BME 695K/IPPH 690W

Polymers in Biomedical & Pharmaceutical Systems

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Polymers in Everyday Life

- Tooth Brush
- Shaving blade
- Shampoo
- Lotions
- Sun screens
- Mascara
- Cosmetics
- Nail enamels

1. Introduction to polymers

Polymer: a substance whose molecules consist of many (poly-) parts (meros, greek) or units.

Plastic: a polymer-based material that can be molded, cast, extruded, drawn, or laminated into objects, films, or filaments.

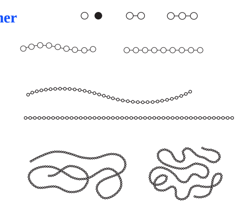
Oligomers and Polymers

Monomer, Dimer, Trimer

Multimer

Oligomer
(N = 30-200)

Polymer
(N = >200)



Molecular weight: heterogeneous → average

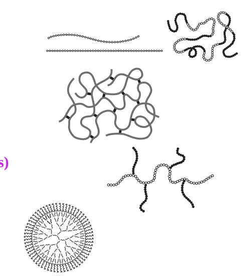
Synthetic Polymers

Linear polymers (1930's)
Homopolymer, block copolymer

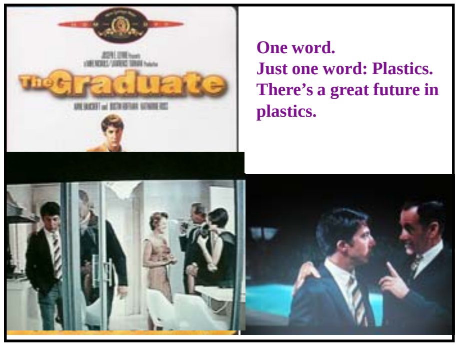
Crosslinked gel (1940's)

Branched polymers (1960's)

Dendrimers (1980's)



Polyhuman. Poly(red human)


The Graduate
One word.
Just one word: Plastics.
There's a great future in plastics.

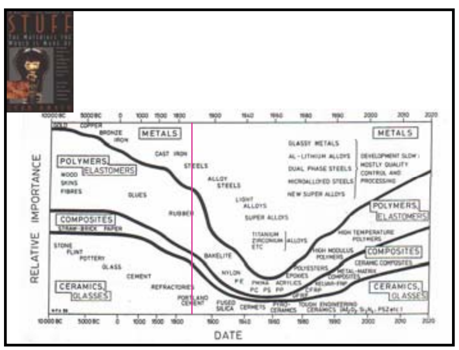

2,000,000
PLASTIC BOTTLES

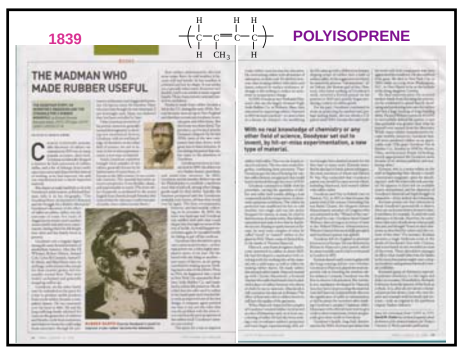

I HAVE JUST ONE WORD FOR YOU: BIOPLASTICS
One word.
Just one word: Plastics.
There's a great future in plastics.

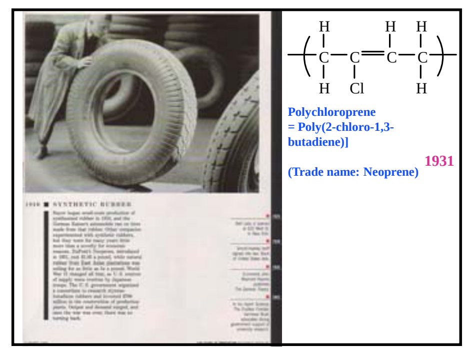

Bioplastic
Fantastic
Bugs that eat sugar and poop polymers could transform industry—and cut oil use too. by Stuart F. Brown
Making plastic


Beginning of the Polymer History: Ivory replacement in 1866
The stuff of history

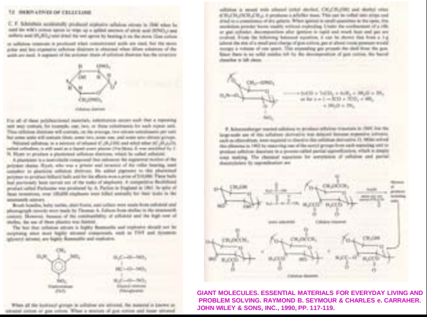

A CENTURY OF SYNTHETICS
1902 First artificial fiber, a rayon yarn, patented
1909 Baekeland patents Bakelite
1915 Pyrex glass
1925 Cellophane
1926 PVC (polyvinyl chloride)
1927 Scotch tape
1928 Safety glass
1929 Latex foam rubber
1930 Polystyrene
1932 Neoprene, the first synthetic rubber
1934 Carothers invents nylon
1935 Plexiglas
1938 Teflon
1940 Formica; mass-produced nylon stockings
1942 Polyurethane foam; bubble wrap
Prometheans in the Lab
1946 Nylon zippers; polyester
1950 Silly Putty
1952 Mylar recording tape
1958 Lycra spandex introduced
1963 Permanent-press clothing
1965 Astroturf installed in Houston Astrodome
1975 Plastic soda bottles
1976 Kevlar bulletproof vests
1985 60-atom carbon, buckminsterfullerene ("Buckyballs"), discovered


STUFF
METALS
POLYMERS
ELASTOMERS
COMPOSITES
CERAMICS, GLASSES
RELATIVE IMPORTANCE
DATE


1839
POLYISOPRENE
THE MADMAN WHO MADE RUBBER USEFUL


Polychloroprene
= Poly(2-chloro-1,3-butadiene)]
1931
(Trade name: Neoprene)

1866. CELLULOID™: THE FIRST THERMOPLASTIC. THE FIRST FLEXIBLE PHOTOGRAPHIC FILMS FOR STILL AND MOTION PICTURES



GIANT MOLECULES. ESSENTIAL MATERIALS FOR EVERYDAY LIVING AND PROBLEM SOLVING. RAYMOND B. SEYMOUR & CHARLES e. CARRAHER. JOHN WILEY & SONS, INC., 1990, PP. 117-119.

1891. Rayon: artificial silk.

Regenerated man-made fibers of cellulose from cuprammonium cellulose, viscose (cellulose xanthate), or cellulose acetate.

Sutdy on silkworm by Louis Marie Hilaire Bernigaut, Paris: Silkworm secretes a liquid from a narrow orifice that hardens upon exposure to air (silk).

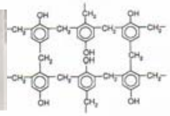
Idea: Pass a liquid that has similar characteristics to silk before being secreted through a man-made apparatus to form fibers that can spun and feel like silk.

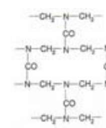
Natural strength. Proteins in strands of silk emerging from a spider's spinnerets combine resilience with extreme toughness.

Beginning of Polymers

1907. Bakelite
Phenol-formaldehyde resin.

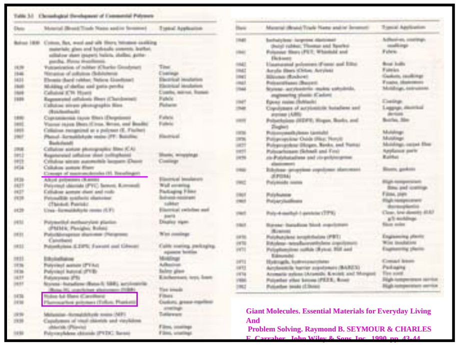
The first completely man-made substance.
The first thermoset plastic.





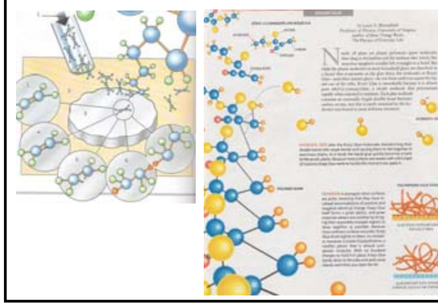
Urea-formaldehyde Resin (1929)

1907



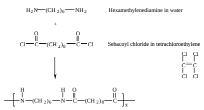
Giant Molecules. Essential Materials for Everyday Living And
Problem Solving. Raymond B. SEYMOUR & CHARLES E. Carraher. John Wiley & Sons, Inc., 1990, pp. 43-44

Vinyl Polymerization



Condensation Polymerization (Step-reaction Polymerization)

Nylon 6-10



WALLACE HUME CAROTHERS: THE FATHER OF NYLON

Fortune would not be as kind to the century's other great plastics pioneer, Wallace Hume Carothers. A brilliant chemist but a troubled soul, Carothers was hired by DuPont in 1928 from his bastion at Harvard to run the company's newly minted Purity Hall. Executives in charge of DuPont's diversification from gunpowder into synthetics made a bet—unusual at the time—that an investment in "pure" science would pay off.

They were right. Carothers was given a state-of-the-art lab, a bright young research staff and instructions to do basic research on polymers like Bakelite, cellulose and silk, whose molecular structure was a matter of intense debate. Carothers, applying the new ideas of quantum mechanics to some novel theories about the structure of polymers, correctly deduced that they were long chains of enormous numbers of small molecules chemically linked together.

Once he knew how natural polymers worked, making synthetic ones was relatively easy. Carothers' first success was neoprene, a rubber-like substance that DuPont started selling in 1932. His tour de force, however, was an artificial silk that Carothers called 66 polyamide but that DuPont dubbed nylon.

Nylon was an instant hit when it was introduced at the 1939 World's Fair. DuPont promoted it with fervor, using 30-ft.-long mannequin legs to show it off. Public demand for the stuff—especially nylon stockings—was overwhelming. Women bought more than 4 million pairs in one day; newspapers reported "nylon riots" in the department stores. During World War II, when all DuPont's nylon production went into the war effort (for parachutes, tire cords, flak vests and rope), "a pair of nylon stockings could buy you anything," as one Navy researcher recalled.

Carothers, however, saw none of this. A chronic depressive, he killed himself by drinking cyanide in a Philadelphia hotel room in 1937, two years before nylon hit the market.

—By Ivan Amato

HIS SYNTHETIC RUBBER WAS A HIT, BUT NYLON SET OFF RIOTS IN THE STORES

1939

DuPont begins to market nylon

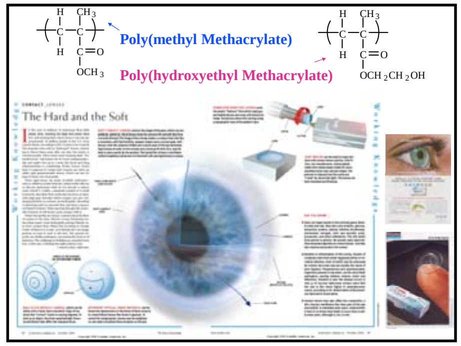
Nylon mania looks set to sweep the nation with the unprecedented demand for clothes made from the world's first synthetic fiber. People caught their first glimpse of nylon at this year's World's Fair in New York. The chemical giant DuPont has also begun to manufacture nylon commercially. Initially developed five years ago by a research team led by Wallace Carothers, nylon is produced in a reaction between an acid and an amine. Through varying the reaction components, it is possible to change the properties of the fiber from hard and tough to soft and rubbery.

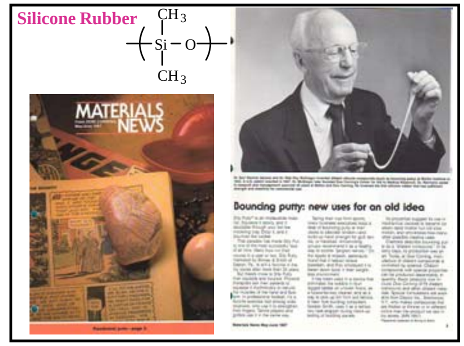
Wallace Hume Carothers

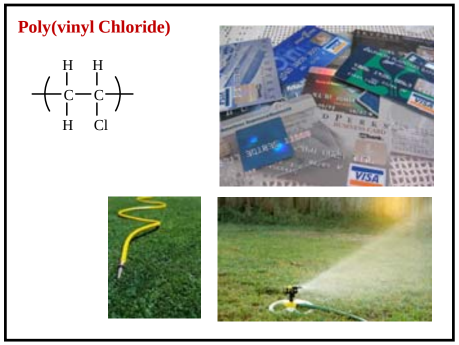
▲ Stockings were one of the first items to be made from nylon.

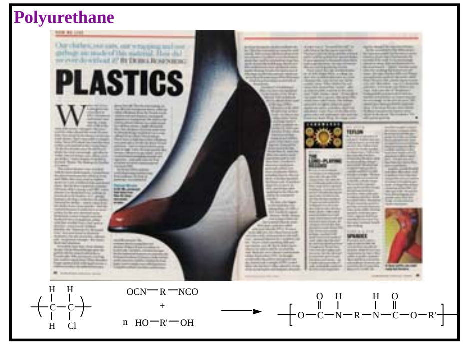
Need For New Tough Plastic.

Synthesis of nylon based on Staudinger's theory on polymeric nature of plastics.









Emergence of Synthetic Polymers

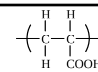
Year 1960 - present

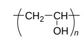
1. Large scale operations.
2. Applications in daily lives, transportation, communications, education, & leisure.
3. Polymer composites
4. Polymers as biomaterials.
5. Functional polymers
   Polymers with bioactivity
6. Smart polymers and hydrogels
7. Biodegradable polymers

Silicone Rubber

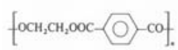

Cohesive silicone gel implants, such as this one made by McGhan, a division of Inamed,

Poly(acrylic acid)





POLY(ETHYLENE TEREPHTHALATE)



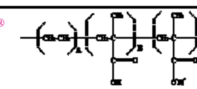
TRADENAMES:
- DACRON
- VYCRON (FIBERS)
- MYLAR (FILMS)

APPLICATIONS:
- BIOMATERIALS
- FILM
- RECORDING TAPES
- BOTTLES

Carbon Fiber

Result of a failure of making high strength polymeric adhesive

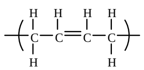
Surlyn®



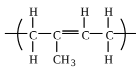
Surlyn® is the random copolymer poly(ethylene-co-methacrylic acid). The incorporation of methacrylic acid is typically low (< 15mol. %). Some or all of the methacrylic acid units can be neutralized with a suitable cation, commonly Na^+ or Zn^{+2}.

Surlyn®: Distance
Polyurethane: Spin

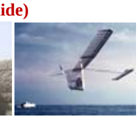
Polybutadiene



Polyisoprene (Natural Rubber)



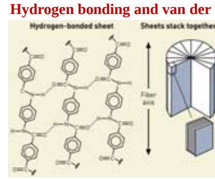
Kevlar (Poly(*p*-phenylene terephthalamide)

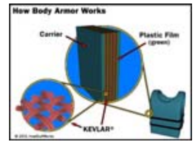


Stephanie Kwolek

"Gossamer Albatross" crossed the English Channel in 1979. It was constructed frpm a variety of plastics, including Kevlar film, Teflon, Delron, acetral resin, molded polystyrene, and carbon-reinforced polymer (E.I., DuPont).

Hydrogen bonding and van der Waals forces





Polyethylene

Workers cover the ski slopes on the Pitztal Glacier in Austria with an innovative white fleece in an effort to protect the mountain from glacier melting.

A Plastic with Hues You Can Use

The gel changes hue with shifts in temperature, moisture, acidity, or pressure

Here's an invention that seems more like a mood ring than an industrial technology: It's a gelatinous material that can be formed to any shape – from a flat sheet to an autumn leaf – and responds to changes in temperature, pressure, moisture, or acidity by changing color.

Developed by materials science professor Edwin Thomas and teammates at Massachusetts Institute of Technology, it's made up of repeating, ultrathin layers of polystyrene and a patented polymer whose molecules change shape, from short and coiled to flat and long, as conditions shift.

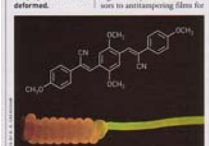
When the molecules extend and contract, they reflect different wavelengths of light, determining the hue. One use could be to identify food that's gone bad: "You want your potato chips to be dry and crisp," says Thomas. "So if a bit of gel in the packaging goes blue, you know moisture has crept in."

MATERIALS SCIENCE

STRESSED POLYMERS CHANGE COLOR

Materials incorporate fluorescent dyes as internal strain sensors

HUE AND CRY Dye molecules, such as the one shown below, change their emission color when the polymer matrix is deformed.



Light-emitting polymer blends that respond to stresses and strains by changing their hue have potential uses ranging from early internal failure sensors to antitampering films for packaging, according to the polymer scientists who developed the materials at Case Western Reserve University, Cleveland.

Associate professor Christoph Weder and graduate student Brent R. Crenshaw prepared blends of conventional polymers such as linear low-density polyethylene and a series of highly photoluminescent dyes [*Chem. Mater.*, 15, 4717 (2003)].

"The dyes serve as integral sensors," Weder says. They allow a material's mechanical deformation to be traced through a change in its fluorescence – for example, from red to green. Under UV light, the effect is readily seen by the naked eye.

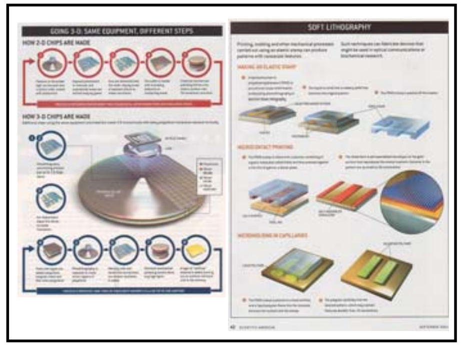
The phenomenon relies on phase separation of small aggregates of the cyano-oligo(*p*-phenylene vinylene) dye molecules in the polymer matrix. The phase behavior of the blend is controlled by varying the dye's chemical structure, the blend composition, and the processing conditions.

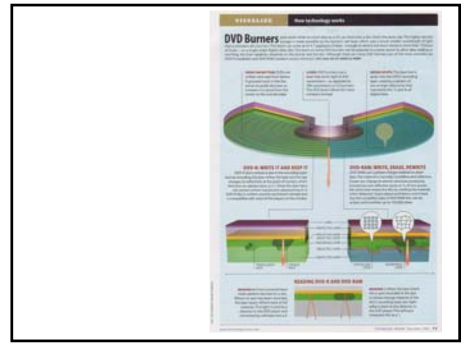
Dissolved "isolated" dye molecules exhibit "monomer emission." When the molecules are assembled as aggregates, in a polymer matrix for example, they display "excimer emission," which has a different fluorescence color.

"Our work indicates that the color change requires numerous very small aggregates of the dye molecules embedded in the polymer matrix," Weder explains. "Only with this architecture can mechanical deformation of the matrix efficiently break up the dye aggregates and lead to dispersion and dissolution of the dye molecules.

"We are currently working on applying the concepts to other polymer systems – for example, elastomers, in which the effect can be reversible," Weder adds. "We are also extending the approach to other stimuli, such as changes in temperature." – MICHAEL FREEMANTLE

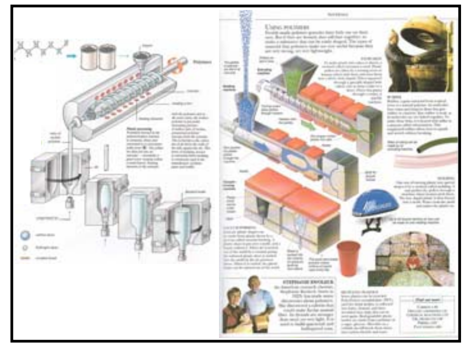

NEWS OF THE WEEK
NOVEL MOLECULAR THERMOMETERS
Thermosensitive polymers begin to glow above a threshold temperature
Sea Snails Shod With Iron Sulfide Scales

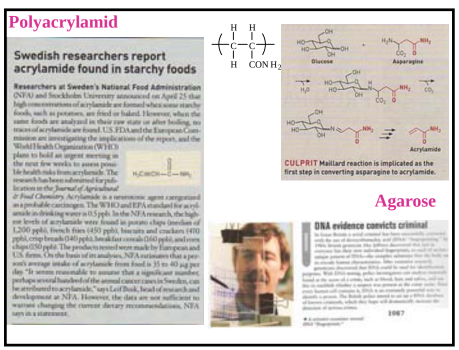

GOING 3-D: SAME EQUIPMENT, DIFFERENT STEPS
SOFT LITHOGRAPHY


DVD Burners

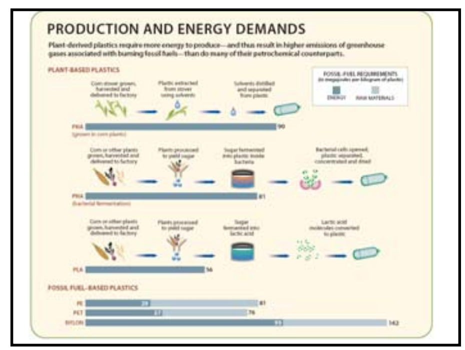

Science & Technology Electronics
Just Two Words: Plastic Chips
They can endow just about anything with computer smarts—and they'll be cheap


Self Healing Plastics
Plastics that can heal themselves
Plastic, heal thyself




Polyacrylamid
Swedish researchers report acrylamide found in starchy foods
Agarose
DNA evidence convicts criminal


Biodegradable Polymers
how green are green plastics?

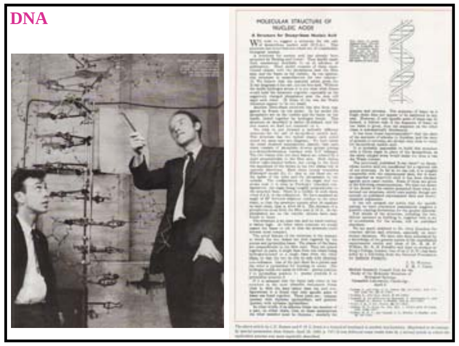

PRODUCTION AND ENERGY DEMANDS
Plant-derived plastics require more energy to produce—and thus result in higher emissions of greenhouse gases associated with burning fossil fuels—than do many of their petrochemical counterparts.
PLANT-BASED PLASTICS
FOSSIL FUEL-BASED PLASTICS

Natural Polymers

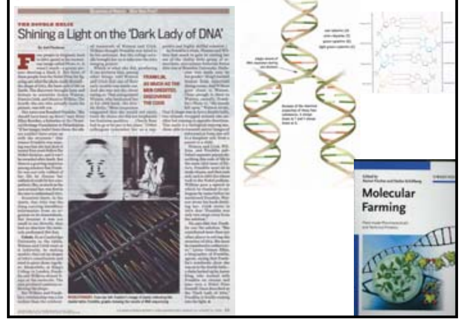
Nucleic acids
Proteins
Polysaccharides

Are natural polymers safe?

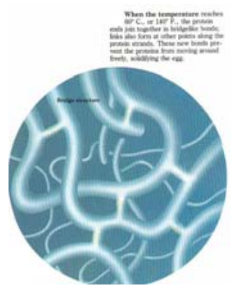
DNA

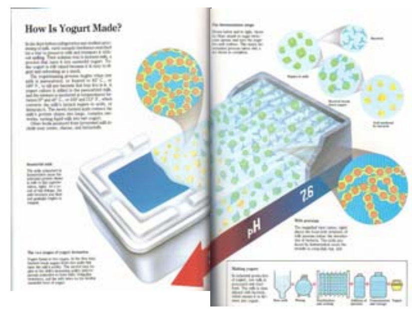


DNA



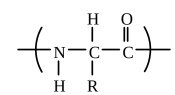
Protein

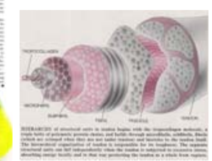




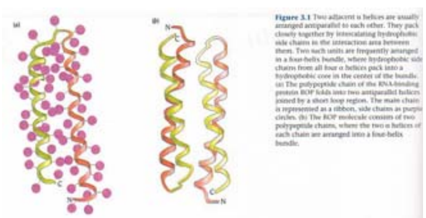
Gelatin

Peptide bond

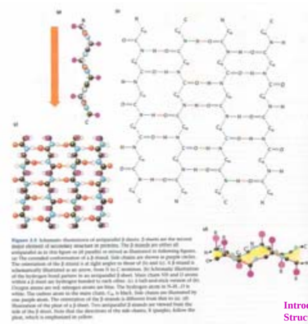




Protein Folding

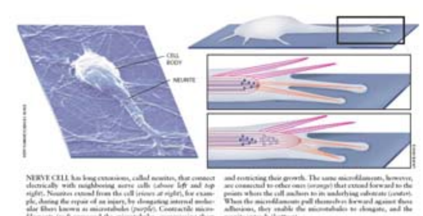


Introduction To Protein Structure
Carl Branden & John Tooze, 1991

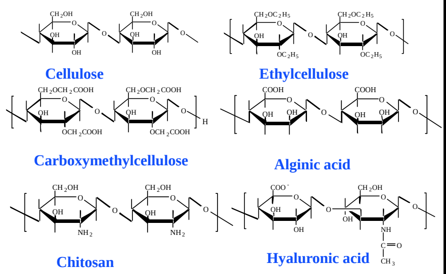


Introduction To Protein Structure
Carl Branden & John Tooze

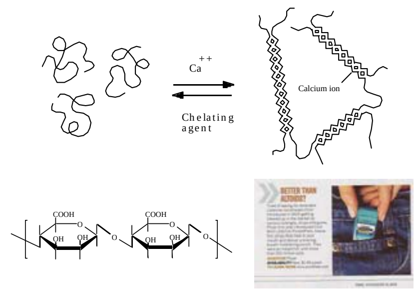
Microtubules, Microfilaments



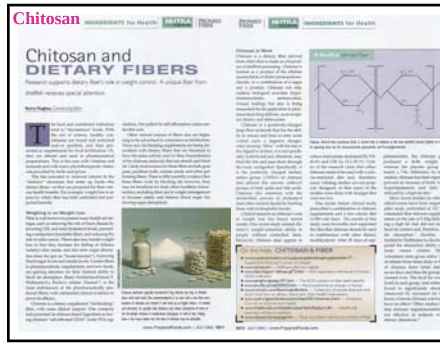
Polysaccharides

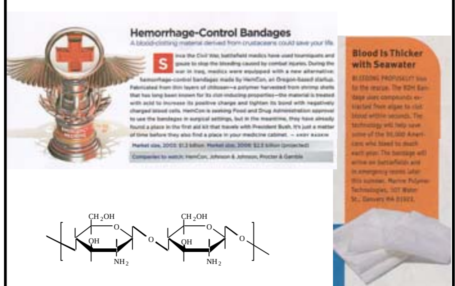


Alginic Acid



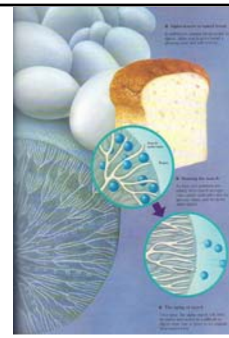
Chitosan





Starch

Bread:
Soft
Hard



Guar Gum, Xanthan Gum

Pectin

Polymers:

They are indispensable in our daily life and in the biomedical and pharmaceutical systems.