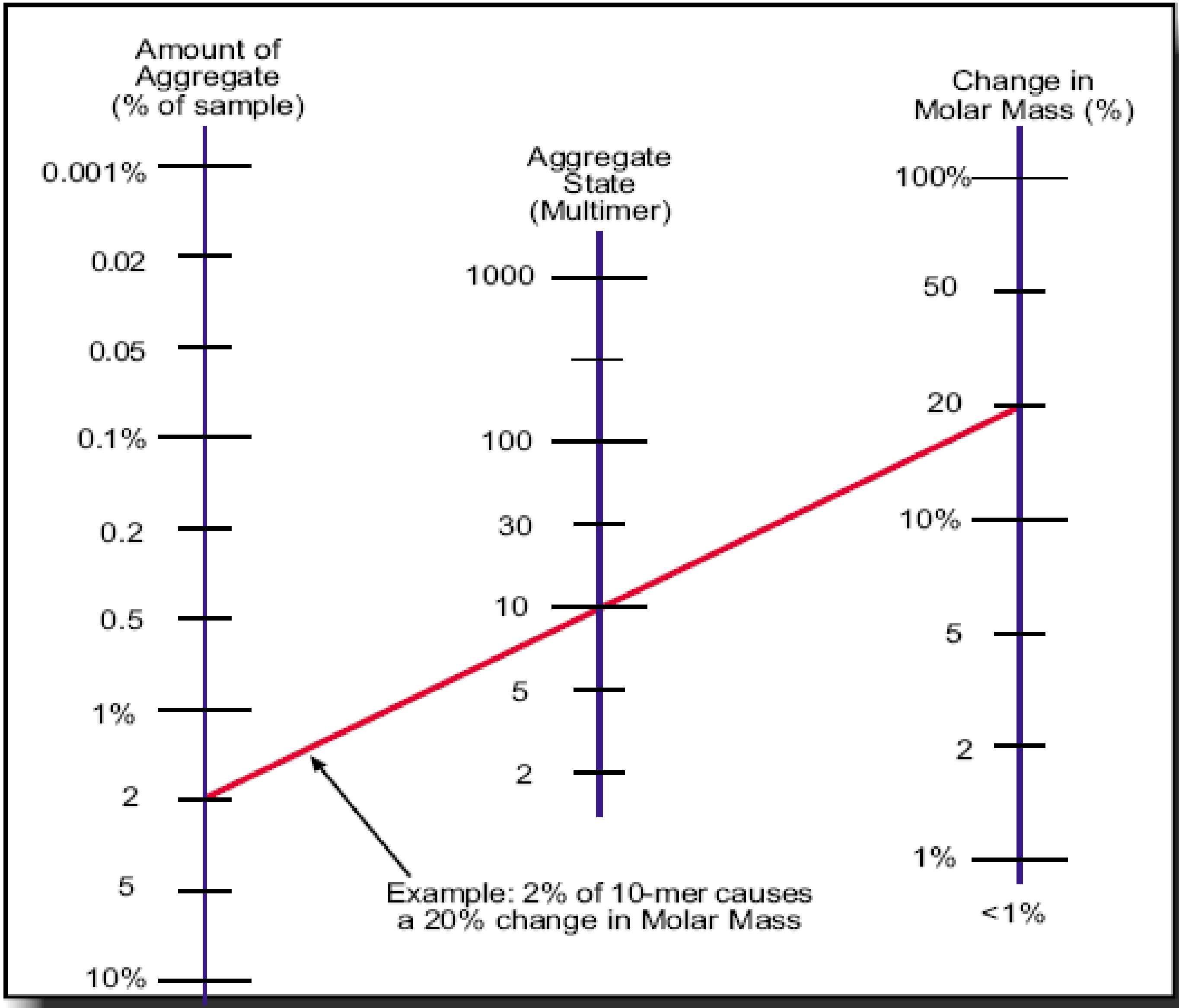
- varies with the mass and concentration according to the Rayleigh Expression
- is proportional to
  - M_w
  - M_n^2
  - R^6
- is non-invasive
- is ideal for aggregate detection & quantification in low volume, low concentration biological samples.





Peak	D_I (nm)	%I	%M
1	5.95	5	93
2	46.0	94	6

Static Light Scattering

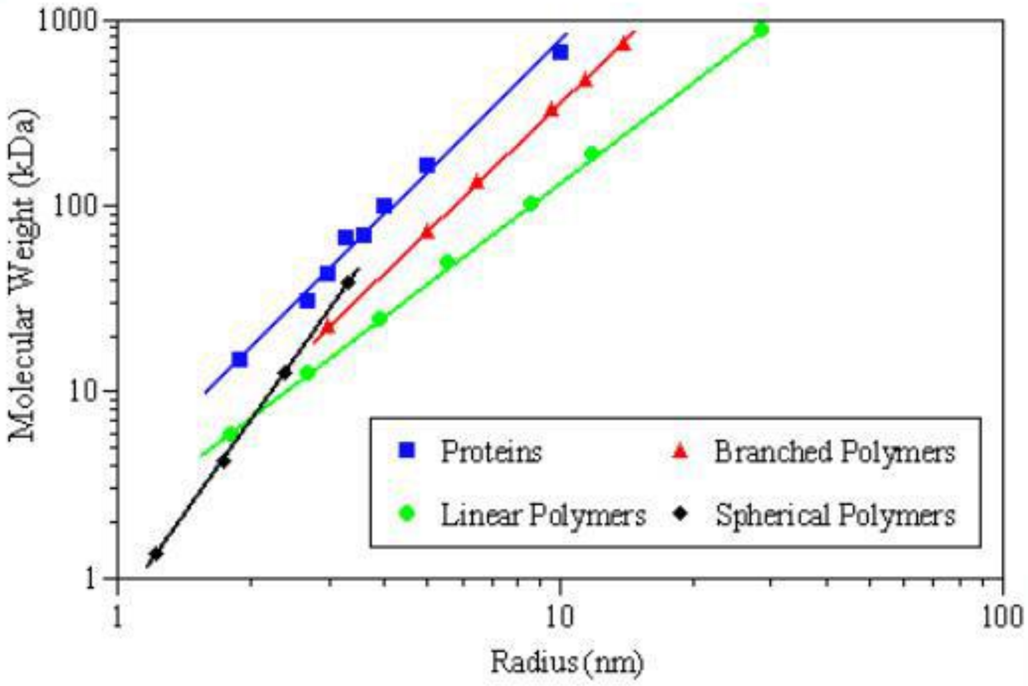


Example: 2% of 10-mer causes a 20% change in Molar Mass

Static Light Scattering

Estimated Molecular Weight

MW estimated from empirical MW vs. R_H relationships, similar to GPC techniques.



Chain Dimensions - Scattering Function

$$\frac{Kc}{R_\theta} = \frac{1}{\overline{M}_W} + \frac{1}{\overline{M}_W}\frac{16}{3}\pi^2\frac{\langle r^2\rangle}{6\lambda^2}\sin^2\frac{\theta}{2} + 2A_2c$$

where:

K - contrast factor

c - concentration of scattering species

R_θ - Rayleigh ratio (reduced intensity)

r - distance from scattering center to detector.

I_0 - incident wave intensity

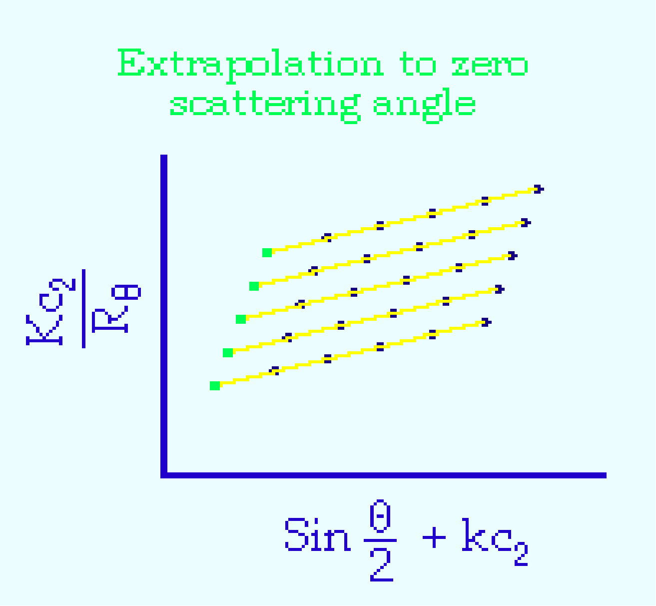
A_2 - 2nd virial coefficient

$$R_\theta = \frac{4\pi^2 n_{solv}^2\left(\frac{dn}{dc}\right)^2 Mc}{N_A\lambda^4} = KMc$$

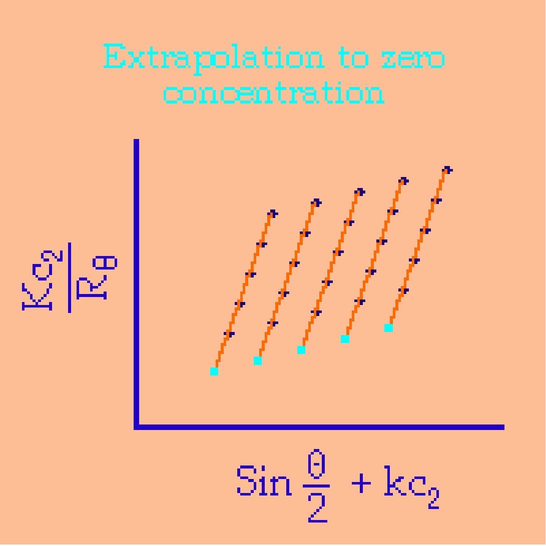
Chain Dimensions

Generation of a Zimm Plot

$$\lim_{\theta\to 0}\frac{Kc}{R_\theta}=\frac{1}{\overline{M}_W}+2A_2c$$

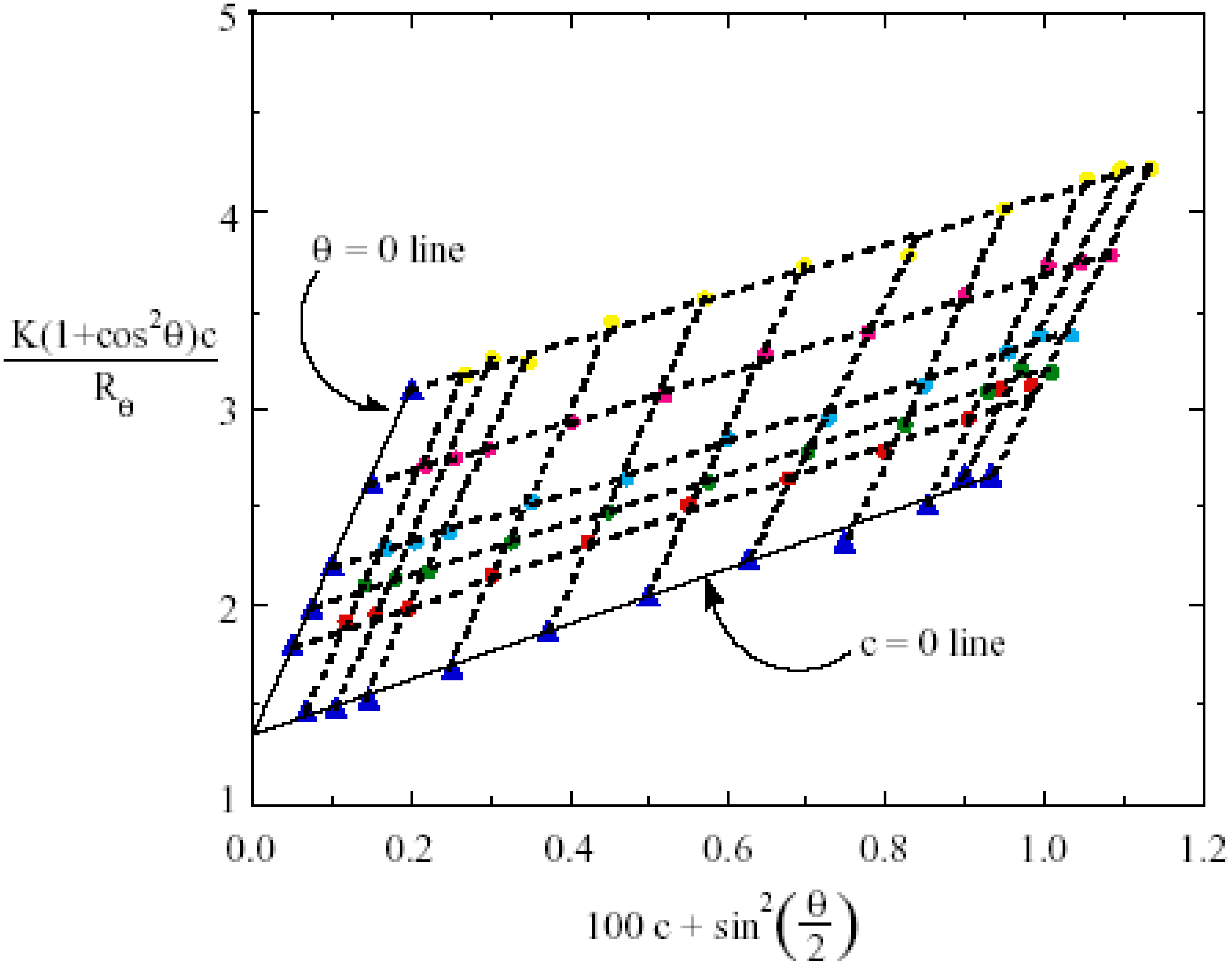


$$\lim_{c\to 0}\frac{Kc}{R_\theta}=\frac{1}{\overline{M}_W}+\frac{1}{\overline{M}_W}\frac{16}{3}\pi^2\frac{\langle r^2\rangle}{6\lambda^2}\sin^2\frac{\theta}{2}$$



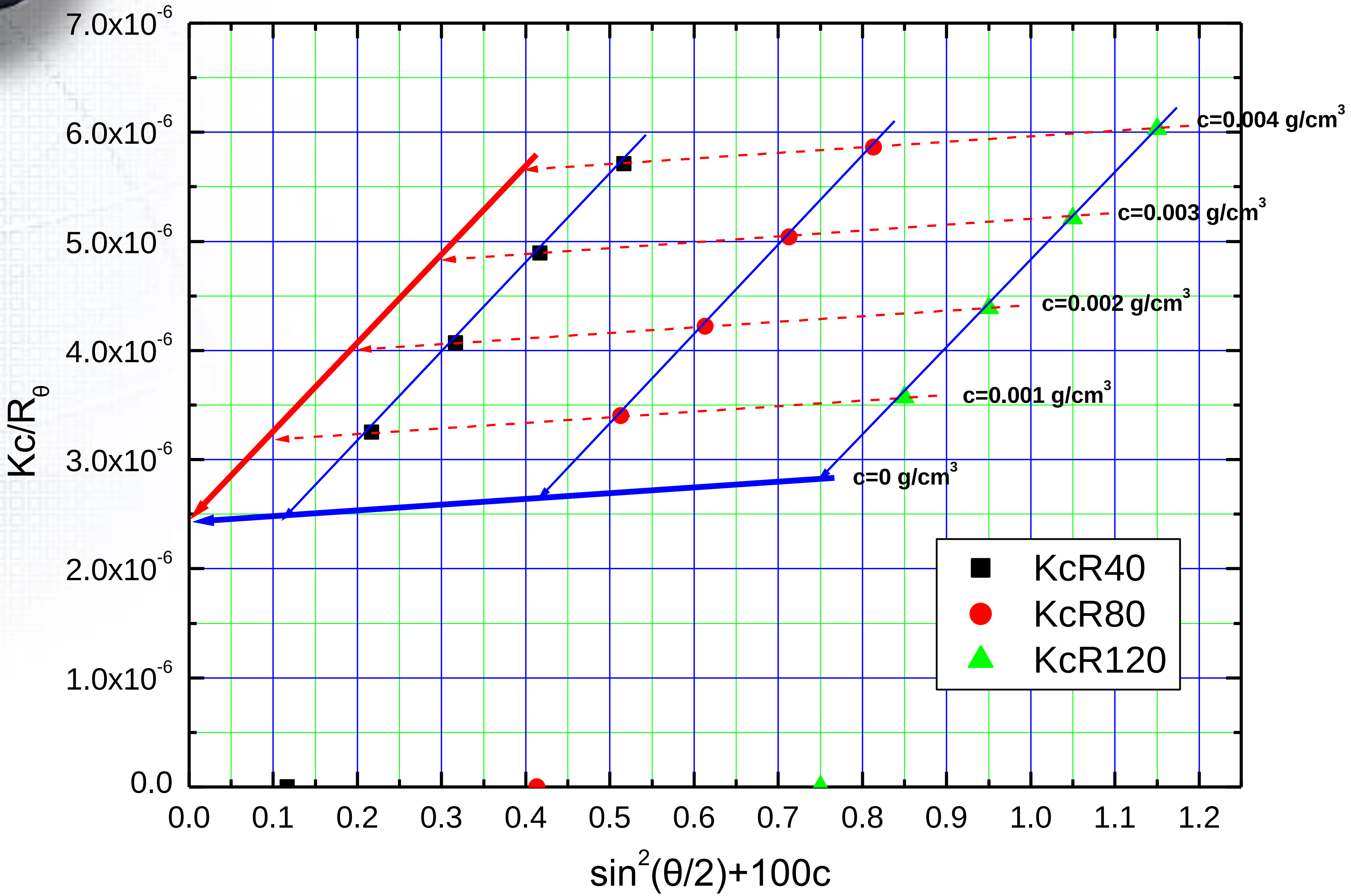
Chain Dimensions

Generation of a Zimm Plot

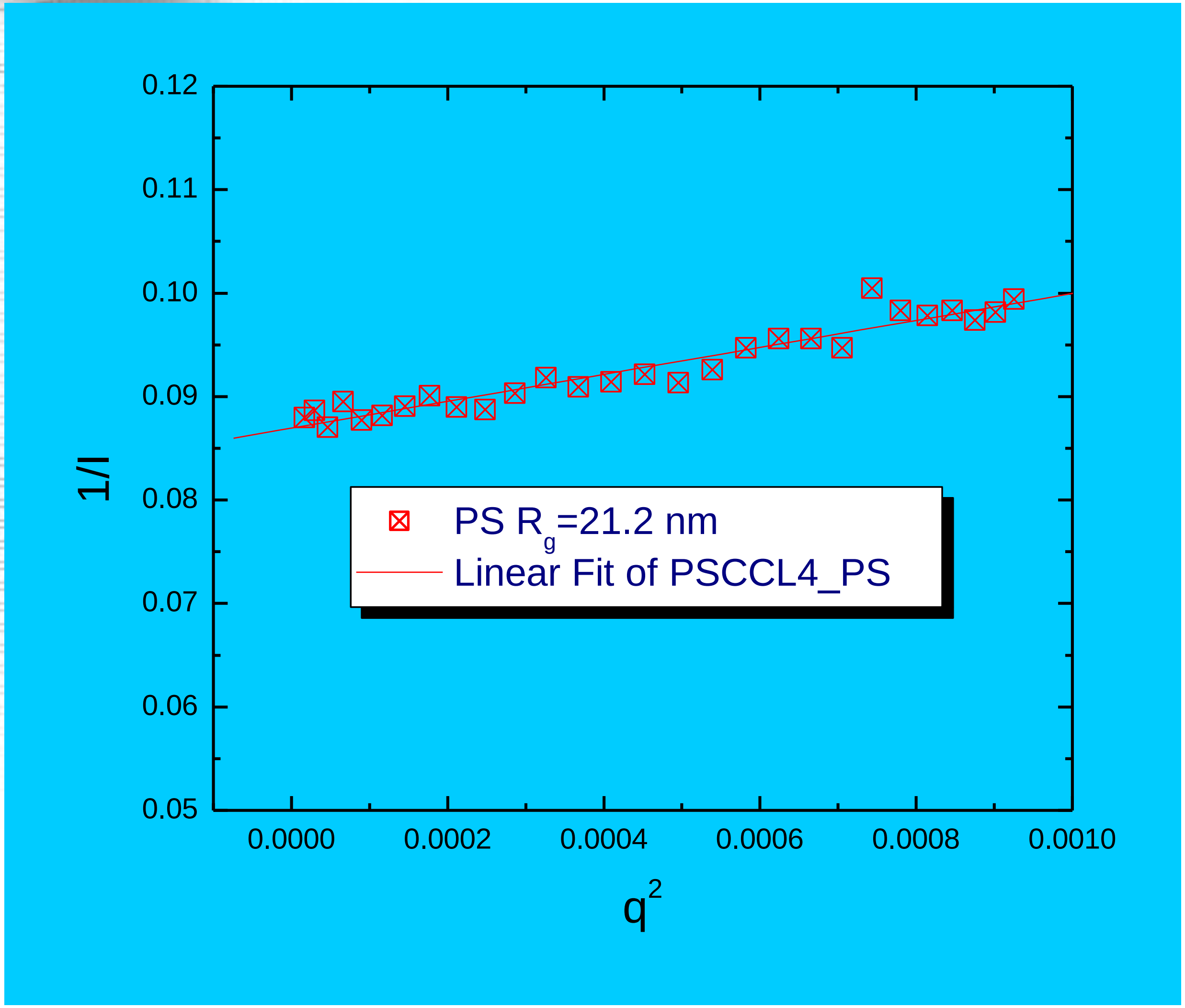


Chain Dimensions

Generation of a Zimm Plot



Static Laser Light Scattering



$$\frac{1}{I} = \frac{1}{KcM_W}\left(1 + \frac{R_g^2}{3}q^2\right) \Rightarrow \frac{1}{I} = A + Bq^2$$

$$A = \frac{1}{KcM_W}$$

$$B = \frac{R_g^2}{3}A \Rightarrow R_g = \sqrt{\frac{3B}{A}}$$

Dynamic light scattering experiment

- The scattered electric field time autocorrelation function measured in a dynamic light scattering experiment is proportional to the time autocorrelation function of the fluctuations in refractive index.

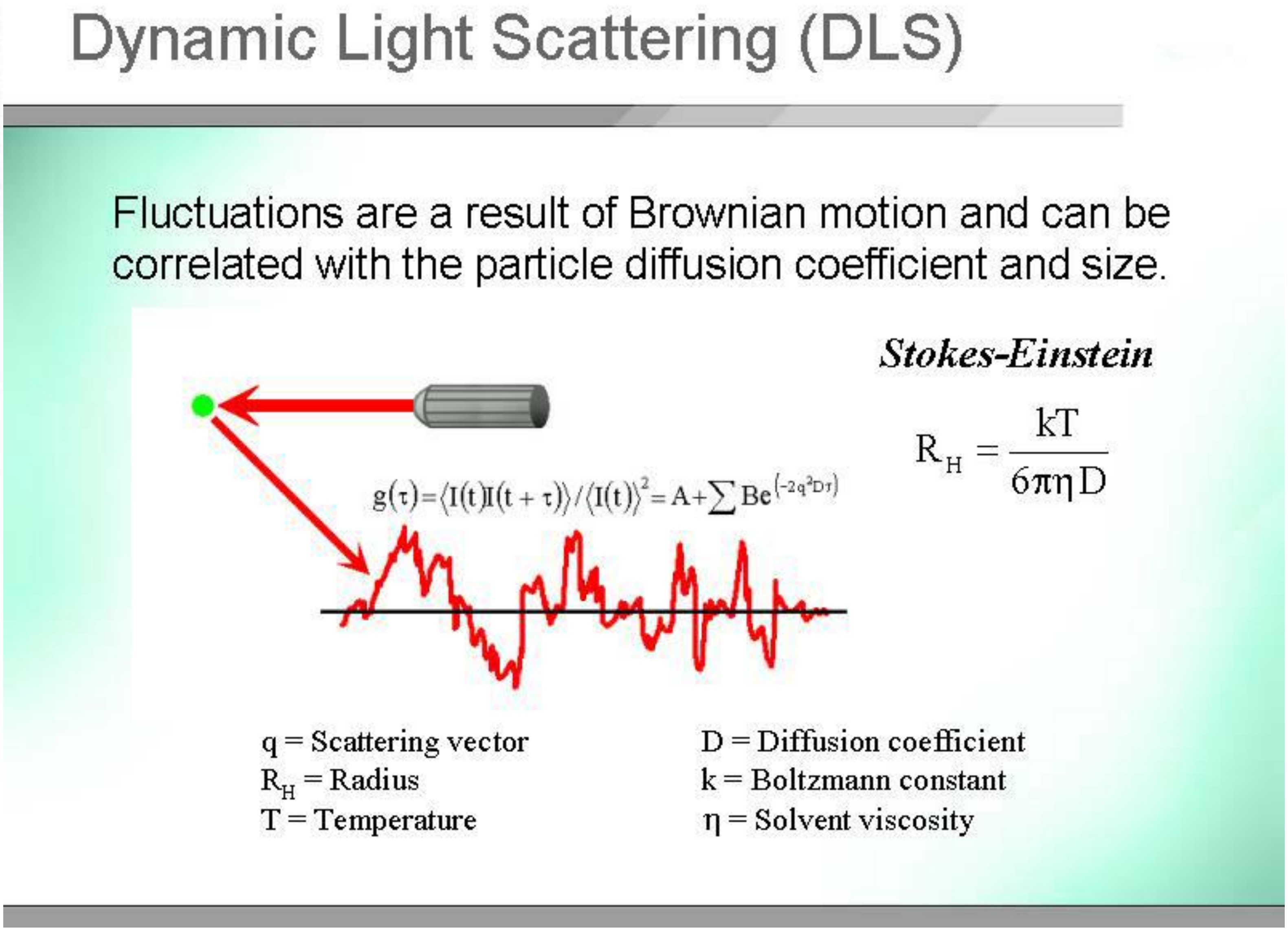
$$g^{(1)}(t) = <\delta n_{\mathrm{if}}(q,0)\delta n_{\mathrm{if}}(q,t)>$$

q is the scattering vector: $q = |\vec{q}| = \left|\vec{k}_f - \vec{k}_i\right| = (4\pi n / \lambda)\sin(\vartheta / 2)$

- Correlation functions are Laplace transforms of the spectrum of relaxation time:

$$g^{(1)}(t) = \int_0^\infty A(\tau) e^{-t/\tau} d\tau$$

Dynamic Light Scattering



Dynamic Light Scattering (DLS)

Fluctuations are a result of Brownian motion and can be correlated with the particle diffusion coefficient and size.

$$g(\tau)=\langle I(t)I(t+\tau)\rangle/\langle I(t)\rangle^2 = A+\sum Be^{(-2q^2D\tau)}$$

Stokes-Einstein

$$R_H = \frac{kT}{6\pi\eta D}$$

q = Scattering vector
R_H = Radius
T = Temperature

D = Diffusion coefficient
k = Boltzmann constant
η = Solvent viscosity

Dynamic light scattering experiment

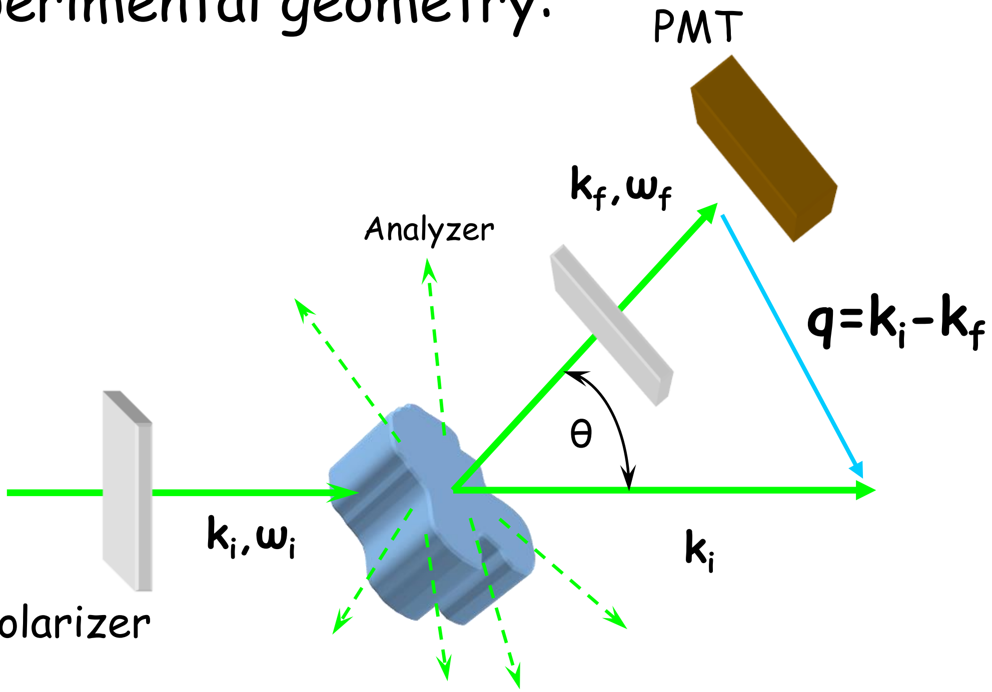
$\boxed{G(\tau)=1-e^{-\Gamma t}}$ where $\Gamma=1/\tau \rightarrow \Gamma=q^2D$

D is the diffusion coefficient

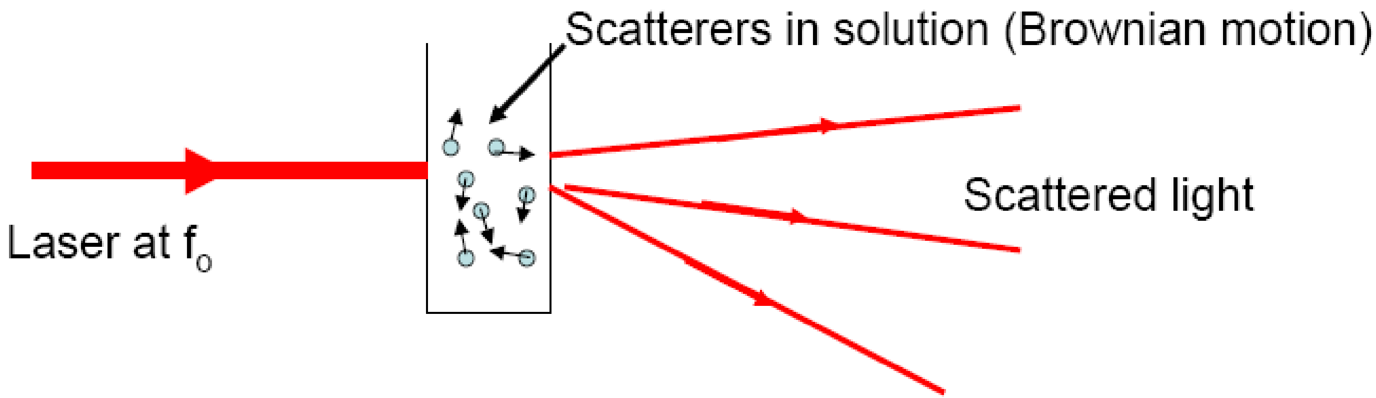
and q is determined by the experimental geometry:

$$|k_i|=|k_f|=2\pi n/\lambda$$

$$q=2k_i\sin(\theta/2)=$$
$$=(4\pi n/\lambda)\sin(\theta/2)$$



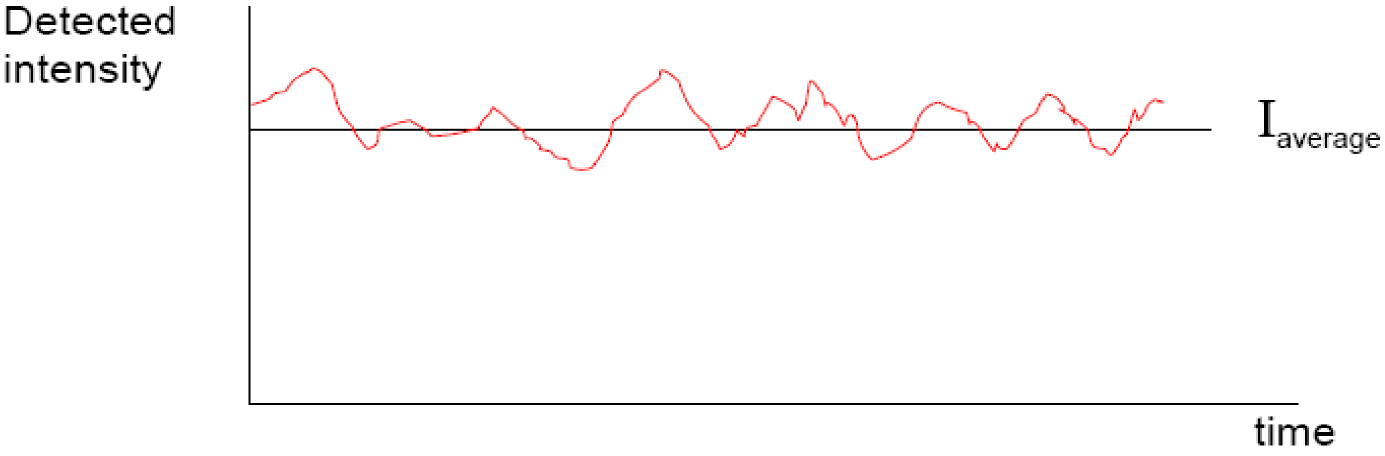
Dynamic Light Scattering Experiment



Scatterers in solution (Brownian motion)

Laser at f_o

Scattered light

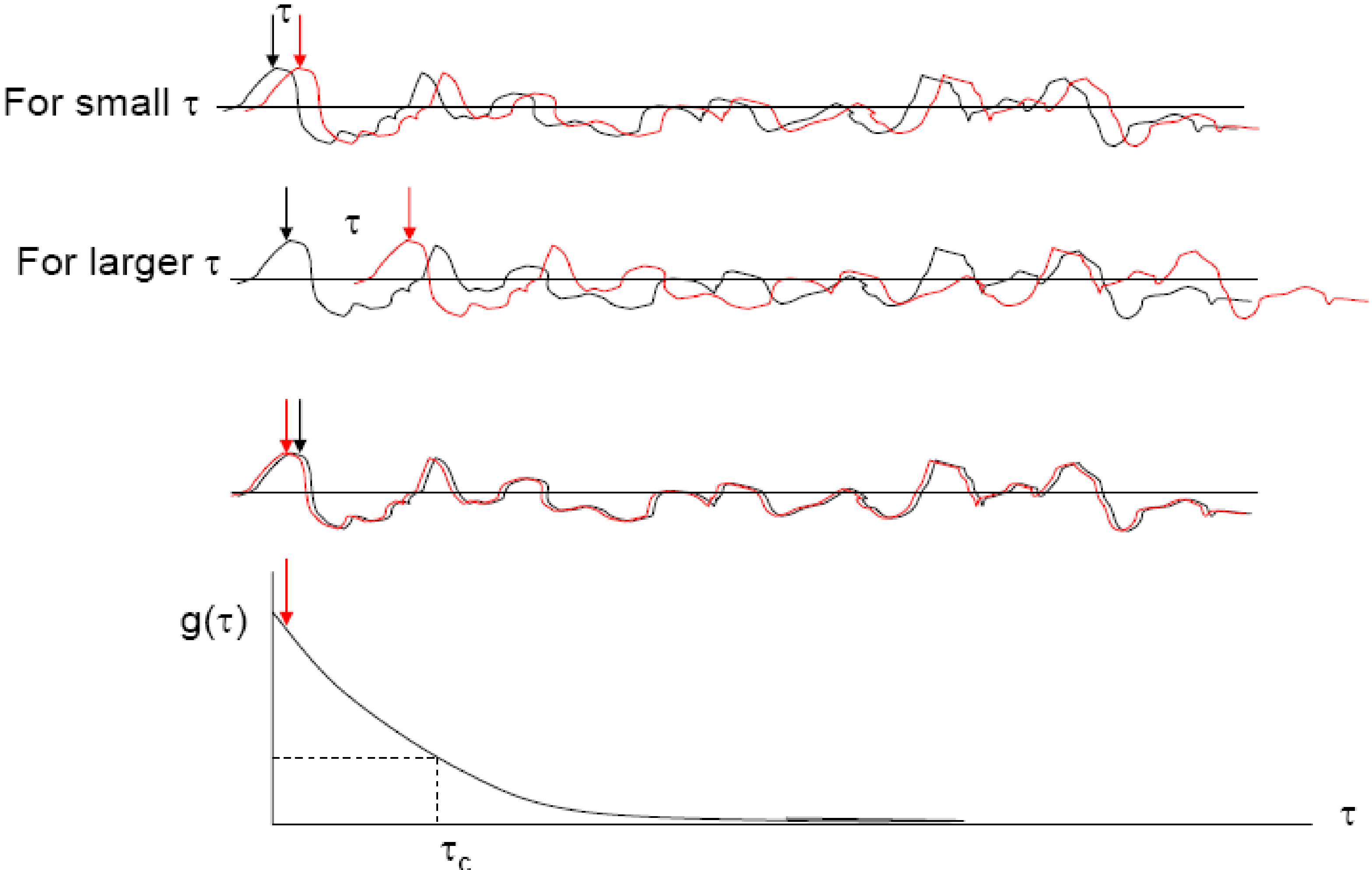


How can we analyze the fluctuations in intensity?

Data = $g(\tau) = \langle I(t)\, I(t+\tau)\rangle_t$ = intensity autocorrelation function

Intensity Autocorrelation

- $g(\tau) = \langle I(t)\, I(t + \tau) \rangle_t$



Time Correlation Function

A **Time Correlation Function** describes : the dynamic behavior of spontaneous fluctuations about the equilibrium state

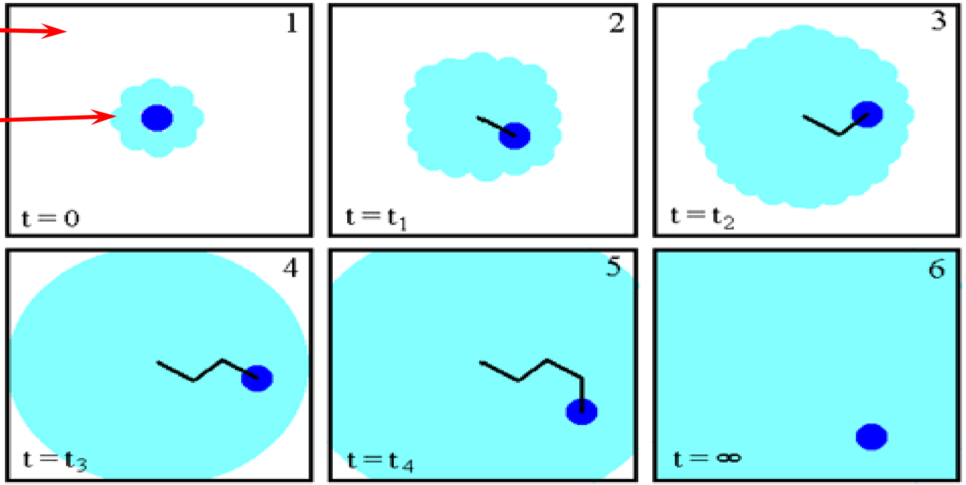
- Qualitatively, a **Time Correlation Function Describes** how long a given property of the system persists until it is averaged out by the microscopic motion of the molecules in the system.

$$G(\tau) = \int_0^\infty I(t)I(t+\tau)dt$$

where τ is the relaxation time

Scattering Volume

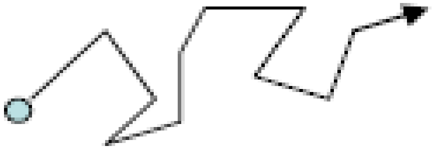
Diffusion Volume



What Determines the Correlation Time?

- Scatterers are diffusing – undergoing Brownian motion – with a mean square displacement given by $<r^2> = 6D\tau_c$ (Einstein)

- The correlation time τ_c is a measure of the time needed to diffuse a characteristic distance in solution

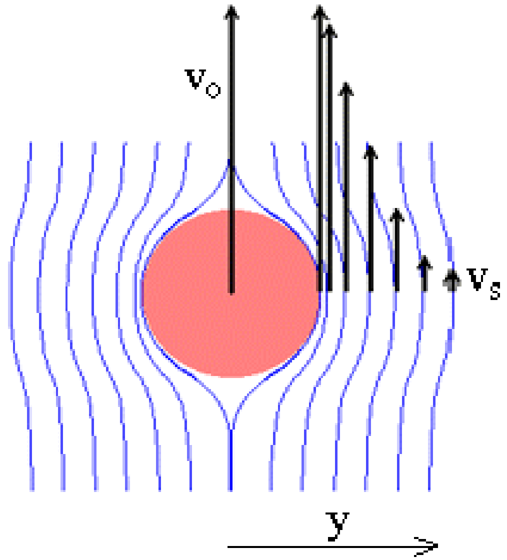


  - this distance is defined by the wavelength of light, the scattering angle and the optical properties of the solvent –
    - ranges from 40 to 400 nm in typical systems

- •Values of τ_c can range from 0.1 μs (in small proteins) to days (in glasses, gels).

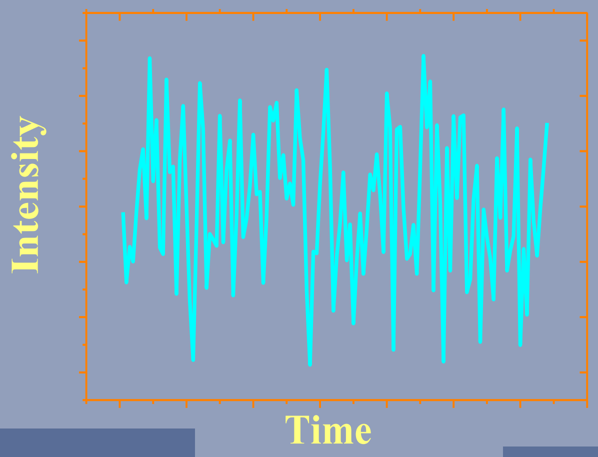
Stokes-Einstein: Hydrodynamic Radius

$f = 6\pi\eta R$

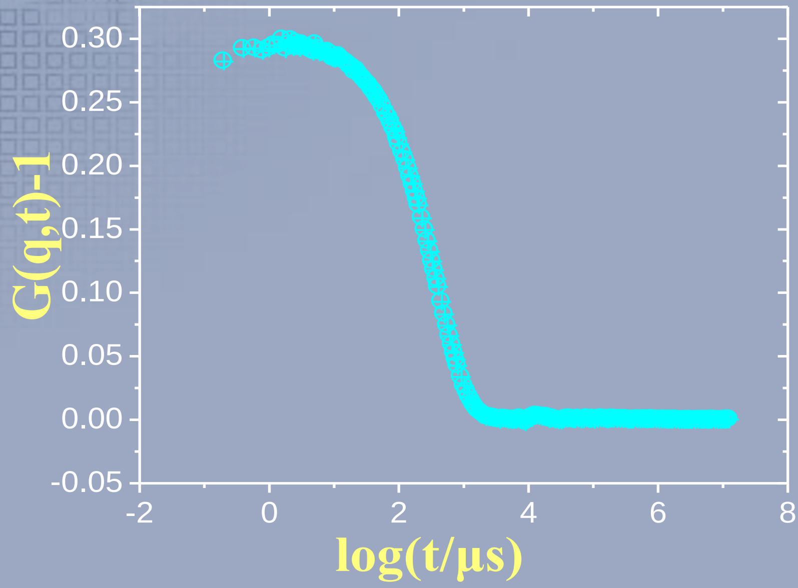


$$D = \frac{kT}{f} = \frac{kT}{6\pi\eta R} \Rightarrow R = \frac{kT}{6\pi\eta D}$$

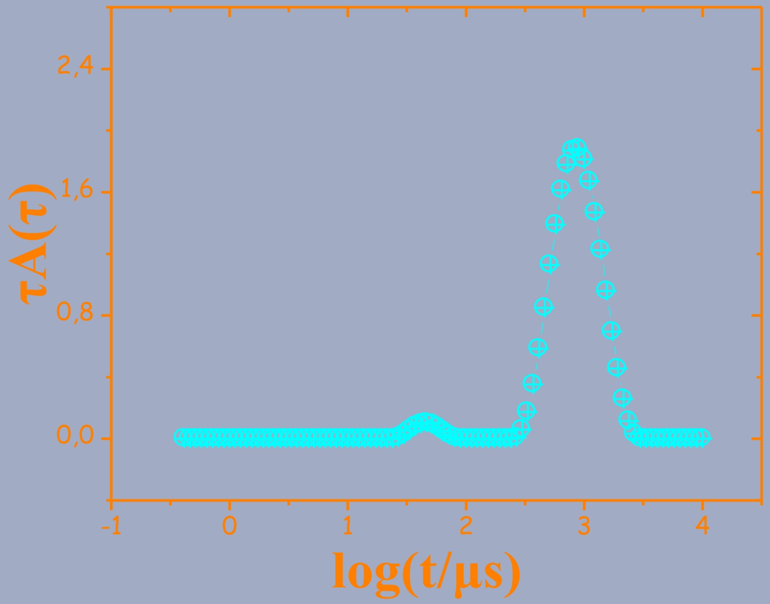
Dynamic light scattering experiment



Correlation Function



Inverse Laplace Transform



Laser Light Scattering

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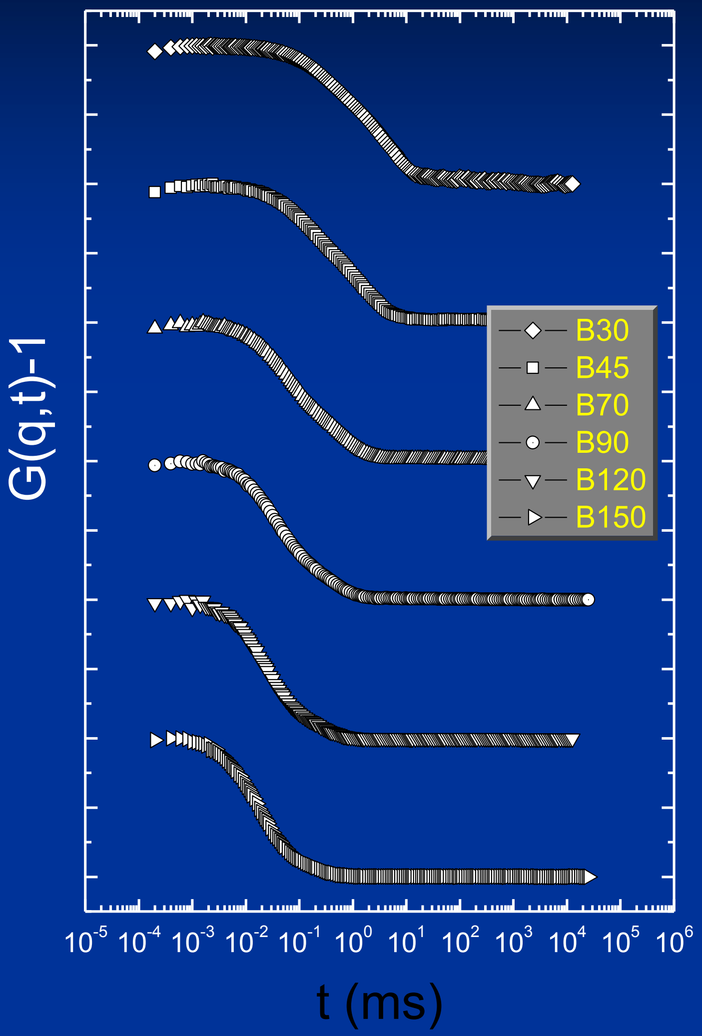
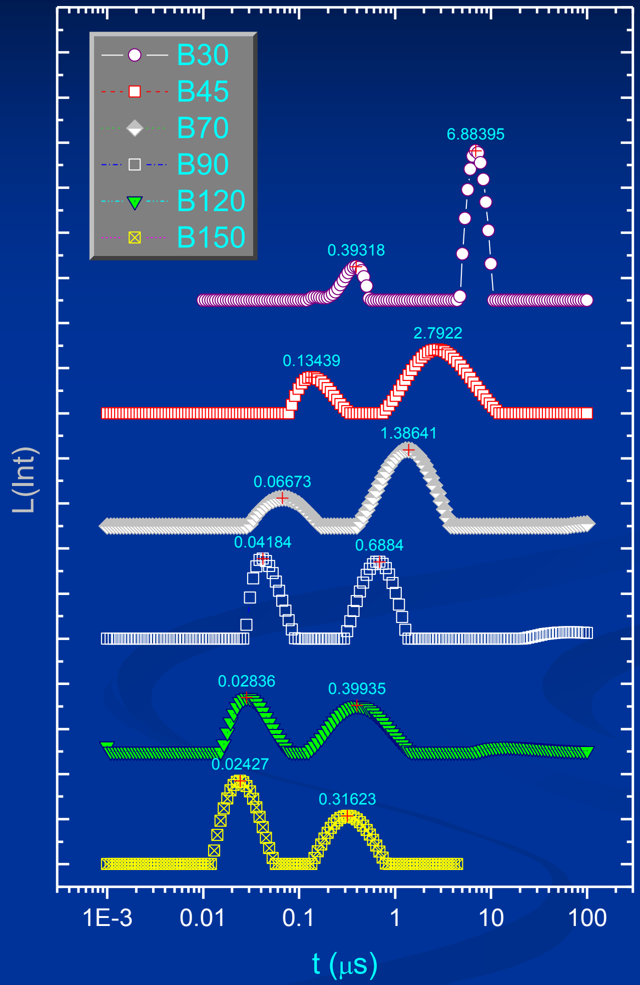




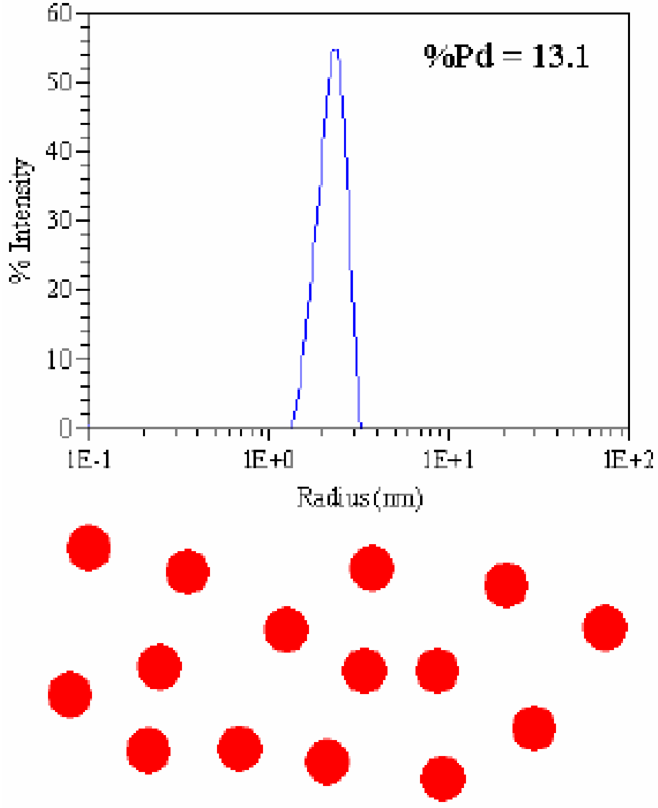
$$\Gamma = \frac{1}{\tau} = Dq^2 \quad [\mathrm{s}^{-1}]$$

$$D = \frac{k_B T}{6\pi\eta R_H} \Rightarrow R_H = \frac{k_B T}{6\pi\eta D} =$$

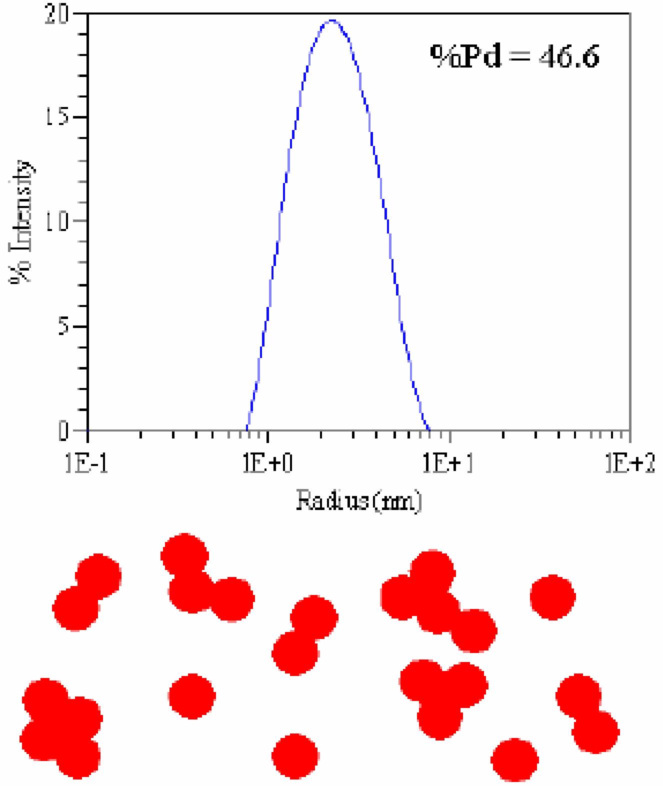
$$= \frac{1.38 * 10^{-23} J/K * 298.2K}{6 * 3.14 * 0.00059 * Pa * s * 3 * 10^{-11} m^2/s} = 12.3 * 10^{-9} m = 12.3nm$$

Polydispersity (Pd) From DLS

Pd is representative of the particle size distribution width, with high polydispersity being indicative of oligomerization and/or aggregation.



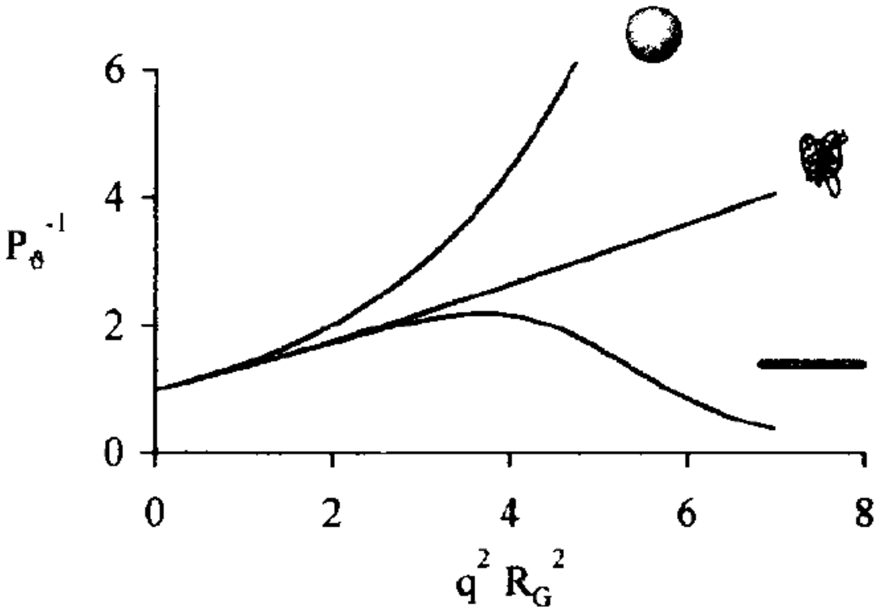
Monodisperse



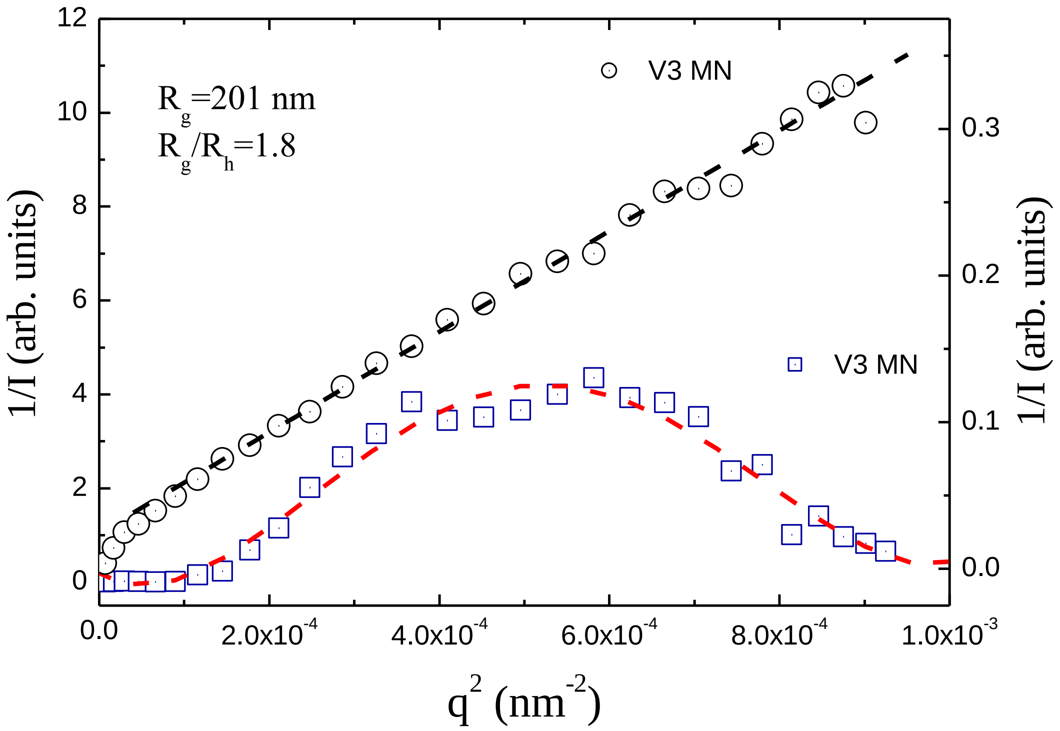
Polydisperse

Calculated reciprocal scattering functions for solid spheres, ideal coils and rigid rods

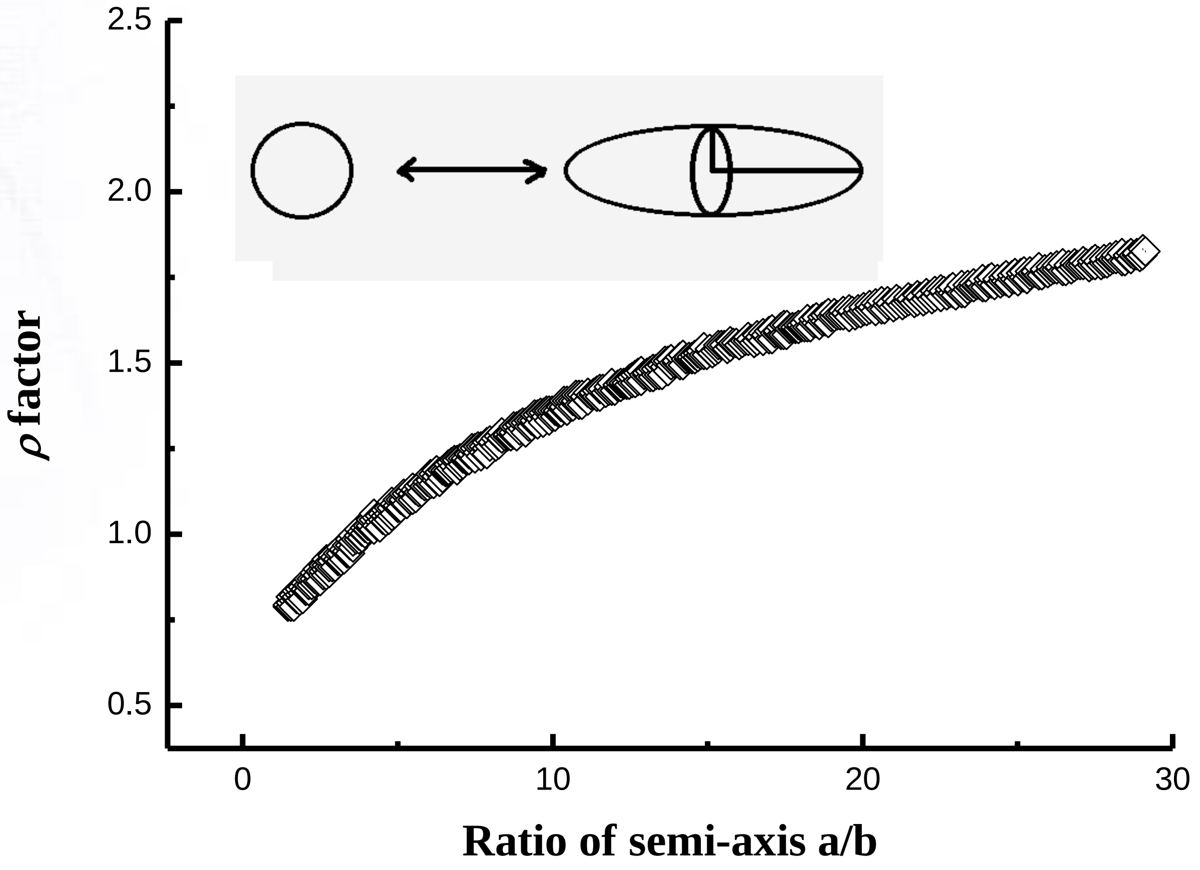
- For large values of qR_G the scattering function P_θ has a significant dependence on molecular shape



Kulicke et. al. (1997) Polymer **38**, 1513



Shape analysis: shape factor $\rho = R_g/R_h$



Rizos, A. K., Spandidos, D. A., and Krambovitis, E., (2003) *Int. J. Med.*,12, 559-563

Conformational information

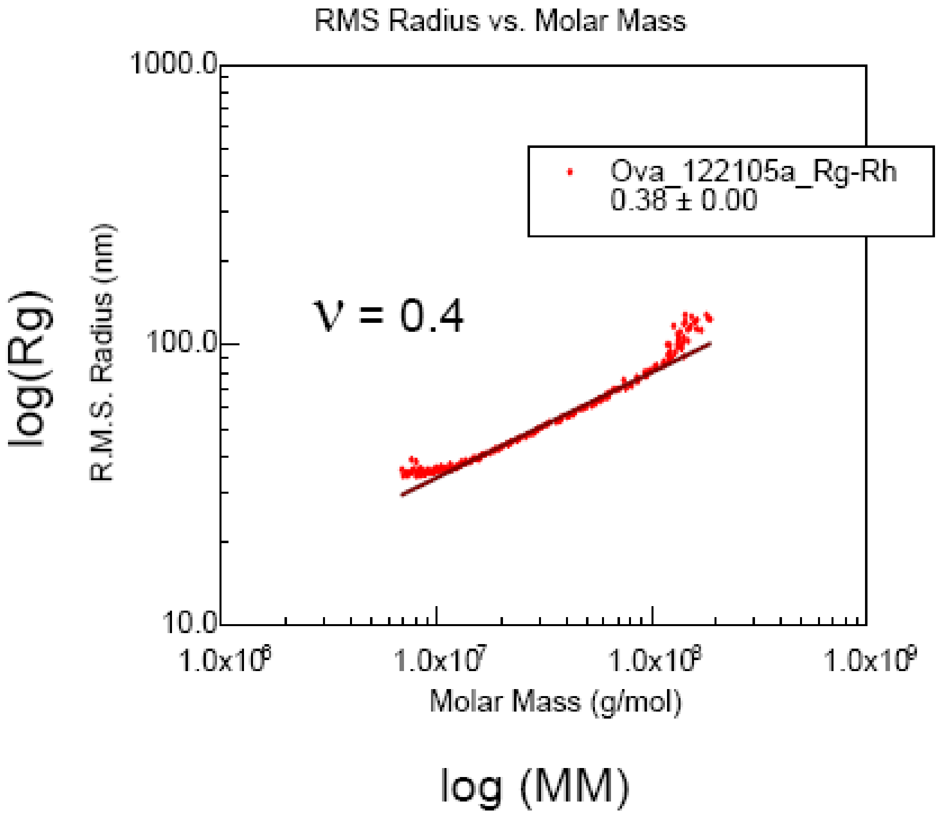
Inferring conformational information from the relationship between molecular size (R_g) and molecular weight (Molar Mass)

$$R_g \sim M^{\nu}$$

$\log(R_g)$ *versus* $\log(MM)$

Slope = ν

For	ν
Sphere	0.33
Coil	0.5
Rod	1



Rollings, J.E. (1992) in *"Laser Light Scattering in Biochemistry"*, Eds. S.E. Harding, D. B. Sattelle and V. A. Bloomfield; p. 275-293

Polyglycerol Polyricinoleate (PGPR).

Chemistry.
Polyglycerol Polyricinoleate (PGPR) also know under the trade names Palsgaard®4125 or Palsgaard®4150, is a food grade emulsifier consisting of poly-glycerol as the hydrophilic group and interesterified ricinoleic fatty acids as the hydrophobic group. (see fig.1)

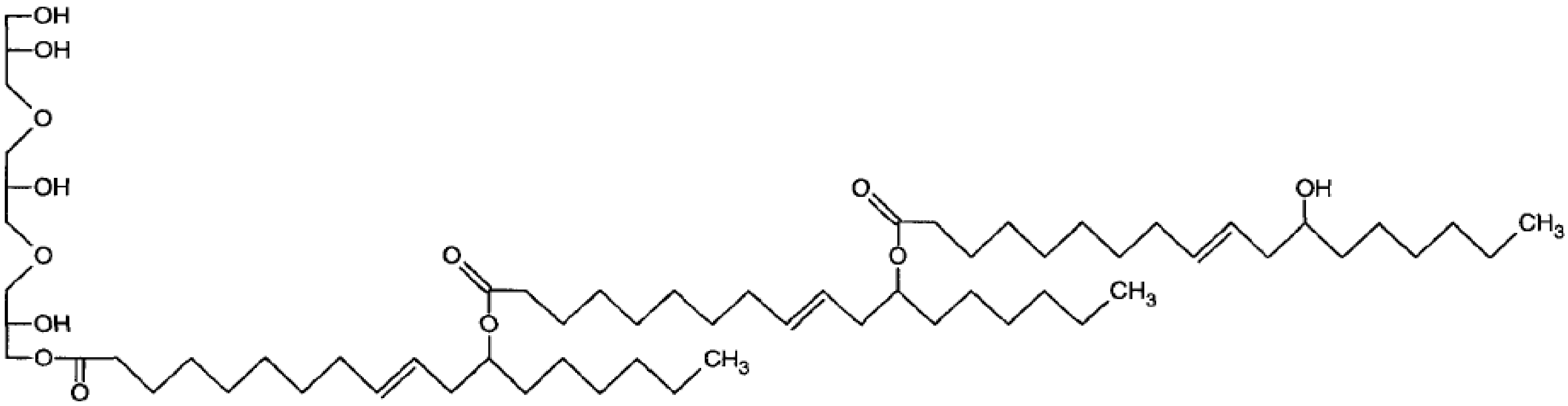


Fig.1. Chemical structure of PGPR. (Here the fraction consisting of Tri-Glycerol Tri-Ricinoleate is shown.)

The polyglycerol part of PGPR is mainly found as di- tri- or tetraglycerol (min 75%) and max 10% of the polyglycerol part will be found as heptaglycerol or higher.

PGPR (E 476)

Application in Foods.

PGPR has a dramatic impact on the flow properties of liquid chocolate and componds based on vegetable fats. In general it is understood that PGPR works by lowering the Yield Value of the chocolate system, whereas the Plastic Viscosity hardly is influenced.

This has the practical implication that PGPR as a general rule always is added as a co-emulsifier in combination with lecithin or ammonium phosphatide. These emulsifiers mainly reduce the plastic viscosity.

Cocoa butter and specialty vegetable fats are quite expensive raw materials, so the manufactures of chocolate and componds can benefit from the effect of PGPR and lower the total fat content in the ready to consume products. Also from a health point of view fat reduction in chocolate and componds is improving the quality in the eyes of the consumers.

Due to the strong effect on the yield value in chocolate it is possible to make the chocolate flow during production by use of much less fat. Therefore PGPR is an important tool in manufacturing of various types of chocolate-type products.

The effect in is further described by Steven T.Beckett. The Science of Chocolate. (Royal Society of Chemistry, 2000. p 81 ff) and by Schantz, b. and Rohm, H. (Lebensm.-Wiss.u.Technol. 38 (2005) p 41-45.

List of National Permissions

1. **USA. Agency Response Letter GRAS Notice No GRN 000009.**
   PGPR to be added to chocolate at a level up to 0.3 %.

2. **USA. Agency Response Letter GRAS Notice No GRN 000179.**
   PGPR to be added to margarines, low fat margarines, spreads, creamers and dairy analogs at levels no greater than 1 % by weight.

3. **EU Parliament and council Directive No 95/2/EC.**
   PGPR to be added to Cocoa-based confectionery, including chocolate up to 5g/kg
   PGPR to be added to Spreadable fats having a fat content below 41% up to 4g/kg
   PGPR to be added to Dressings up to 5g/kg

4. **Australia New Zealand Food Autrority P150 – A joint general standard for Food Additives.**
   PGPR to be added to Chocolate and Cocoa Products (included Compounded chocolate) up to 5000 mg/kg
   PGPR to be added to Margarine and similar products up to 5000 mg/kg

5. **Canada The Food and Drugs Act and Regulations.**
   PGPR to be added to Milk Chocolate ; Sweet Chocolate up to 0.5%
   PGPR to be added to Unstandardized chocolate flavoured confectionery coatings up to 0.25 %

Structure Elucidation of Polyglycerol Polyricinolate (PGPR) by Dynamic Light Scattering, ESI--MS and NMR Spectroscopy

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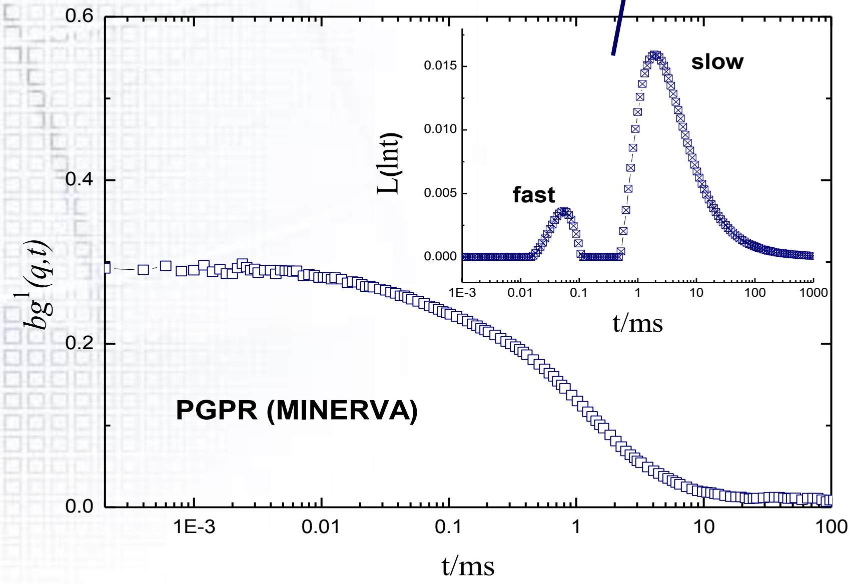
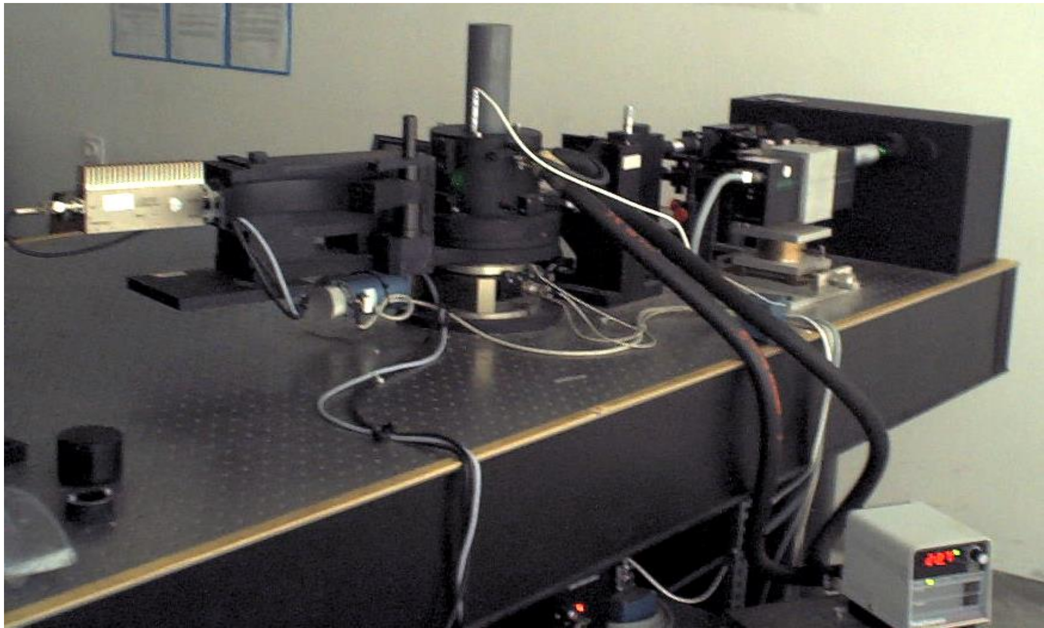
ABSTRACT

Three different analytical techniques, namely NMR spectroscopy, electrospray ionization - mass spectrometry (ESI-MS) and dynamic light scattering (DLS), were employed to unravel the structure of a commercial sample of ricinoleic acid (RA) (purity 80%), and more importantly the morphology of polyglycerol polyricinolate (PGPR), which is used alone or with lecithine as an emulsifier in the preparation of chocolate and other confectionary products. The use of modern 2D NMR techniques allowed the distinction of two separate entities in the commercial RA; the monomeric and oligomeric RA in agreement with literature data that RA forms estolides, i.e. intermolecular esters comprising at least two fatty acid molecules. Different entities were discovered in PGPR as well. ^{1}H and ^{13}C spectra of this material demonstrated signals attributed to glycerol moiety esterified by monomeric and preferably by oligomeric RA and to a lesser extent by oleic and linoleic acids; the latter acids are present in castor oil which is the source of RA preparation. Although ^{13}C diffusion ordered NMR (DOSY) experiments evidenced the presence of more than two species in PGPR, their identity and distribution was confirmed by ESI-MS experiments. The picture obtained from this analysis was as follows: free RA molecules and RA oligomers with degree of polymerization 2-6 are distributed in polyglycerols with degree of condensation 2-6; the concentration of the various entities decreases with increasing degree of polymerization/condensation. DLS experiments identified two distinct relaxation modes attributed to monomeric and oligomeric RA as observed with the ESI-MS and NMR experiments. The hydrodynamic radius (R_h) and shape (ρ) of RA aggregates in PGPR were estimated to be 93±4 nm and 0.72±0.05, respectively. The latter experimental value can be correlated with a spherical shape. Finally, the average molecular weight of PGPR determined by NMR compares favorably with that obtained by ESI-MS, but differs with the value estimated by DLS.

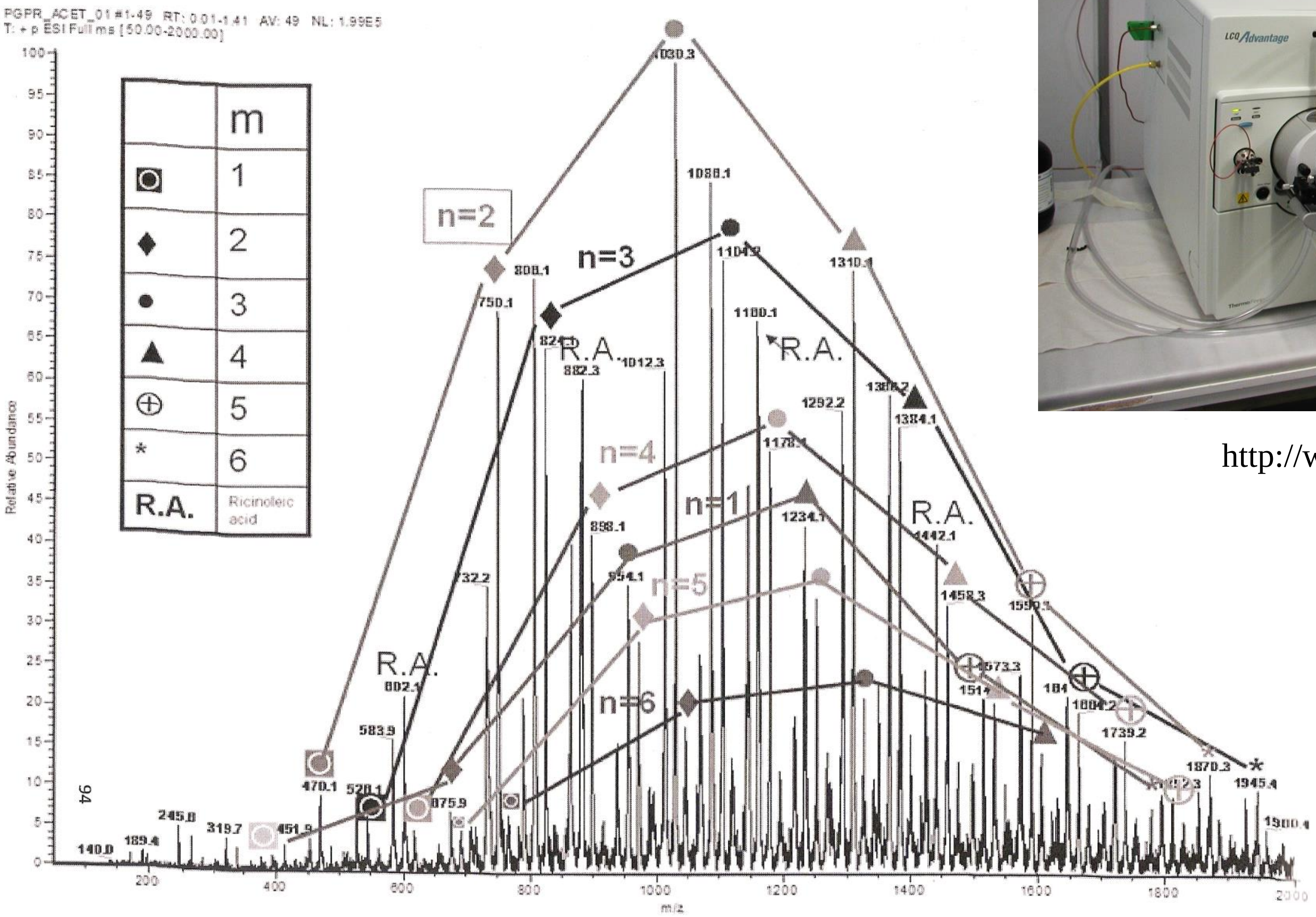
Dynamic Light Scattering

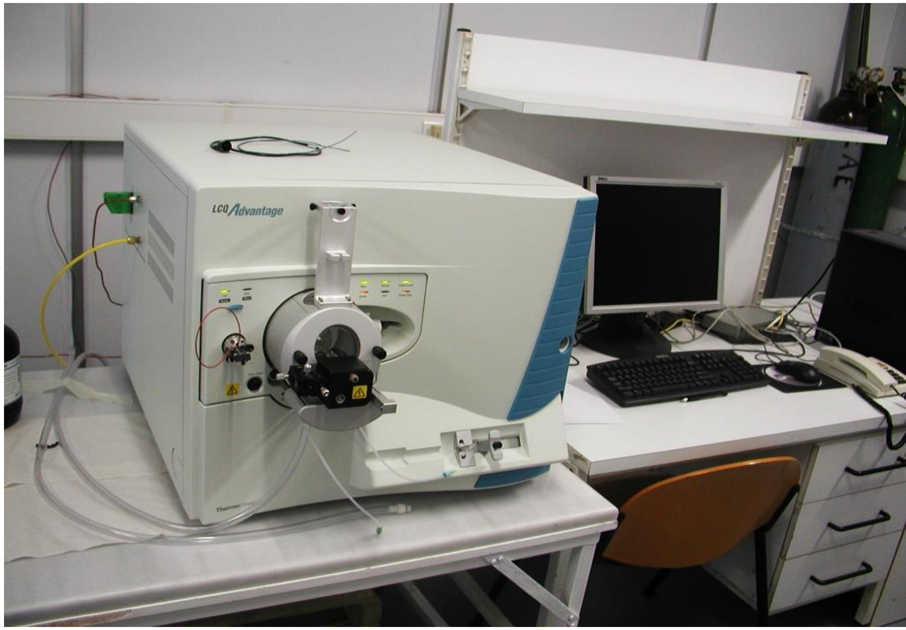
R_h=4.3 nm
(Dimers, trimers to … polymers)





Φασματομετρία μάζας (ThermoFinnigan LCQ Advantage)

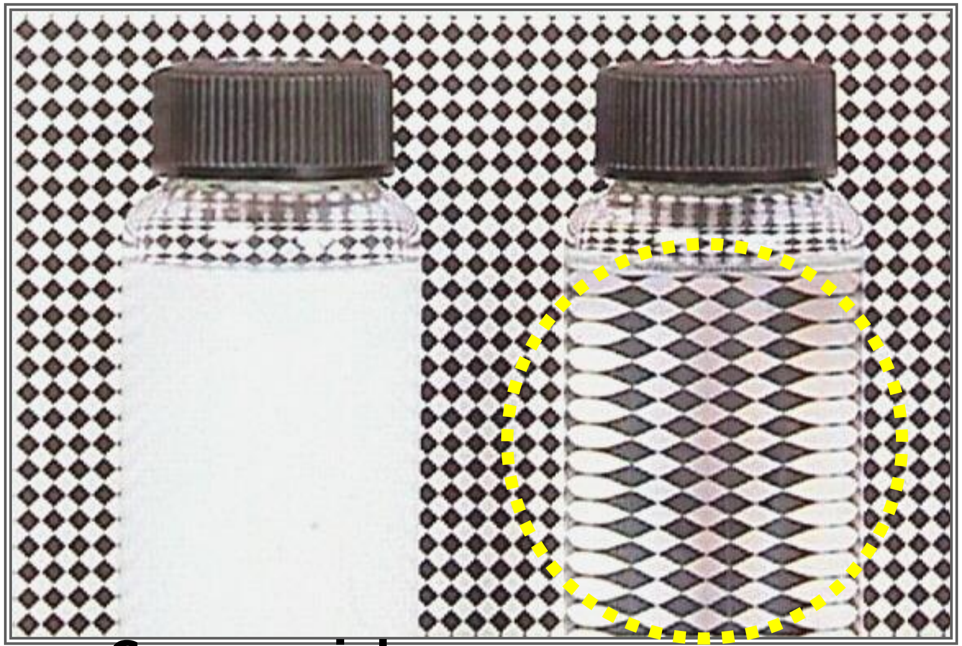




http://www.chemistry.uoc.gr/spergantis/

Effect of Super Emulsion

Vitamin E drink (Vitamin E content 10 mg/100 ml)

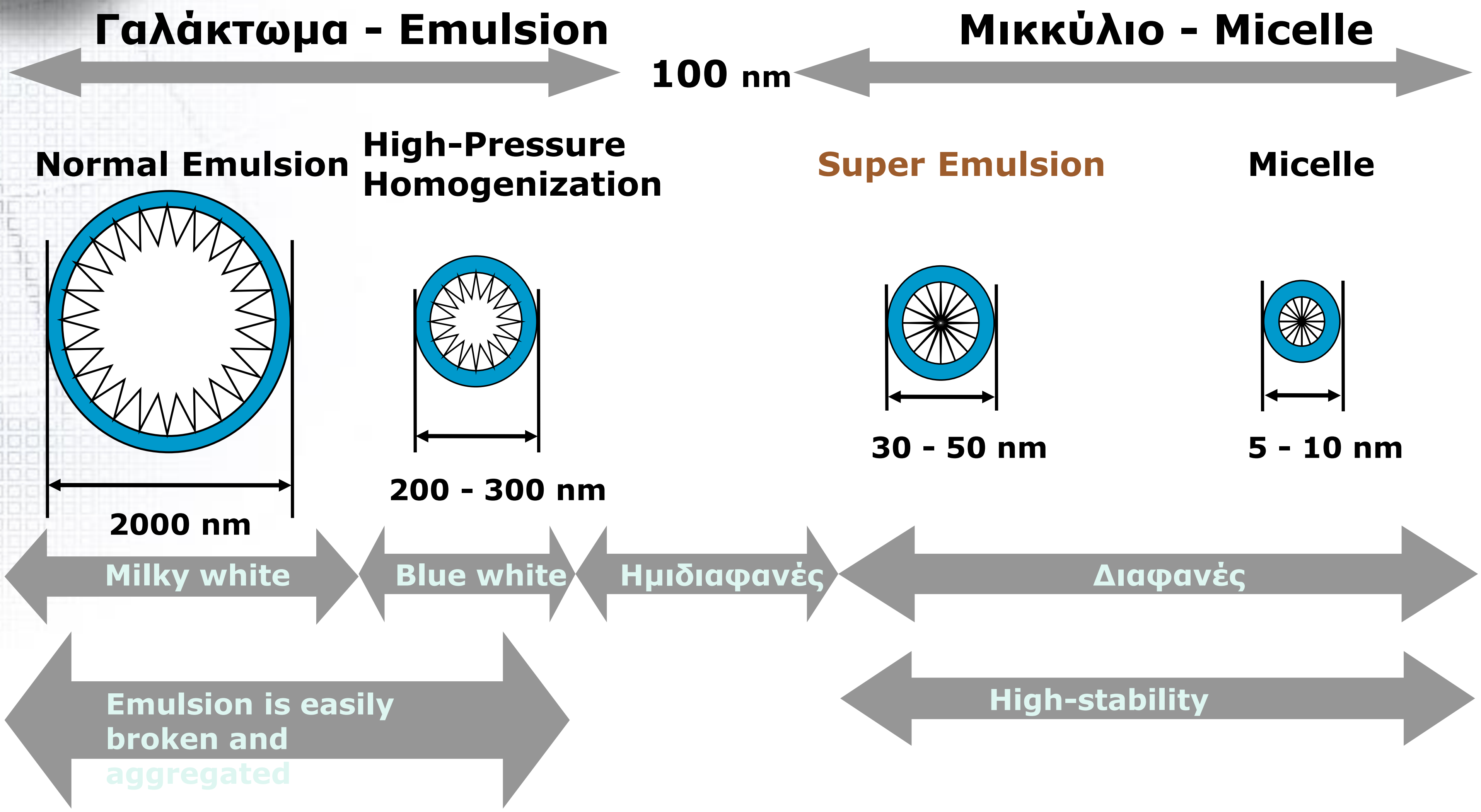


Commercial Vitamin E Emulsifier

"Super Emulsion" Vitamin E

By the use of Super Emulsion Vitamin E series a transparent drink containing vitamin E can be produced.

Particle Size in the Liquid-Liquid Dispersion Model
(a key to the Stability and Deliverability of Vitamins)



Γαλάκτωμα - Emulsion

100 nm

Μικκύλιο - Micelle

Normal Emulsion

High-Pressure Homogenization

Super Emulsion

Micelle

2000 nm

200 - 300 nm

30 - 50 nm

5 - 10 nm

Milky white

Blue white

Ημιδιαφανές

Διαφανές

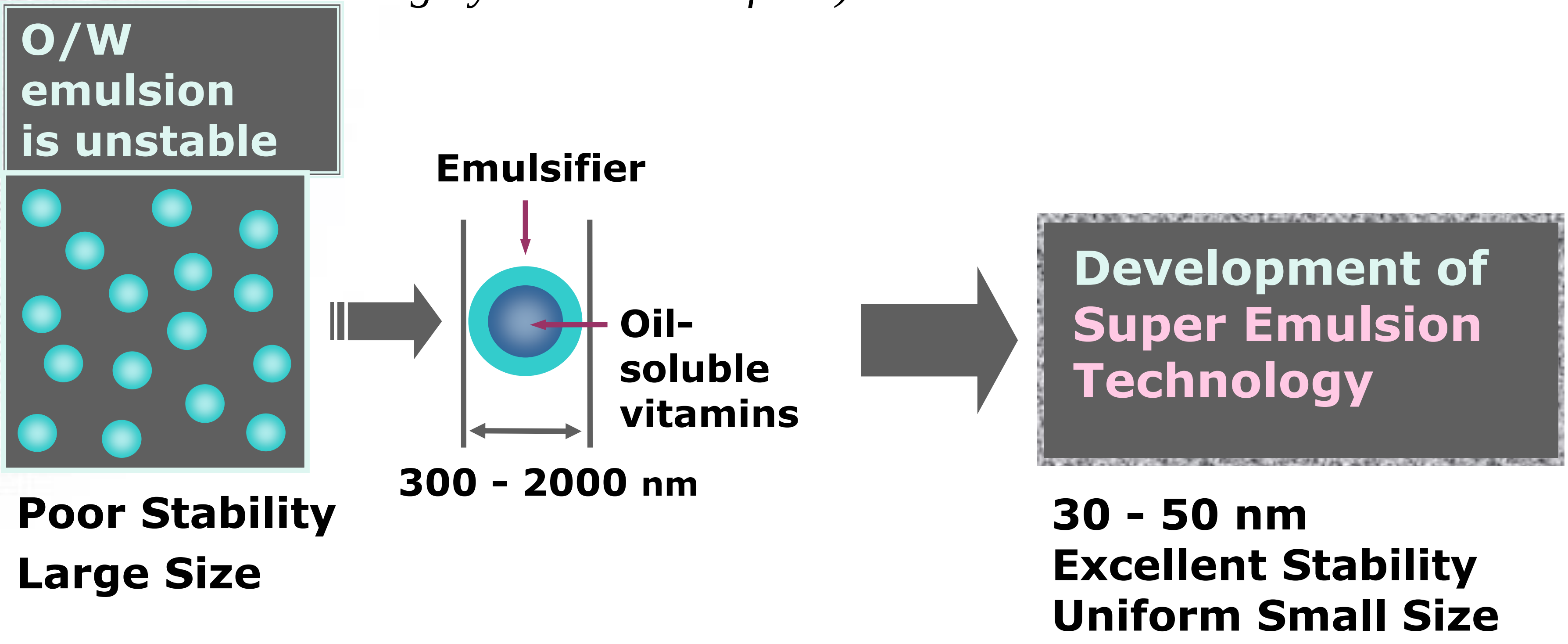
Emulsion is easily broken and aggregated

High-stability

Super Emulsion Oil-Soluble Vitamin Agent

The application of oil-soluble vitamins for water-soluble foods, O/W emulsion technology is required.

(It creates an emulsifier barrier that maintains the uniform nano-particle size of between 30 - 50 nanometers, increases stability and delivers the vitamin in a highly bioavailable form).



O/W emulsion is unstable

Poor Stability

Large Size

Emulsifier

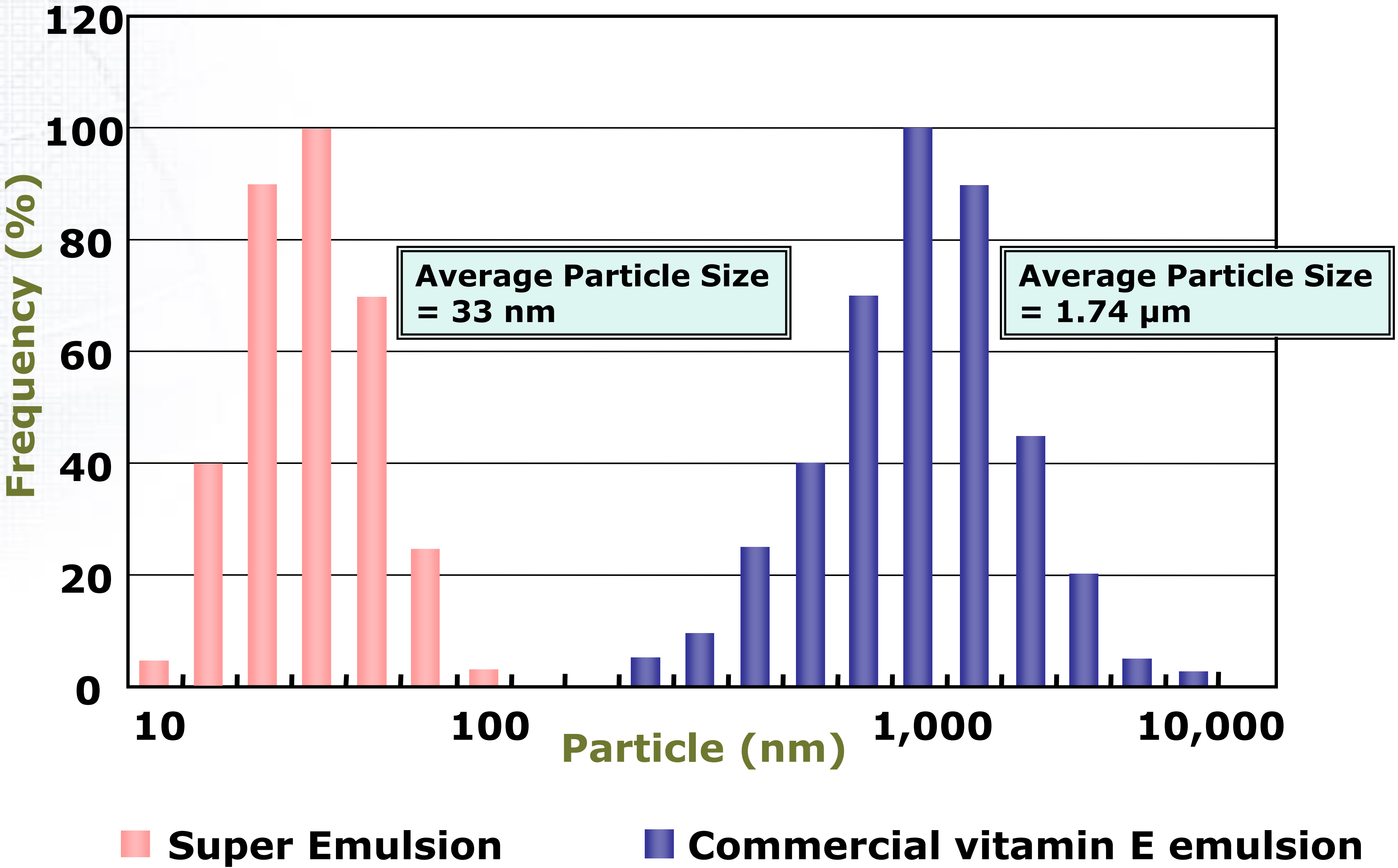
Oil-soluble vitamins

300 - 2000 nm

Development of Super Emulsion Technology

30 - 50 nm
Excellent Stability
Uniform Small Size

Particle Size of Super Emulsion



Average Particle Size = 33 nm

Average Particle Size = 1.74 µm