POLYMER SCIENCE : GLORIOUS PAST, PRESENT CHALLENGES AND EXCITING FUTURE

Dr. S. Sivaram
A 201,Polymers and Advanced Materials Laboratory,
National Chemical Laboratory,
Pune-411 008, INDIA

Tel : 0091 20 2589 2614
Fax : 0091 20 2589 2615
Email : s.sivaram@ncl.res.in

National Chemical Laboratory
Pune

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POLYMER SCIENCE : PAST, PRESENT AND FUTURE

- **What are polymers?**
- **Its origins and history**
- **What are the new frontiers in polymer science ?**

- **How relevant is polymer science today ?**
- **How will this science address some of the most pressing problems of our society ?**
- **The transition from visible to invisible : The future of polymer science**

THE AGES OF HUMAN KIND

Human Civilization has been marked by several ages, which are all material based:

- ***Stone Age***
- ***Bronze Age***
- ***Iron Age (Steel. Aluminum)***

- ***Polymer Materials Age (Carbon based materials)***

-

Polymer (< **Gk *poly* "many" + *meros* "parts"**)

- A substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few constitutional unit. **Source: IUPAC (International Union of Pure & Applied Chemistry)**

- It is solid in its finished state in most cases and can be shaped by flow into a finished article.

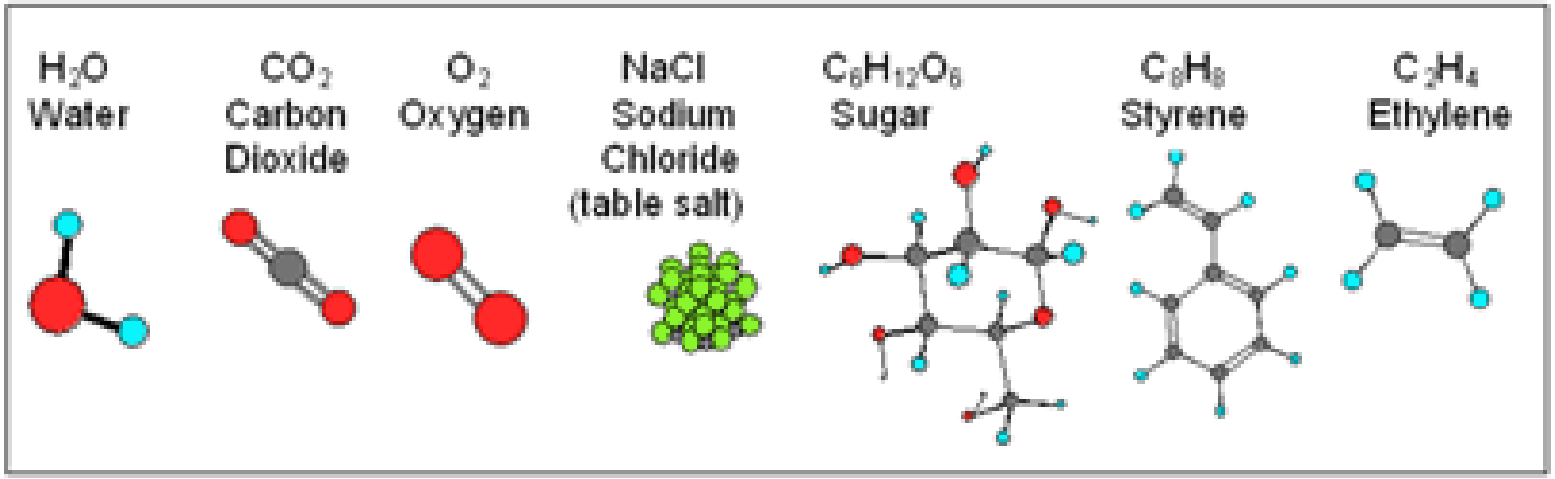
- "Plastic" and "resin" are often used synonomously with "polymer",
  - **"Plastic" & "resin" refers to polymers with various additives (such as pigments and stabilizers) that turn the polymer into a practical product**

What are Polymers?

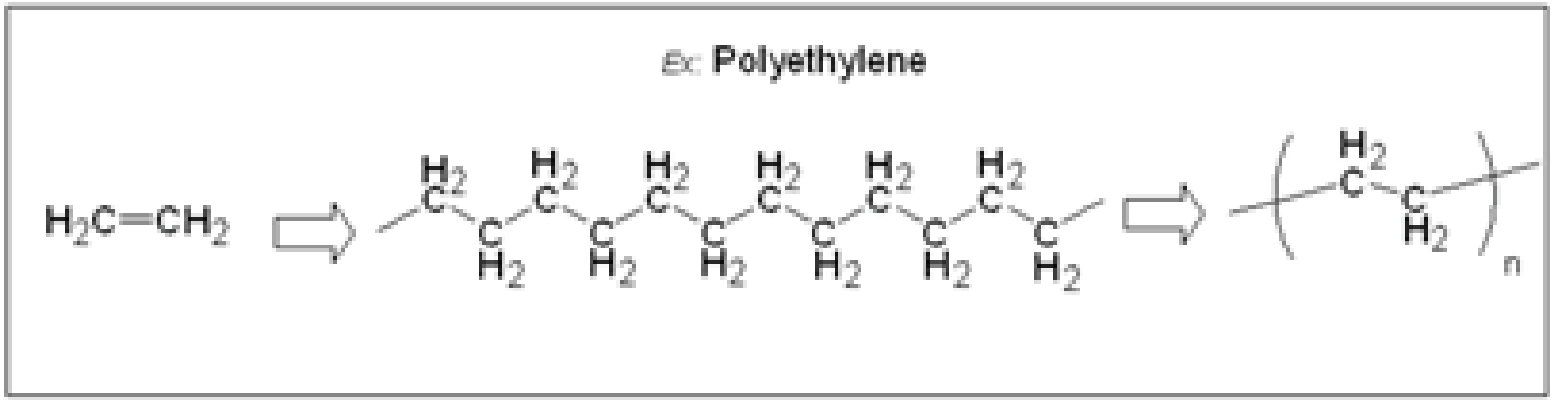
Poly mers *are made up of many* Mono mers

Many Units — One Unit

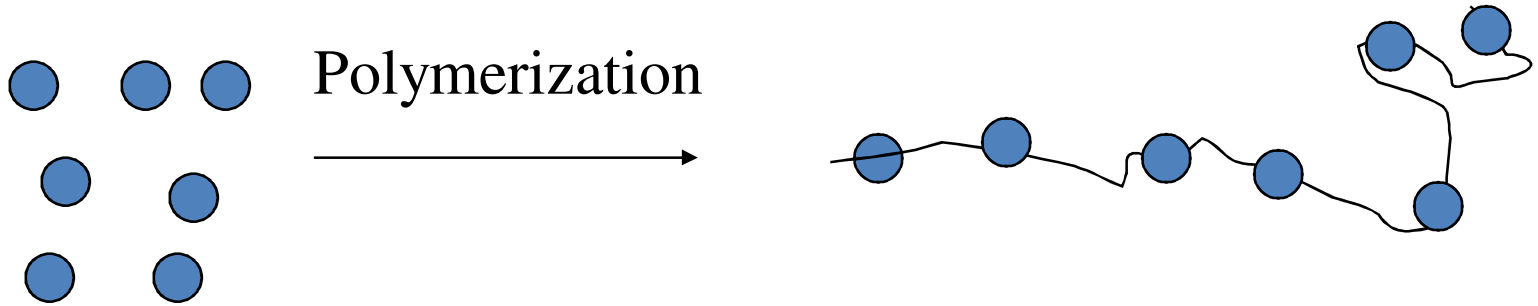
Small Molecules and Monomers:



Macromolecules (Polymers):

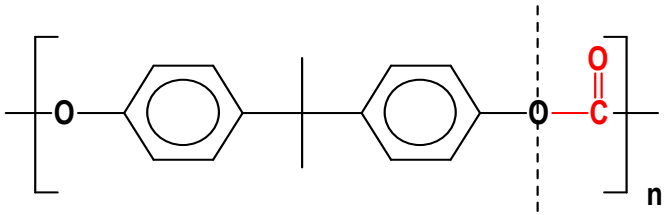


What is polymerization ?



Mono mer

Poly mer



Structural unit from BPA

Structural unit from DPC or $COCl_2$

Repeat Unit

$M_{RU} = 16 + 76 + 42 + 76 + 16 + 12 + 16 = 254$

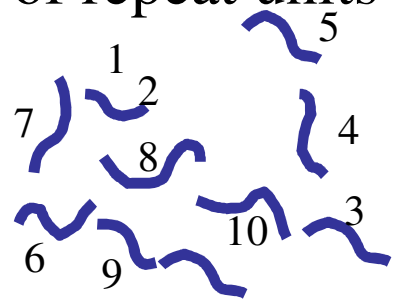
$M = \bar{M}_{SU} \times DP = M_{RU} \times n$

DP = no. SU

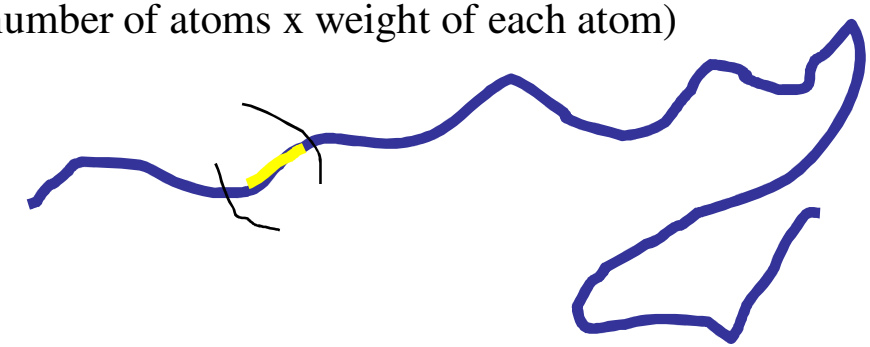
How Big is Big?

The most important feature of a polymer is its "length" or molecular weight.

Repeat Unit Molecular Weight = *M* Number of repeat units = n



(*M* = number of atoms x weight of each atom)



Molecular weight Mw = nM

Each polymer has a minimum molecular weight M_e necessary for entanglements

$M > M_e$ =>
polymer bends and forms knots with itself and other polymers

Example: Polyethylene

Monomer: Ethylene $CH_2=CH_2$

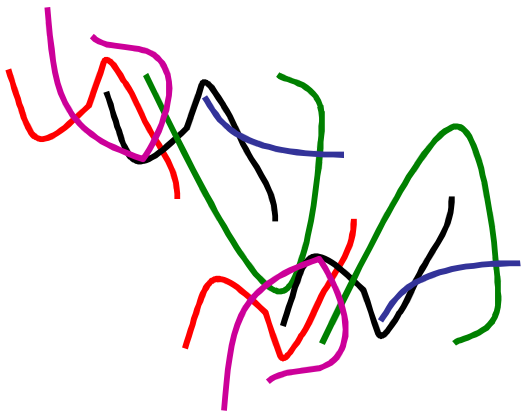
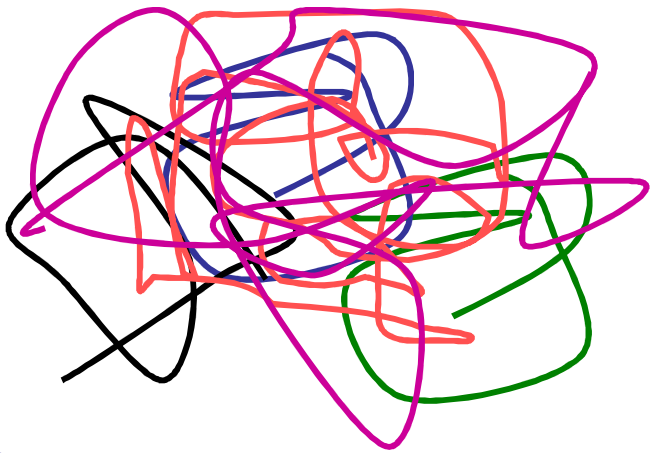
- Molecular Weight = 28 g/mol
- Colorless, Flammable Gas at room Temperature

Polymer: Polyethylene $\cdots - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - \cdots$

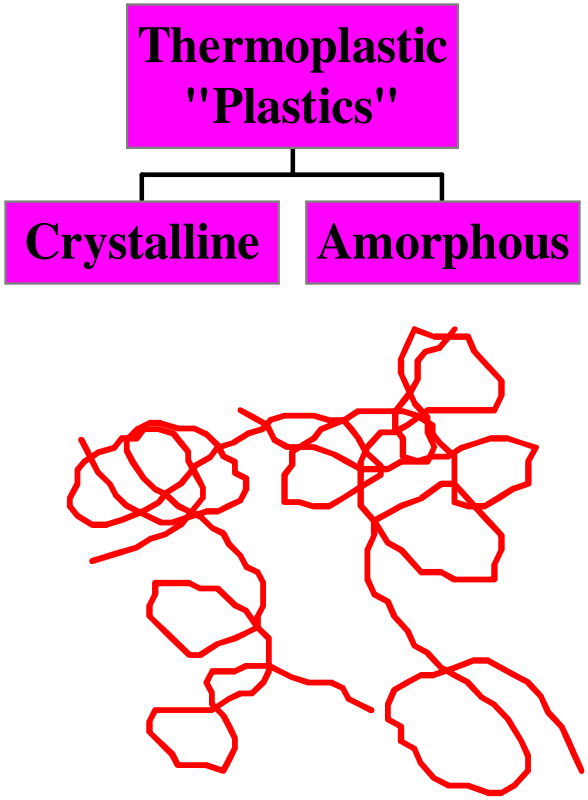
- Composed of hundreds to thousands of ethylene units
- Molecular Weight = 1,500 - 100,000 g/mole
- Milky white plastic solid that "melts" at 85℃ to 100℃

Polymers consist of large number of repeat units

Length + Flexibility Make it Happen...

Short Molecules	**Long Molecules**
	
• Can separate easily • Too short to entangle • Behave independently	• **Completely entangled** • **Molecules do not easily move independently**
Bowl of Rice	Bowl of Spaghetti

Thermoplastic Polymers

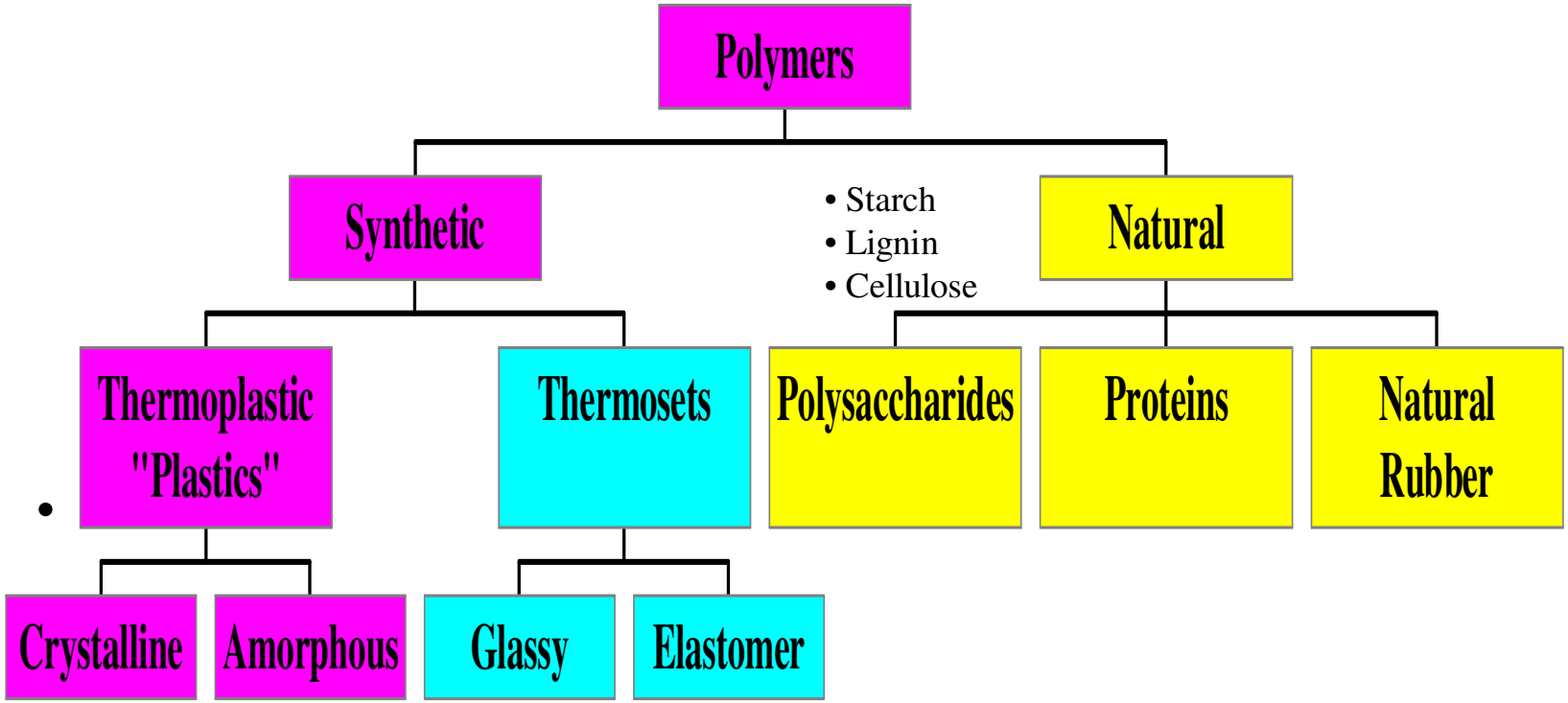


THERMOPLASTIC ("THERMO" = HEAT + "PLASTIC" = FORMABLE)

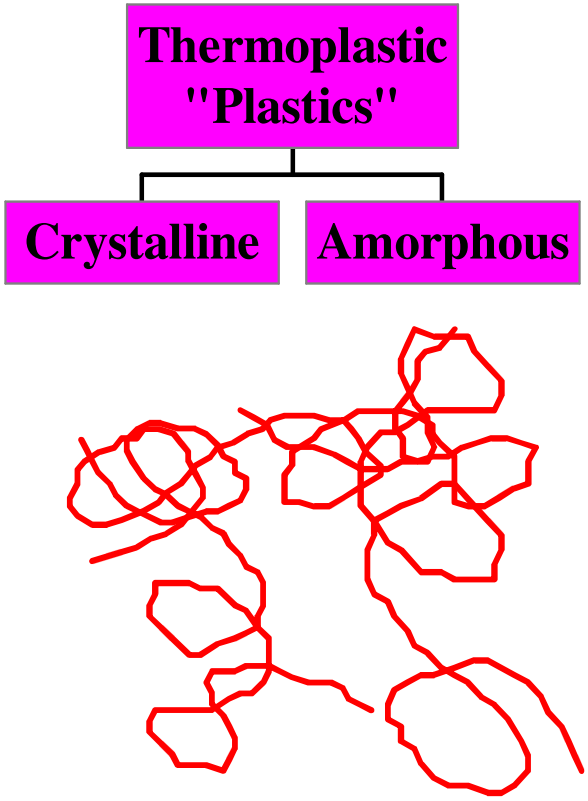
- **Are large, linear, unconnected molecules**
- **Undergo no chemical reaction during molding**
- **Properties:**
  - **soften with heat to a high viscosity melt**
  - **hard at room temperature**
  - **can be re-melted and re-processed (recyclable)**
  - **molecules are entangled but not bonded to one another**
  - **resist breaking but can be attacked by solvents**

Examples: Polyethylene, Polystyrene, Polycarbonate

Polymers : Family Tree



Thermoplastic Polymers



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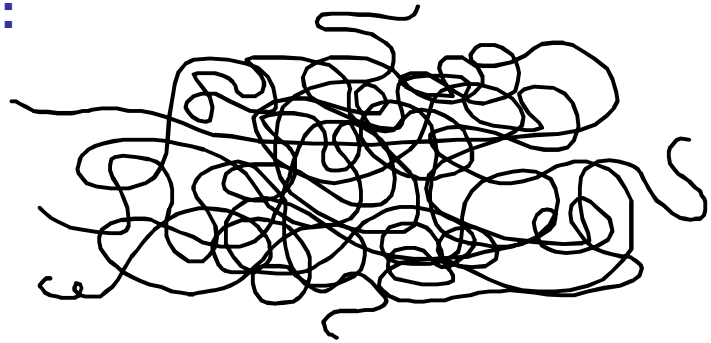
Thermoplastics: Amorphous vs. Crystalline

AMORPHOUS:



Have a glass transition temperature (Tg) - the temperature at which the polymer transforms from glassy state (hard) to rubbery state(soft).

Characteristics:

- **Random Entanglement of Chains**
- **Chemical Susceptibility**
- **Moderate Heat Resistance**
- **Impact Resistance**
- **Low Shrinkage**
- **Wide Softening Range**
- **Typically transparent in thicker sections.**

CRYSTALLINE

- ***Have both crystalline (ordered) and amorphous regions***
- ***Have an amorphous phase Tg; Crystalline phases characterized by melting temperature Tm > Tg.***

Characteristics:

- **Chemical Resistance**
- **High Heat Resistance**
- **Notch Sensitivity**
- **High Shrinkage**
- **Fatigue Endurance**
- **Wear Resistance**
- **Typically opaque in thicker sections**

Thermoset Polymers

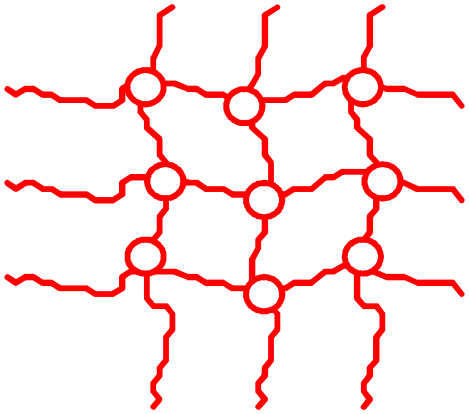
Thermosets

Glassy

- Rigid at room temperature

Elastomer

- Flexible at room temperature



THERMOSET ("THERMO" = HEAT + "SET" = HARDEN)

- Begin as small molecules (low viscosity liquid)
- React ("cures") by heat, catalysis, or other chemical means to form an infinite molecular network
- Properties of Glassy Thermosets
  - rigid at room temperature
  - network is permanent, so it is not re-processable
  - tend to break more easily than thermoplastics ("brittle")
  - solvent resistant

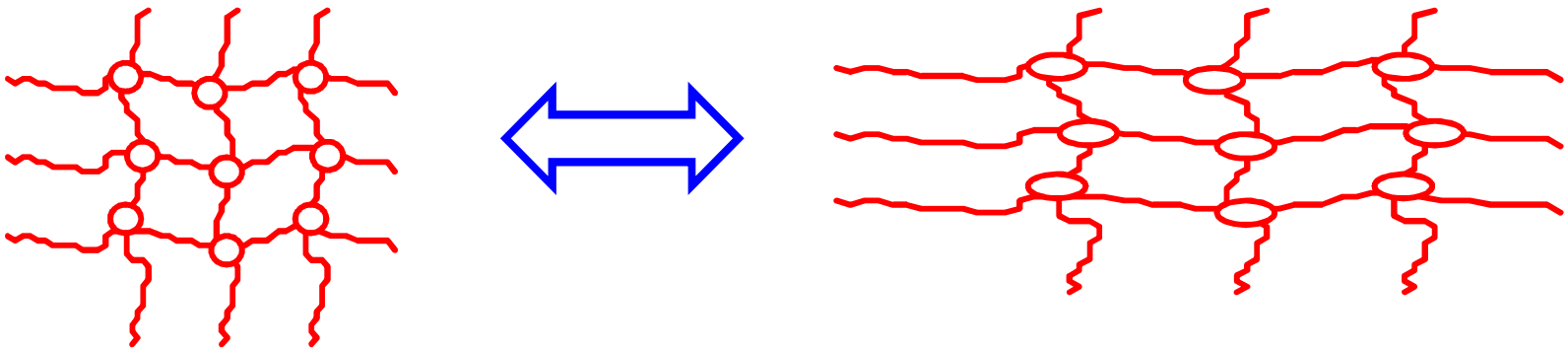
Example: Epoxy, Phenolics

Elastomers

- **Thermosets that are soft at room temperature (above the glass transition temperature)**

- **Stretchy and recover when applied stress is released.**

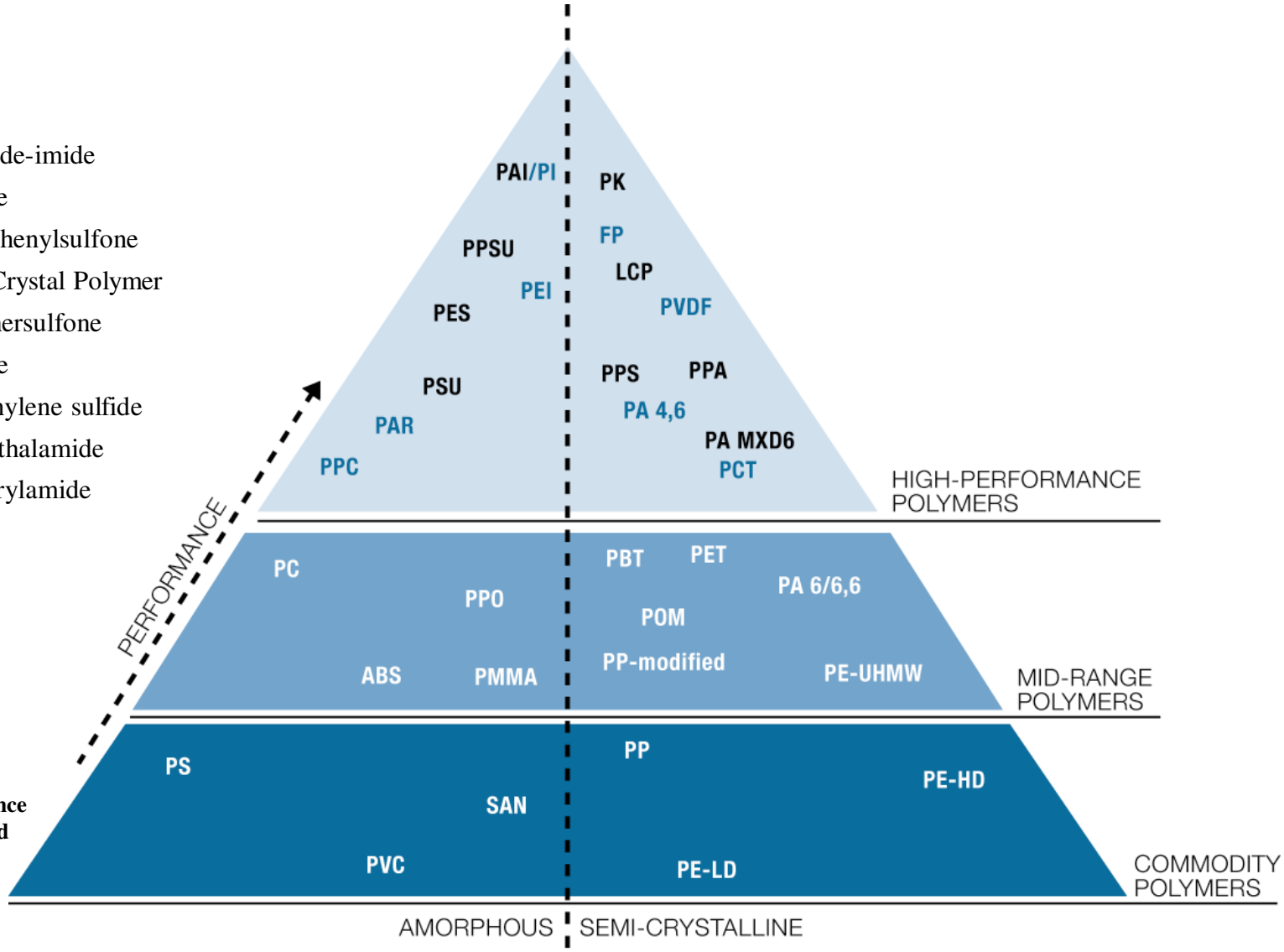
- **"Stretchiness" is due to the fact that polymers extend upon deformation but are prevented from permanent flow by cross-links.**



Examples: "Rubbers", Silicones

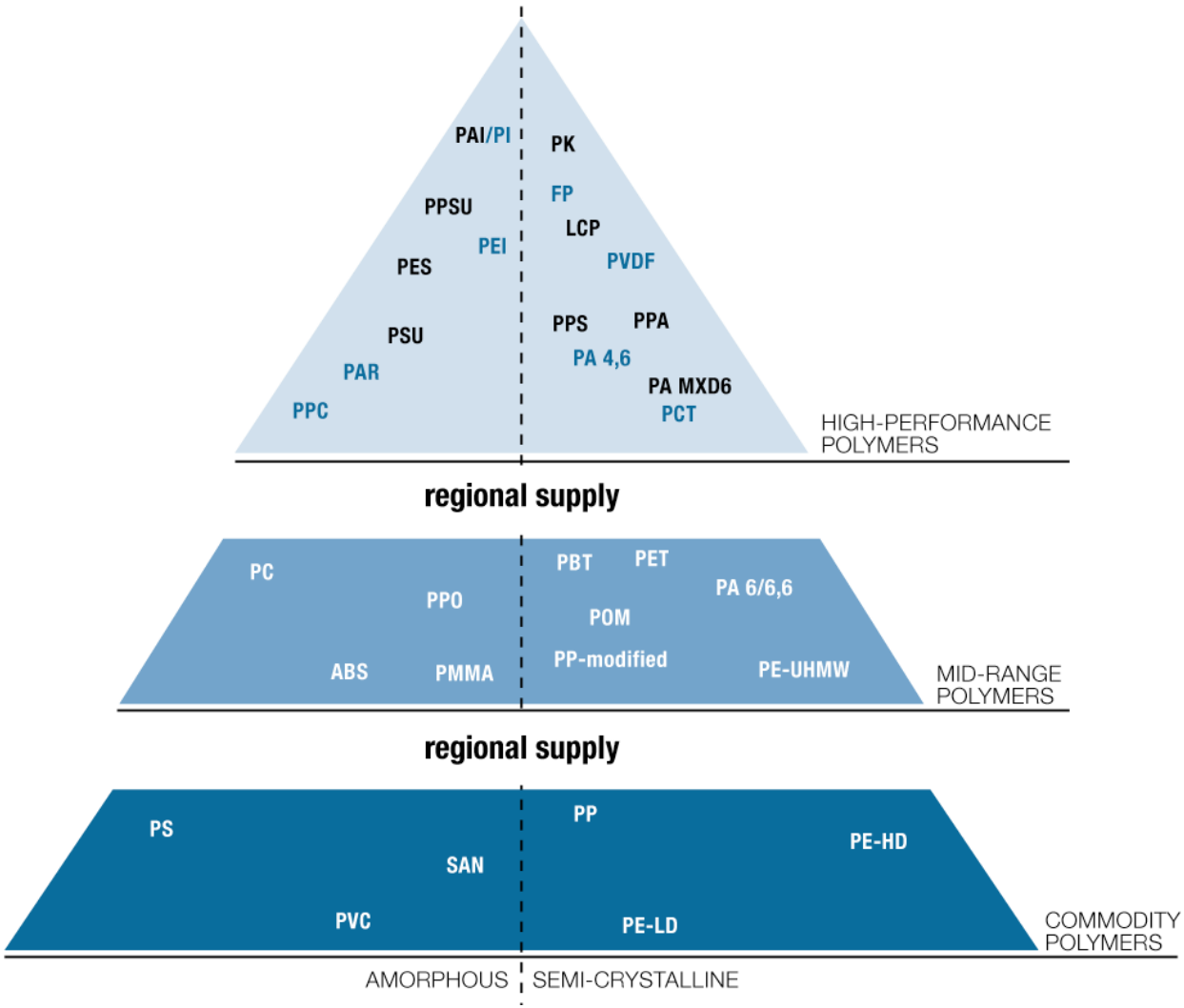
THE POLYMER PYRAMID

PAI = TORLON® polyamide-imide
PK = KADEL® polyketone
PPSU = RADEL® R polyphenylsulfone
LCP = XYDAR® Liquid Crystal Polymer
PES = RADEL® A polyethersulfone
PSU = UDEL® polysulfone
PPS = PRIMEF® polyphenylene sulfide
PPA = AMODEL® polyphthalamide
PA MXD6 = IXEF® polyarylamide



Acronyms for high-performance plastics from Solvay Advanced Polymers are shown in black

Number of Producers		Volume of Producers
1-4	global supply	<1-100 million lbs.
5-10	regional supply	2-5 billion lbs.
50-70	regional supply	>50 billions lbs.



The Periodic Table of the elements by Medvedev was a historic achievement in chemistry and enabled chemists to see the relationship between structure and properties of the basic elements.

Polymers also have a strong relationship between structure and properties and this 'Periodic Table of Polymers' is a first attempt to provide a simple codification of the basic polymer types and structures.

The diversity of polymer types makes it impossible to include all of the variations in one simple table and this table only includes the most common polymers.

Tangram Technology
Periodic Table of Thermoplastics

TANGRAM TECHNOLOGY | Consulting Engineers

Increasing performance

Amorphous → **Semicrystalline**

Increasing crystallinity

Random molecular orientation in both molten and solid phases.

General Characteristics
- Soften gradually.
- Generally transparent.
- Lower Tensile Strength and Tensile Modulus.
- Lower Density.
- Low Creep Resistance.
- High Dimensional Stability.
- Low fatigue resistance.
- Easy to bond using adhesives and solvents (high surface energy).

Commodity					Engineering				Performance				
PS-HI High Impact Polystyrene	**PS-GP** General Purpose Polystyrene	**ABS** Acrylonitrile Butadiene Styrene (Copolymer)	**SAN** Styrene Acrylonitrile (Copolymer)		**PMMA** Polymethyl methacrylate (Acrylic)	**PPO** (Modified) Polyphenylene Oxide	**PC** Polycarbonate		**PAR** Polyarylate	**PSU** Polysulphone	**PES** Poly-ethersulphone	**PPSU** Poly-ethersulphone (Block copolymer)	
PVC-P Plasticised Poly-vinylchloride	**SBS** Styrene-Butadiene-Styrene (Copolymer)	**SMA** Styrene-Maleic Anhydride (Copolymer)	**ASA** Acrylonitrile Styrene Acrylate (Copolymer)	**SB** Styrene-Butadiene (Copolymer)						**PEI** Polyetherimide	**PAI** Poly-amideimide	**PI** Polyimide	**PBI** Polybenzimide azole
PVC-U Unplasticised Poly-vinylchloride	**CA** Cellulose Acetate	**CAB** Cellulose Acetate Butyrate	**CAP** Cellulose Acetate Propionate	**CP** Cellulose Propionate	**PET-G** Glycolised Polyethylene terephthlate	**PVC-UX** Crosslinked Unplasticised PVC	**PVC-C** Chlorinated PVC						
PVC-U High-Impact Unplasticised PVC								**PA 6/3/T** Amorphous polyamide	**PPA** Poly-phthalamide (Amorphous)	**PARA** Polyaryl amide			

Random molecular orientation in molten phase, densely packed crystallites in solid phase.

General Characteristics
- Sharp melting point.
- Generally translucent or opaque.
- Higher Tensile Strength and Tensile Modulus.
- Higher Density.
- High Creep Resistance.
- Low Dimensional Stability.
- High fatigue resistance.
- Difficult to bond using adhesives and solvents (low surface energy).

PE-LD Low Density Polyethylene	**PE-LLD** Linear Low Density Polyethylene	**PE-MD** Medium Density Polyethylene	**PMP** Polymethyl pentene	**EVA** Ethylene-vinyl Acetate (12% VA)	**PE-X** Crosslinked Polyethylene	**PB** Polybutene-1 (Polybutylene)	**PE-UHMW** Ultra-high Molecular Weight PE	**PA 11** Polyamide 11 (Nylon 11)	**PA 12** Polyamide 12 (Nylon 12)	**PPA** Poly-phthalamide	**PA 46** Polyamide 46 (Nylon 46)	**PEK** Poly-etherketone	**PEEK** Polyetherether ketone
		PE-C Chlorinated Polyethylene	**PE-VLD** Very Low Density Polyethylene	**EMA** Ethylene-methyl Acrylate	**PBT** Polybutylene-terephthlate	**PA 6** Polyamide 6 (Nylon 6)	**PA 66** Polyamide 66 (Nylon 66)		**LCP** Liquid Crystal Polymer (Aromatic copolyester)	**PFA** Perfluoroalkoxy	**ECTFE** Ethylene-chlorotrifluoro-ethylene	**PCTFE** Polychloro-trifluoro-ethylene	**PTFE** Poly-tetrafluor-ethylene
	PP Polypropylene (Homopolymer)	**PP** Polypropylene (Copolymer)			**PET** Crystalline Polyethylene-terephthlate	**PA 6/10** Polyamide 6/10 (Nylon 6/10)	**PA 6/12** Polyamide 6/12 (Nylon 6/12)	**POM** Poly-oxymethylene (Acetal Copolymer)	**EVOH** Ethylene-vinyl Alcohol	**PPS** Polyphenylene Sulphide	**FEP** Fluorinated ethylene-propylene	**ETFE** Ethylene-tetrafluoro-ethylene	**PVDF** Poly-vinylidene-fluoride
PE-HD High Density Polyethylene								**POM** Poly-oxymethylene (Acetal Homopolymer)					

KEY TO MAJOR POLYMER FAMILIES: Styrenes | Polyolefins | Vinyls | Cellulosics | Polyesters | Polyamides | Acrylics | Polycarbonates | Acetals | Polysulphones | Imides | Fluoropolymers

Reduced Version. Issue 2: February 2008

Synthetic Polymers

- Poly (ethylene terephthalate) {PET}
  - Soda bottles, laundry detergent containers

- High Density Polyethylene {HDPE}
  - Milk jugs, shampoo bottles, landfill liners

- Poly (Vinyl Chloride) {PVC}
  - Shower curtains, siding, piping

- Low Density Polyethylene {LDPE}
  - Garbage bags, tape, disposable diapers

- Polypropylene {PP}
  - Chip and cookie bags, tupperware

- Polystyrene {PS}
  - Packing foam, disposable cups

CHEMISTRY

CHEMISTRY OF MATERIALS

- Natural materials
- Synthetic materials
- Hybrid Materials
- Nanomaterials

CHEMISTRY OF LIFE

- Origin of life
- Understanding biological processes
- Understanding diseases/ search for cure
- Deeper insight into consciousness and human aging

CHEMISTRY OF ENERGY

- Newer forms of energy
- Light and water as energy
- Interconversion of energy
- Efficient use of energy

CHEMISTRY OF ENVIRONMENT

- Global climatic changes
- Stratosphere ozone depletion
- Conservation of biosphere
- Quality of air / water
- Adverse consequence of excessive consumption on environment

POLYMER MATERIALS : HISTORY

- **Polymers were the product of post war renaissance in chemical industry driven by the promise of inexpensive petroleum derived feed-stocks**
- **The fifties and sixties saw the introduction of many polymers that changed the face of human civilization**
- **From early curiosities polymers became an indispensable part of our daily living and so ubiquitous that we no longer realize how addicted we are to polymer materials !**

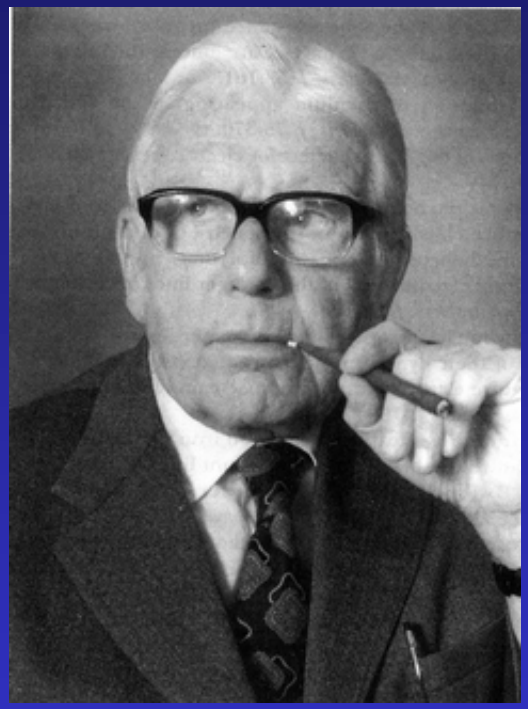
Chemistry creates its own object. This creative power, similar to that of arts distinguishes it fundamentally from the other natural and historical sciences

Marcellin Bertholet, 1860

(1827- 1907)

Bertholet gave the first general discussion on polymerism, that is, materials which have the same chemical composition, but differ only in their molecular weights

THE TALE OF TWO HERMAN(N)'S : THE POLYMER PIONEERS



X Ray Crystallography of macromolecules to show that a molecule could be larger than its unit cell (1926-28)

Herman Mark (1895-1992)

Concept of macromolecules as large molecules linked together by covalent bonds (1920)

Hermann Staudinger (1881-1965)

STAUDINGER AND THE ORIGIN OF MACROMOLECULAR CHEMISTRY

- He propounded the revolutionary concept, that macromolecules can be formed by linking of a large number of small molecules by means of covalent bonds
- Created the " molecular blueprint " that led to the explosive growth of man made organic materials
- Through sheer audacity of intuition and imagination, he proposed that polymers were composed of large number of base units linked together by covalent bonds *(Ber. Dtsch. Chem. Ges., 53, 1073 (1920).* At that time he had no experimental evidence for his hypothesis.
- Wieland told him " Dear colleague, abandon your idea of large molecules; organic molecules with molecular weights exceeding 5000 do not exist. Purify your products and they will turn out to be low molecular weight materials "
- His ideas met with much resistance and criticism from eminent chemists of the period, notable amongst them, Emil Fischer. People called the chemistry being pursued by Staudinger as "Grease Chemistry". After one of the lectures given by Staudinger in Zurich in 1925, one of the speakers termed Staudinger`s championship of long chain molecules as akin to some traveler in Africa reporting that he had seen a zebra 400 meters long !
- Staudinger persevered in spite of being ostracized by the scientific community. From 1926, he abandoned research in organic chemistry and shifted exclusively to macromolecules.

STAUDINGER AND THE ORIGIN OF MACROMOLECULAR CHEMISTRY

- **First experimental evidence for existence of long chains came in 1922. Hydrogenation of natural rubber was not accompanied by the formation of volatile cyclic hydrocarbons *(Staudinger and Fritschi,Helv.Chim.Acta,5, 785 (1922)***

- **First time the term "macromolecules" was used in chemistry**

- **The first definition of macromolecules: "For such colloid particles, in which the molecule is identical with the primary particle, and in which the individual atoms of this colloid molecule are linked together by covalent bonds, we propose for better differentiation the name macromolecule *(Staudinger,Ber.Dtsch.Chem.Ges.,57,1203(1924)***

- **Much of the rigorous proof for the existence of macromolecules will come from physical measurements (viscosity measurements, molecular weight measurements by ultracentrifuge, osmometry and light scattering as well as X Ray diffraction)**
- **But being quintessentially an organic chemist, Staudinger was skeptical of physical measurements. Staudinger believed polymers to possess "rigid rod like structure", a belief he will not abandon for several years. When evidence began building up that polymers have flexible chains, Staudinger ignored them.**

HERMAN MARK AND THE EVOLUTION OF THE STRUCTURE OF POLYMERS

- Mark, along with Staudinger and Carothers can be credited as a cofounder of Polymer Science

- Mark was trained as an organic chemist. His PhD thesis was on the chemistry of free radicals under the supervision of Schlenk

- With Polanyi , Mark began to explore the technique of Crystallography (X Ray and electron diffraction)for the study of organic molecules at Kaiser Wilhelm Institute

- One of the materials chosen was cellulose fiber. They found that cellulose fiber upon stretching leads to increase in modulus

Mark presents his results in a meeting of the Society of German Natural Scientists at Dusseldorf in 1926 ; He says that important information can be obtained from unit cells and space groups, even if detailed molecular structures are not known; He proposes that in polymers "lattice forces are comparable to intramolecular forces and the entire crystallite behaves like a large molecule"

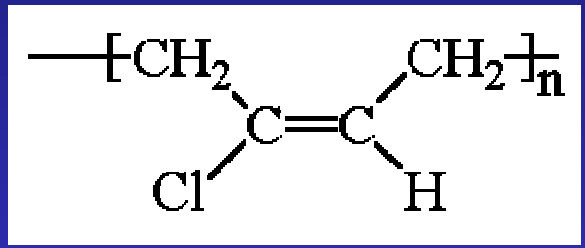
HERMAN MARK AND THE POLYMER INDUSTRY

- In 1926, Mark becomes the Director of research at IG Fabenindustrie in Ludwigshafen, a large producer of rayon and cellulose acetate. Here he develops the first commercial process for producing styrene
- Mark and Meyer solve the crystal structure of Cellulose in 1928, the first crystal structure of a polymer which reconciles the X-Ray pattern with the chemical composition.
- Using X Ray, Mark establishes that natural rubber is a polymer of isoprene, namely, 1,4-polyisoprene and that isoprenes are in a *cis* configuration in the polymer chain
- It is interesting that although Mark provided the most unequivocal support to the macromolecular hypothesis of Staudinger, he and Staudinger were not in good terms. Staudinger felt that macromolecular chemistry was his field and he looked upon physicists and physical chemists as interlopers, who stole his ideas.
- Mark left IG Farben in 1932 and returned to the University of Vienna . It was in Vienna that he along with Eugene Guth proposed the statistical theory of rubber elasticity and developed the Mark Houwink relationship, relating dilute solution viscosity of a polymer solution to its molecular weight
- One of his famous students in Vienna was Max Perutz who went on to found the Medical Research Council at Cambridge which became a centre of excellence in protein crystallography

WALLACE CAROTHERS AND THE BIRTH OF RATIONAL POLYMER SYNTHESIS

1896-1937

- Trained as an organic chemist with Roger Adams, PhD, 1924
- Hired as a faculty at Harvard
- DuPont lured him to Wilmington Delaware to lead a fundamental research programme in organic chemistry and polymers
- by 1931, he had synthesized chloroprene and polymerized to a new synthetic rubber, called by DuPont as Neoprene
- Publishes his seminal paers in JACS in 1929 where in he establishes the equivalence of organic and polymer forming reactions, namely esterification and polyesterification



Poly(chloroprene)

WALLACE CAROTHERS AND THE BIRTH OF RATIONAL POLYMER SYNTHESIS

With Julian Hill, extends the reaction to adipic acid and hexamethylene diamine, a polyamide forming reaction , leading to the first synthesis of Nylon-66 in 1934. Nylon-66 goes into production in 1939

Develops a theoretical understanding of the polycondensation reaction relating the average degree of polymerization to fractional conversions (Carother`s Equation)

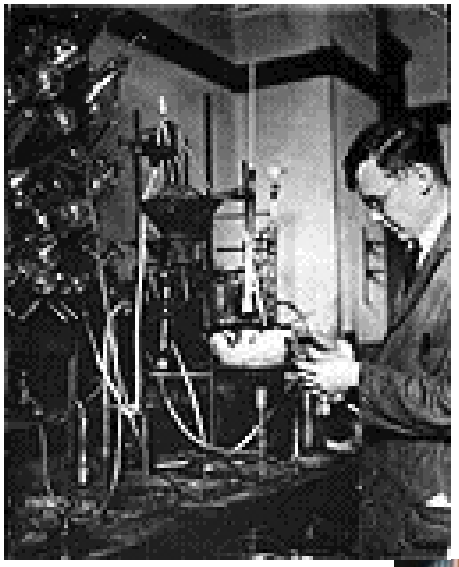
Carothers had been troubled by periods of mental depression since his youth. Despite his success with nylon, he felt that he had not accomplished much and had run out of ideas

His unhappiness was compounded by the death of his sister, Isobel, and on the evening of April 28, 1937 he checked into a Philadelphia hotel room and committed suicide by drinking a cocktail of lemon juice laced with potassium cyanide

His daughter, Jane, was born seven months later on November 27, 1937.

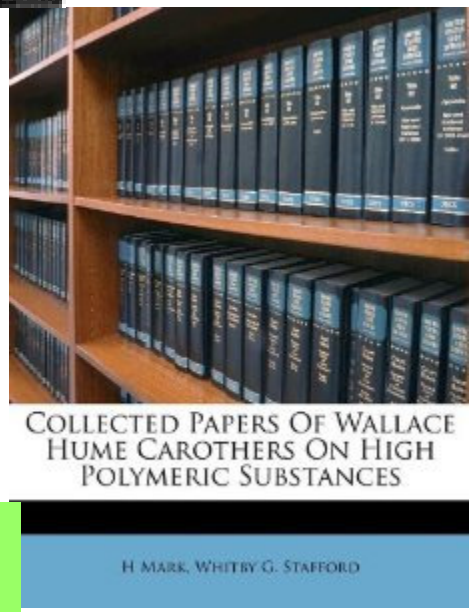
A young man joins Carothers at DuPont in 1934 who will go on to make history

ALIPHATIC POLYESTERS : PIONEERING CHEMISTRY OF WALLACE HUME CAROTHERS



1896-1937

54 papers 400 pages



Enough for one lifetime !

Published 1940

STUDIES ON POLYMERIZATION AND RING FORMATION

Twenty eight papers from 1929 to 1935

Carothers addressed one important question:

(a) If two bifunctional molecules, e. g., one dibasic acid and one glycol or diamide, react, two possibilities occur. The reaction can result (1) in a chain polymer of lower or higher molecular weight, which still bears either hydroxyl or carboxyl terminal groups or (2) in a smaller or larger ring, which does not contain the reactive group.

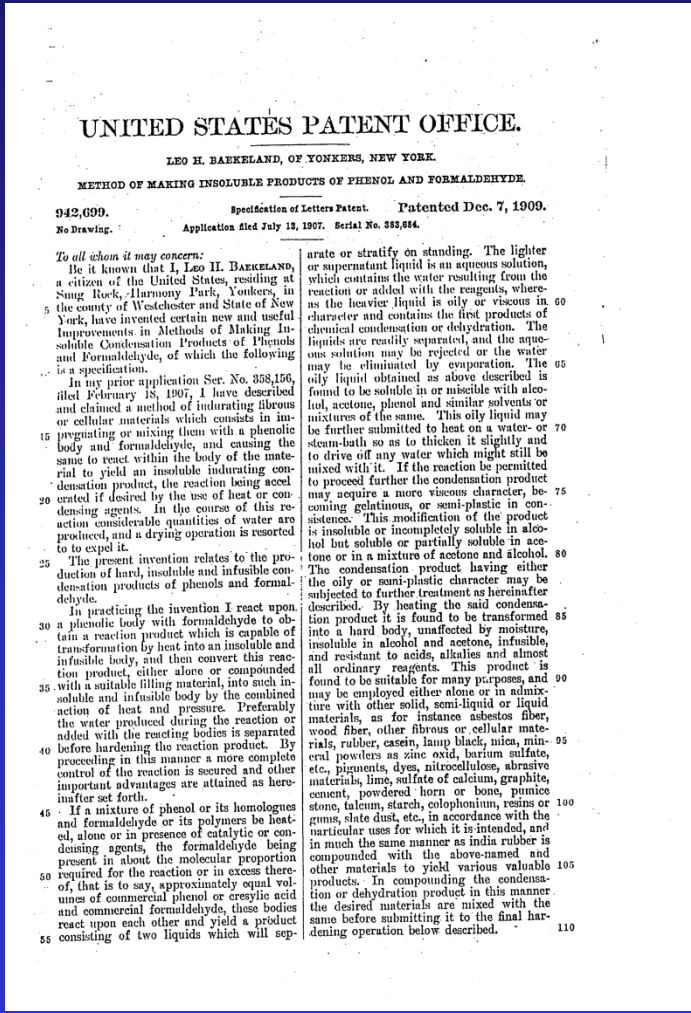
Under what conditions does either of these two possibilities take place and what is the molecular weight of the resulting compound?

IX. Polymerization*

TABLE OF CONTENTS

* *Wallace H. Carothers; Chemical Reviews 8, 353-426 (1931); Communication No. 55 from the Experimental Station of the E. I. du Pont de Nemours and Company.*
Received March 21, 1931. Published June 1931.

THE DAWN OF THE CHEMICAL INDUSTRY: THE MANUFACTURE OF BAKELITE



UNITED STATES PATENT OFFICE.

LEO H. BAEKELAND, OF YONKERS, NEW YORK.

METHOD OF MAKING INSOLUBLE PRODUCTS OF PHENOL AND FORMALDEHYDE.

942,699. Specification of Letters Patent. Patented Dec. 7, 1909.

No Drawing. Application filed July 13, 1907. Serial No. 383,684.

To all whom it may concern:

Be it known that I, LEO H. BAEKELAND, a citizen of the United States, residing at Snug Rock, Harmony Park, Yonkers, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Methods of Making Insoluble Condensation Products of Phenols and Formaldehyde, of which the following is a specification.

In my prior application Ser. No. 358,156, filed February 18, 1907, I have described and claimed a method of indurating fibrous or cellular materials which consists in impregnating or mixing them with a phenolic body and formaldehyde, and causing the same to react within the body of the material to yield an insoluble indurating condensation product, the reaction being accelerated if desired by the use of heat or condensing agents. In the course of this reaction considerable quantities of water are produced, and a drying operation is resorted to to expel it.

The present invention relates to the production of hard, insoluble and infusible condensation products of phenols and formaldehyde.

In practicing the invention I react upon a phenolic body with formaldehyde to obtain a reaction product which is capable of transformation by heat into an insoluble and infusible body, and then convert this reaction product, either alone or compounded with a suitable filling material, into such insoluble and infusible body by the combined action of heat and pressure. Preferably the water produced during the reaction or added with the reacting bodies is separated before hardening the reaction product. By proceeding in this manner a more complete control of the reaction is secured and other important advantages are attained as hereinafter set forth.

If a mixture of phenol or its homologues and formaldehyde or its polymers be heated, alone or in presence of catalytic or condensing agents, the formaldehyde being present in about the molecular proportion required for the reaction or in excess thereof, that is to say, approximately equal volumes of commercial phenol or cresylic acid and commercial formaldehyde, these bodies react upon each other and yield a product consisting of two liquids which will separate or stratify on standing. The lighter or supernatant liquid is an aqueous solution, which contains the water resulting from the reaction or added with the reagents, whereas the heavier liquid is oily or viscous in character and contains the first products of chemical condensation or dehydration. The liquids are readily separated, and the aqueous solution may be rejected or the water may be eliminated by evaporation. The oily liquid obtained as above described is found to be soluble in or miscible with alcohol, acetone, phenol and similar solvents or mixtures of the same. This oily liquid may be further submitted to heat on a water- or steam-bath so as to thicken it slightly and to drive off any water which might still be mixed with it. If the reaction be permitted to proceed further the condensation product may acquire a more viscous character, becoming gelatinous, or semi-plastic in consistence. This modification of the product is insoluble or incompletely soluble in alcohol but soluble or partially soluble in acetone or in a mixture of acetone and alcohol. The condensation product having either the oily or semi-plastic character may be subjected to further treatment as hereinafter described. By heating the said condensation product it is found to be transformed into a hard body, unaffected by moisture, insoluble in alcohol and acetone, infusible, and resistant to acids, alkalies and almost all ordinary reagents. This product is found to be suitable for many purposes, and may be employed either alone or in admixture with other solid, semi-liquid or liquid materials, as for instance asbestos fiber, wood fiber, other fibrous or cellular materials, rubber, casein, lamp black, mica, mineral powders as zinc oxid, barium sulfate, etc., pigments, dyes, nitrocellulose, abrasive materials, lime, sulfate of calcium, graphite, cement, powdered horn or bone, pumice stone, talcum, starch, colophonium, resins or gums, slate dust, etc., in accordance with the particular uses for which it is intended, and in much the same manner as india rubber is compounded with the above-named and other materials to yield various valuable products. In compounding the condensation or dehydration product in this manner the desired materials are mixed with the same before submitting it to the final hardening operation below described.

US Patent 942, 699, December 7, 1909

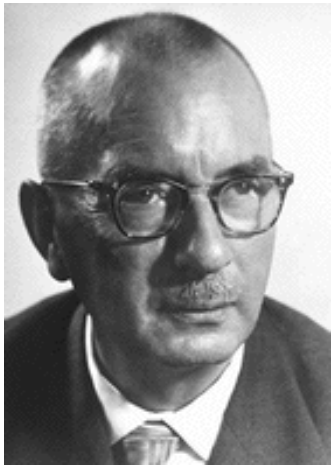
- Baekland set out to discover a substitute for Shellac, then wholly supplied by India to the world
- In the process he made the first man made material, heralding the age of plastics, a discovery considered as revolutionary
- Heat resistant and insulating, demand from the burgeoning electrical goods industry
- Baekland named his new material Novolak
- He founded a company called General Bakelite Corporation in 1910 to manufacture the product

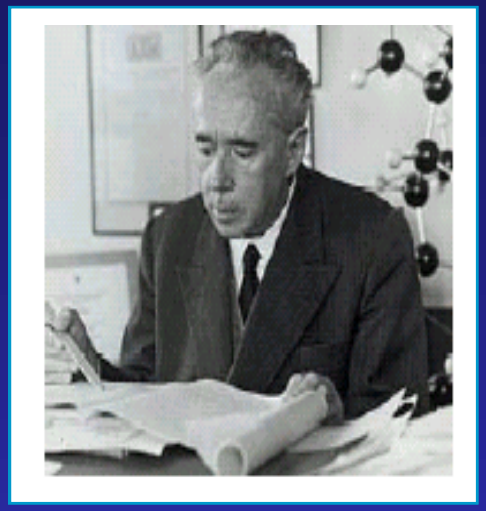
THE DAWN OF THE CHEMICAL INDUSTRY: THE MANUFACTURE OF BAKELITE

Leo Baekland (1863-1944)

When asked why he chose to work in the field of synthetic resins, he replied, "to make money"

POLYETHYLENES AND POLYPROPYLENES





BUNDESREPUBLIK DEUTSCHLAND

AUSGEGEBEN AM 14. APRIL 1960

DEUTSCHES PATENTAMT

PATENTSCHRIFT

Nr. 973 626

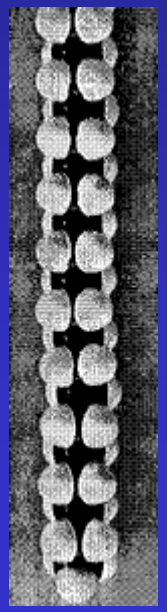
KLASSE 39c GRUPPE 25ca

INTERNAT. KLASSE C08f

Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr,
Dr. Heinz Breil, Oberhausen (Rhld.), Dr. Erhard Holzkamp, Düsseldorf,
und Dr. Heinz Martin, Mülheim/Ruhr
sind als Erfinder genannt worden

Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr

Verfahren zur Herstellung von hochmolekularen Polyäthylenen



CRYSTALLINE HIGH POLYMERS OF α-OLEFINS

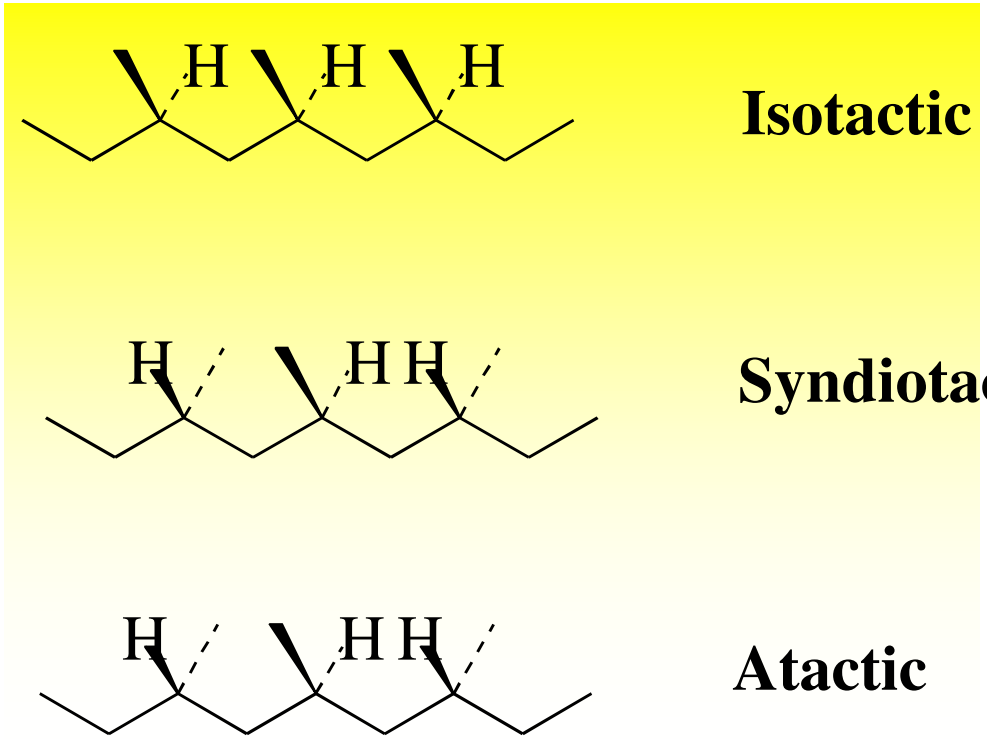
Sir:

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained[1] by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

DE 973626
Nov 18, 1953

G.Natta
JACS 77, 1708, 1955
(March 20, 1955)

Tacticity in Polymers: eg., Polypropylene



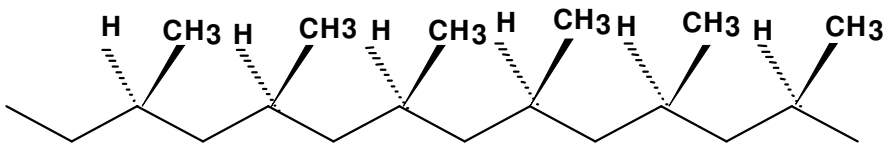
Polymerization with stereo-specificity/ regio-specificity:

Stereoisomerism in polymers arises from different spatial arrangements or configuration of the atoms or substituents which can be inter-converted only by the breakage and reformation of the chemical bond

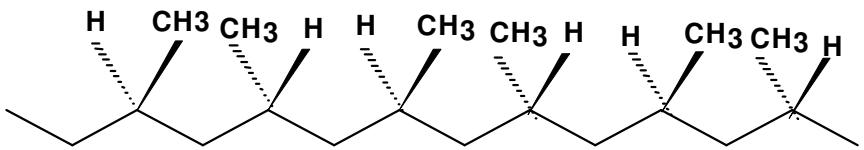
Regularity in configuration of successive chiral, asymmetric or pseudochiral carbon (C*) determines the tacticity of the polymer chain

POLYPROPYLENE

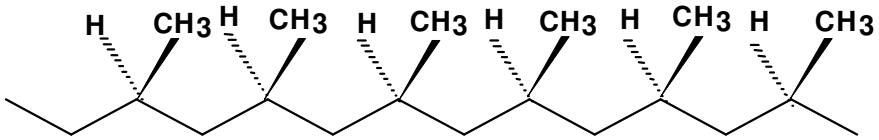
$CH_2=CH-CH_3$ "PROCHIRAL"



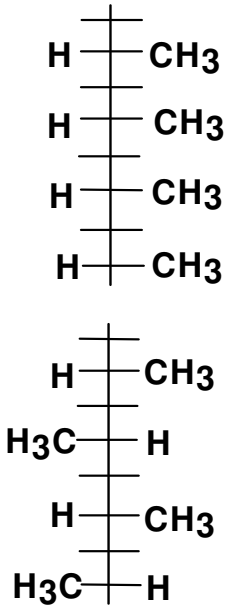
ISOTACTIC



SYNDIOTACTIC



ATACTIC



FISCHER PROJECTIONS

	Tm°C	% X
ISOTACTIC	165-170	55-65
SYNDIOTACTIC	125-131	50-70
ATACTIC	-	0

Tacticity in Polymers

- Isotactic and syndiotactic polymers have ordered arrangements of groups. Hence, the chains can pack closely together and develop high crystallinity.
- Atactic polymers cannot and, therefore, are generally amorphous in nature.

POLYMER SCIENCE DRIVEN INDUSTRY

- **Global chemical industry today is valued at US $ 3 trillion. Bulk petrochemicals and polymers account for one third of this value, US $ 1 trillion. Asia including Japan accounts for a one third share, ~US $ 0.3 trillion**

- **Today we consume ~ 250 million tons of polymer materials**

- **Growth is driven predominantly by India and China. India will become the third largest consumer of polymers by 2012**

Polymer Demand Outlook

Country	2000 (MMT)	Country	2010 (MMT)	*2010/ 2000*
USA	27.3	USA	38.9	*3.6%*
China	16.6	China	38.8	*8.1%*
Japan	9.1	**India**	**12.5**	***14.1%***
Germany	6.4	Japan	9.9	*2.3%*
S. Korea	4.7	Germany	9.4	*3.9%*
Italy	4.7	S. Korea	6.8	*4.8%*
France	4.1	Italy	6.8	*3.8%*
UK	3.5	Brazil	6.7	*7.0%*
Brazil	3.4	CIS	6.2	*9.1%*
India	**3.3**	France	6.1	*4.1%*
Taiw an	3.3	UK	5.2	*4.0%*

Source: CPMA

POTENTIAL TO BE THE 3RD, LARGEST MARKET BY 2010

NEW TO THE WORLD POLYMERS : THE GOLDEN ERA IN POLYMER SCIENCE

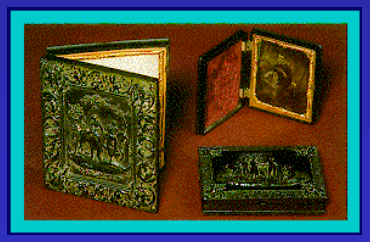
- **PVC (1927) : Replaces natural rubber as cable insulation/ sheathing**
- **Polystyrene (1930) : First commercial production by IG Farben**
- **Neoprene, Poly(chloroprene (1931) : The first man made elastomer**
- **LDPE (1935) : radar, telecommunication cables**
- **PMMA (1936) : Canopies and cockpit covers for airplanes**
- **Nylon (1938) : Replaces silk and rayon, used in parachutes**
- **Poly(ethylene terephthalate) (1941) : The Terylene (ICI) and Dacron (DuPont) fibers**
- **Synthetic rubber (1940-45): Replaces NR; GR-S (SBR), Butyl , the largest mobilization of chemists and engineers towards war effort, part of the Manhattan project. Synthetic rubber capacity grew from close to zero in 1940 to 700, 000 tpa in 1945**
- **Silicones (1943): Eugene Rochow, GE R&D**
- **Poly(tetrafluoroethylene) (1946) : Teflon by DuPont**
- **Epoxy Resins(1947) : Araldite by CIBA**

POLYMERS FULFILLING MATERIAL NEEDS OF SOCIETY…
(Global consumption exceeds 250 million tons)

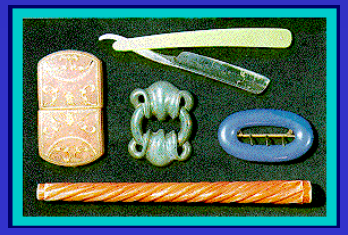
Precursor 19th Century → Semi Synthetics

1839 : Natural Rubber
1843 : Vulcanite / Gutta Percha
1856 : Shellac / Bois Durci
1862 : Parkesine
1863 : Celluloid
1894 : Viscose Rayon
1898 : Poly Carbonate

Natural Polymers



Semi Synthetics



1900 – 1950 → Thermoplastics

1908 : Cellophane
1909 : Bakelite
1926 : Vinyl or PVC
1927 : Cellulose Acetate
1933 : Polyvinylidene chloride
1935 : Low density polyethylene
1936 : Polymethyl Methacrylate
1937 : Polyurethane
1938 : Polystyrene
1938 : Teflon
1939 : Nylon and Neoprene
1941 : PET
1942 : LDPE
1942 : Unsaturated Polyester

1950 onwards → Growth Phase

1951 : HDPE
1951 : PP
1954 : Styrofoam
1960 : PC, PPO
1964 : Polyamide
1970 : Thermoplastic Polyester
1978 : LLDPE
1985 : Liquid Crystal Polymers

Plastics in Packaging

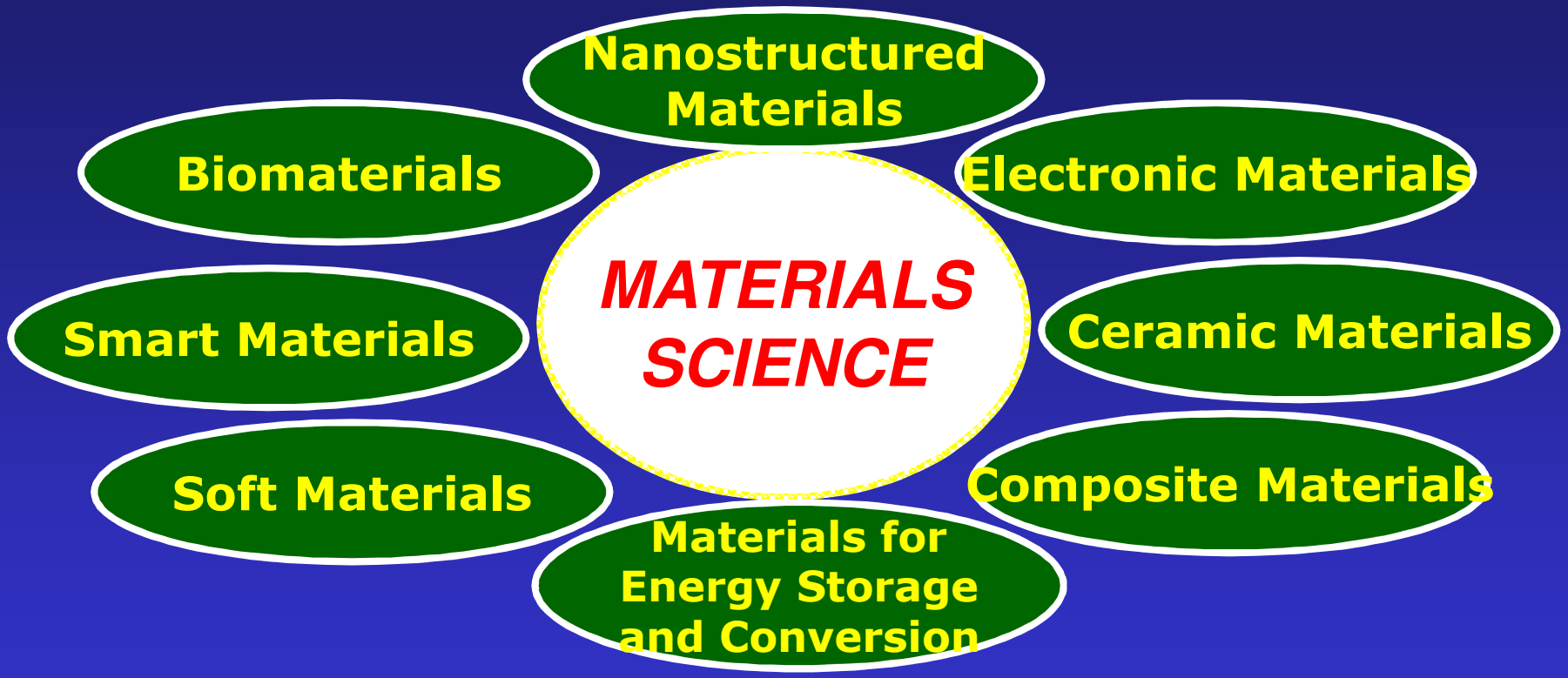
High Performance Plastics

I am inclined to think that the development of polymerization is, perhaps, the biggest thing that chemistry has done, where it has the biggest effect on everyday life

Lord Alexander Todd (1907-1997)

Nobel Laureate, 1957

THE NEW DIMENSIONS OF MATERIAL SCIENCE



INCREASINGLY POLYMER SCIENCE WILL BE AN ENABLING SCIENCE ; TO CREATE ADVANCED MATERIALS WITH USEFUL FUNCTIONS IN COMBINATION WITH OTHER MATERIALS

BIOINSPIRED STRUCTURAL MATERIALS

STRUCTURAL MATERIALS → **FUNCTIONAL MATERIALS**

MACROCOMPOSITES
- Shear
- wetting
- Orientation

BIOCOMPOSITES
- Molecular self assembly
- Hydrogen bonding
- Hydrophobic interaction

NANOCOMPOSITES
- Intercalation and exfoliation
- In-situ polymerization
- Polymerization in constrained spaces
- Nanofibers and nanotubes

ADCVANCED AND FUNCTIONAL MATERIALS

- Functional polymers
- Polymers with precisely defined shape, size and topology (e.g Dendrimers and hyper branched polymers)
- Stimuli responsive materials
- Super and supra-molecular materials
- Nano-materials
- Bio-molecular materials

Research driven by emerging developments in electronics, photonics, information technology and medicine. All new discoveries likely to occur at the interface of polymer science with chemistry, biology and physics

COMPLEX POLYMER SYSTEMS

- **Organic –inorganic hybrids, stimuli responsive polymers, polymer networks with defined functions and control, block and hetero- copolymers, polymers that self assemble into large supramolecular forms with hierarchical order and polymer materials capable of interacting with other materials, especially biological materials**

- **Key fundamental scientific challenges :**

  - Directing structures via controlled kinetic and thermodynamic pathways

  - Complex structure via chain architecture

  - Entropy driven assembly in multi-component hybrid systems

  - Template assisted synthesis of complex systems

NEW DIRECTIONS IN ADVANCED MATERIALS RESEARCH

- Multiphase polymer blends
- Organic - inorganic hybrid materials
- High temperature resistant materials
- Easy processing polymers
- Stiff main chain materials
- Novel processing techniques
  - –Reactive processing
  - –Solid and gel state processing
- Functional polymers with specific electrical, optical, barrier properties
- Intelligent materials
- Biocompatible and bio-molecular materials

SOME UNSOLVED PROBLEMS : THE CHALLENGE OF THE OPPOSITE

- **High molecular weight polymers without chain entanglement**
- **High glass transition temperature with high ductility**
- **High impact with high modulus**
- **Chain stiffening through conventional processing**
- **High optical clarity with electrical conductivity**

POLYMER MATERIALS : FUTURE

- **Speciality or advanced materials**
  - **Functional polymers**
  - **Polymers with precisely defined shape, size and topology**
  - **Stimuli responsive materials**
  - **Super and supramolecular materials**
  - **Nanomaterials**
  - **Biomolecular materials**

Research driven by emerging developments in electronics, photonics, information technology and medicine. All new discoveries likely to occur at the interface of polymer science with chemistry, molecular biology and physics

POLYMER MATERIALS : FUTURE

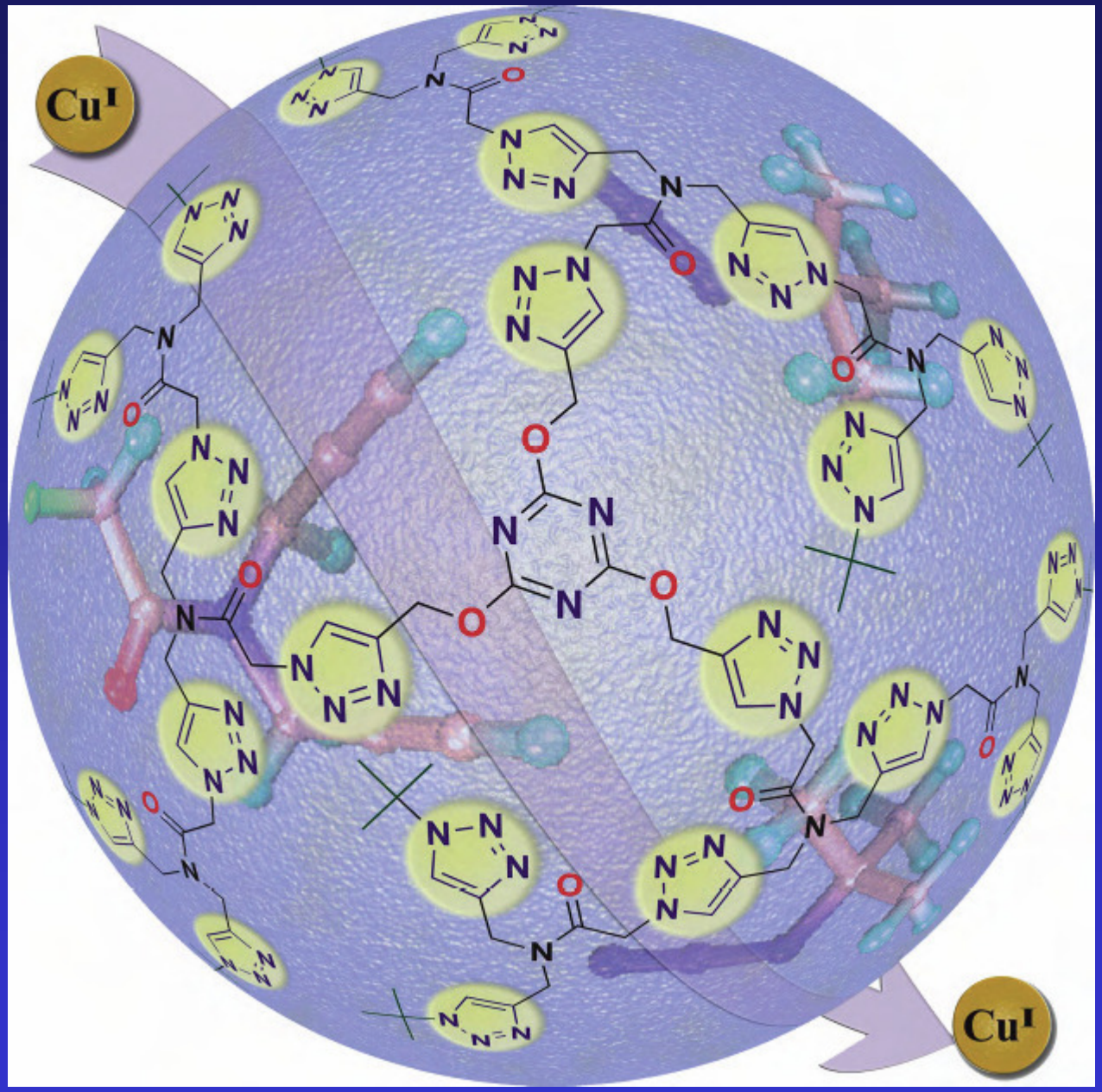
- **Commodity and engineering polymers**
  - **Improved properties**
  - **Advanced computational tools and engineering principles**
  - **Reduced manufacturing cost**
  - **Easier process5bility/new processing technique**
  - **Blends, alloys and composites**

New Polymers will emerge, not from new monomers, but by creating new structures from existing inexpensive monomers

INTELLIGENT MATERIALS

- **Heterogeniety**
- **Dynamics**
- **Cooperativity**

Time dependent response of a surface to an external stimuli / environment is often called "Intelligence"


Cu I
Cu I

INTERDISCIPLINARY ROLES OF DENDRIMERS AND DENDRIGRAFTS

LIFE SCIENCES

Dendrimer (DNA, antibodies, proteins) conjugates

Gene therapy

Biomimetics

Drug delivery

Immunoassays

NANO DEVICES

Molecular antennae

Electroconductive dendrimers

Ball and chain constructs (amphiphiles)

MATERIALS SCIENCES

New dendrimer compositions

Molecular ball bearings (flow regulators, processing aids)

Liquid crystal constructs

INTERDISCIPLINARY ROLES OF DENDRIMERS AND DENDRIGRAFTS

INTERFACIAL SCIENCES

Dendrimer catalysts (homogeneous/heterogeneous)

Electro-catalysis

Monolayers/multilayers

Coatings

SUPRAMOLECULAR SCIENCES

Molecular encapsulation

Host-guest interactions

Dendrimer box

Lock and key complexes

Self assembling dendrimers

Micelle mimics and inverted micelle mimics

POLYMER MATERIALS : SUSTAINABILITY CHALLENGE

- **Excessive dependence on fossil fuel ; a finite natural resource**
- **Persist in the environment**

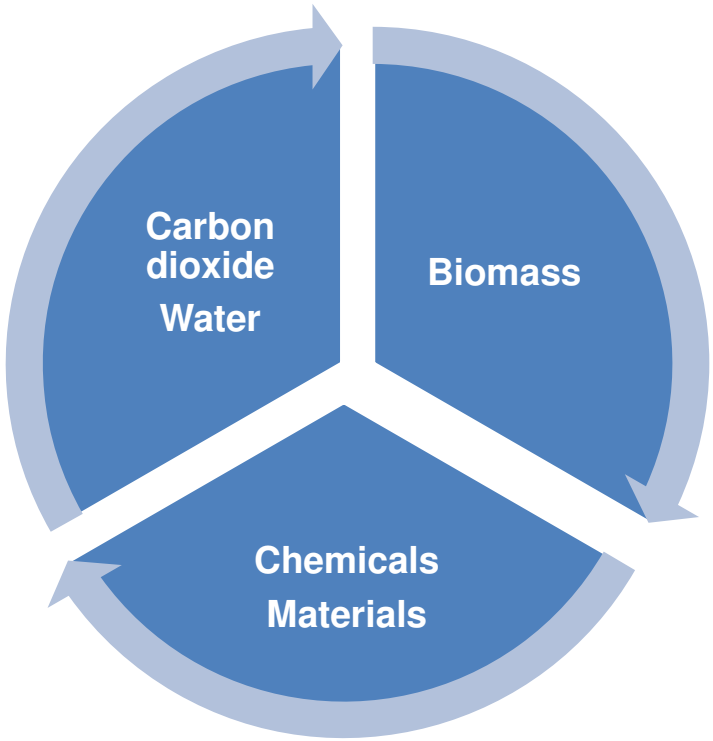
Poly(ethylene terephthalate)

Every second we throw away about 1500 bottles

Over 30 billion liters of bottled water is consumed annually

What is the solution ?

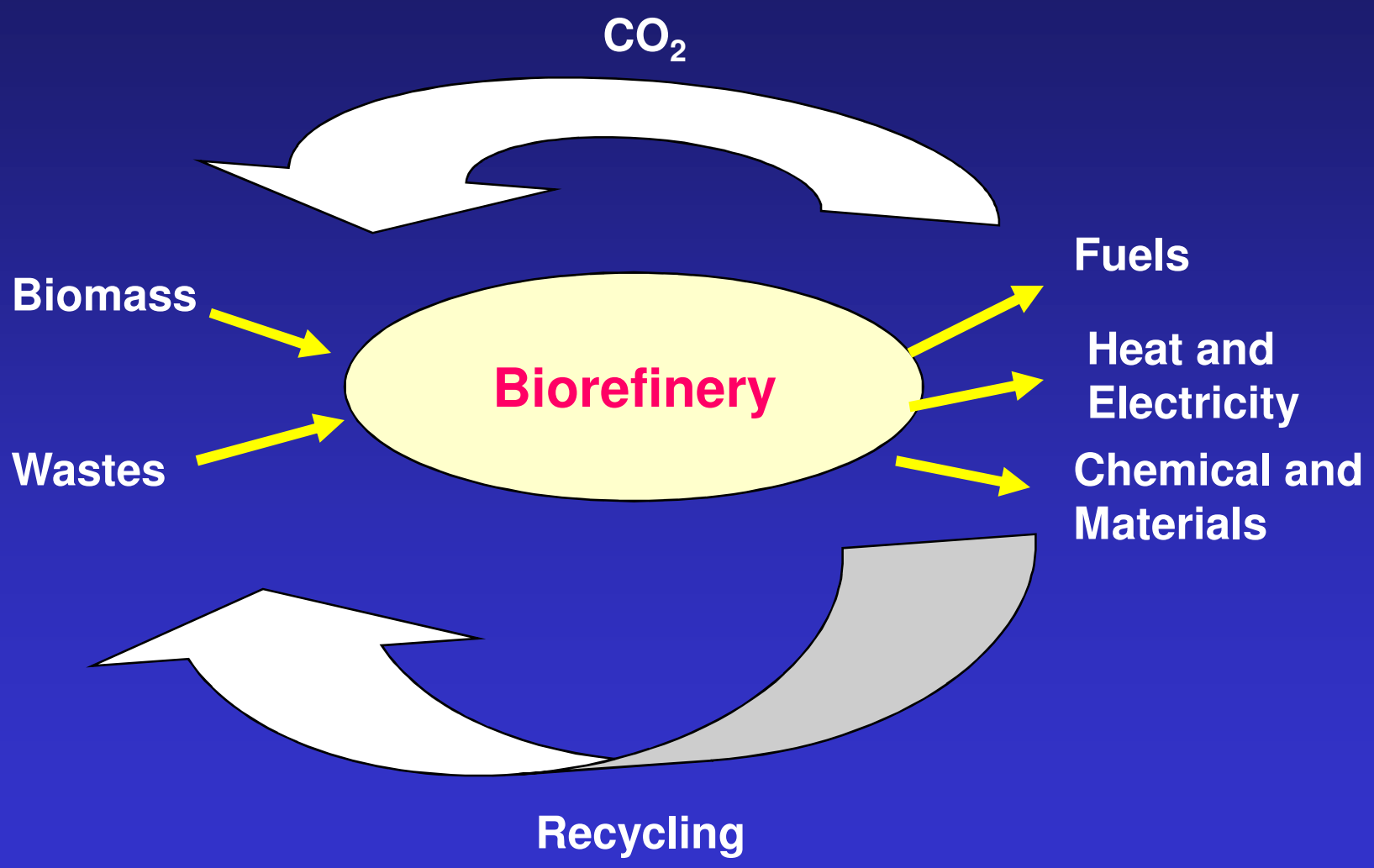
FROM HYDROCARBONS TO CARBOHYDRATES : FROM NON RENEWABLES TO RENEWABLES



Can a part of the chemicals / materials manufacturing progressively shift to renewable carbohydrate resources

Is such a virtuous cycle just a dream ?

FROM PETROLEUM TO BIOREFINERIES



FROM HYDROCARBONS TO CARBOHYDRATES

- **The polymer industry is increasingly focused on the concept of sustainability**
- **There is only so much petroleum on earth and with time, oil will become increasingly rare**
- **Chemicals / feed stocks manufacturing will progressively shift to natural gas in the short term and renewable carbohydrate resources in the long term**

Feed-stocks for polymers will slowly , but certainly, shift to renewable and sustainable resources during the next two decades

POLYMERS FROM RENEWABLE RESOURCES

Biodegradable polymers

- Polyesters
- Starch

Bio-derived monomers and polymers

- PET/PTT / PBS
- Nylon-11
- Ethylene from ethanol and polyethylene

•Environmental sustainability
•CO_2 mitigation – closing the carbon cycle
•Food Vs material

•Reduce cost of feedstock
•Reduce dependence on fossil fuel

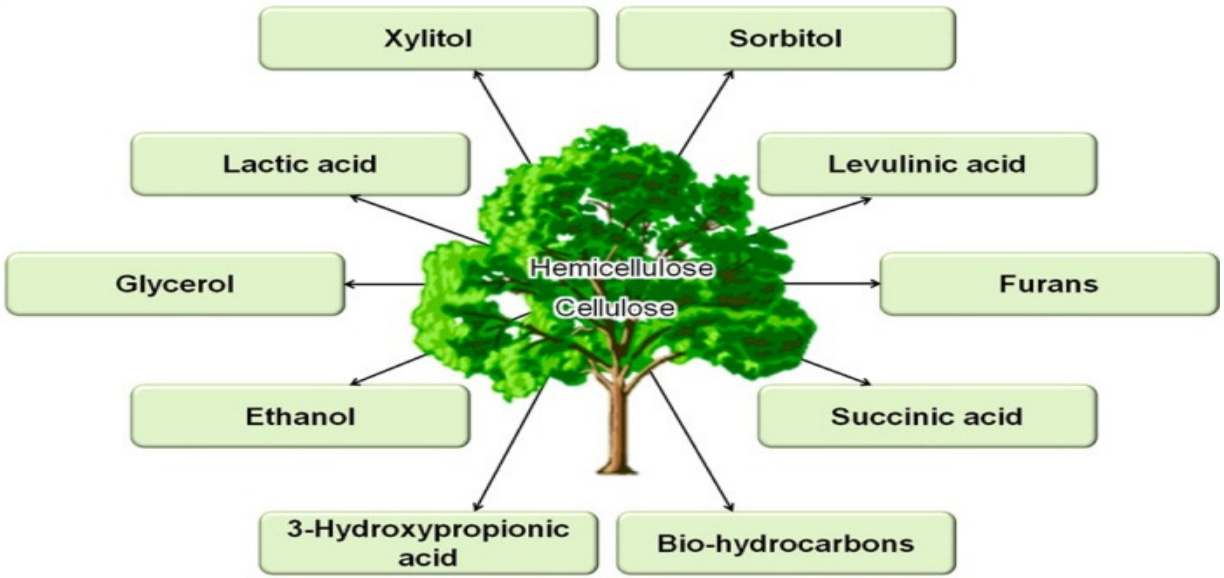
BIO BASED MONOMERS FOR POLYMERS

Scientific Challenges

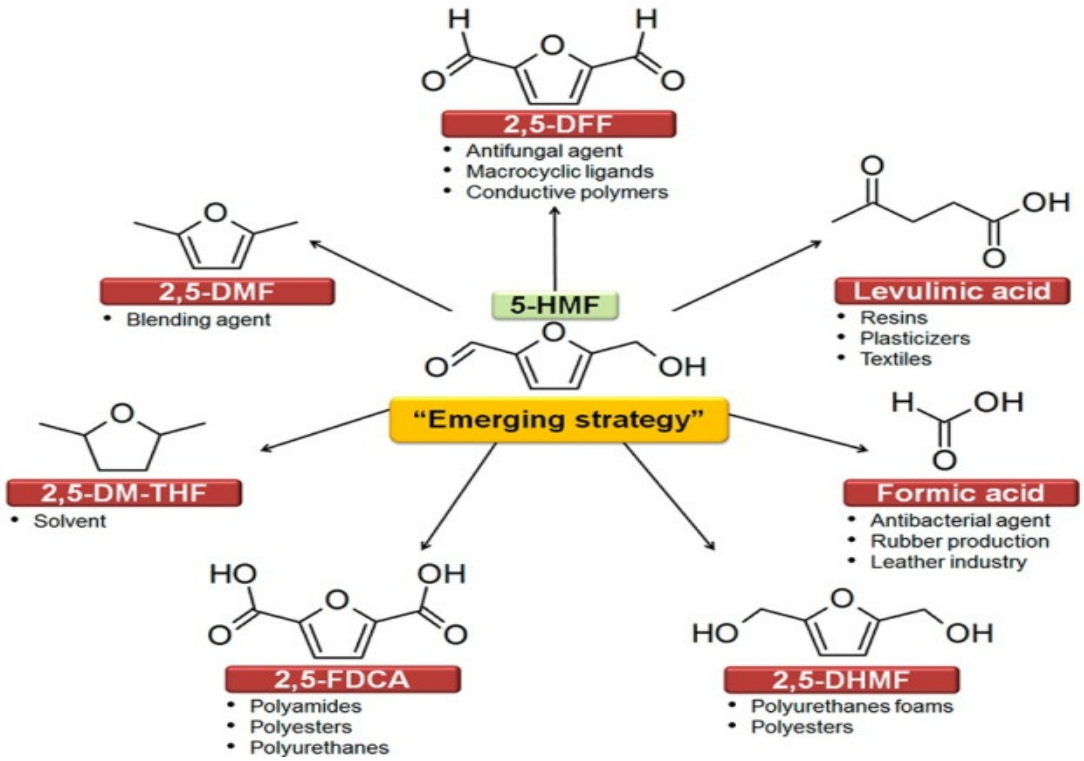
- Creating monomers from fossil fuel based feed-stocks is about selectively introducing functionality (oxidation, dehydrogenation, oxychlorination, epoxidation etc)

- Creating monomers from bio based feeds-tocks is about selectively removing functionality (examples, dehydration, decarboxylation, decarbonylation, deoxygenation)

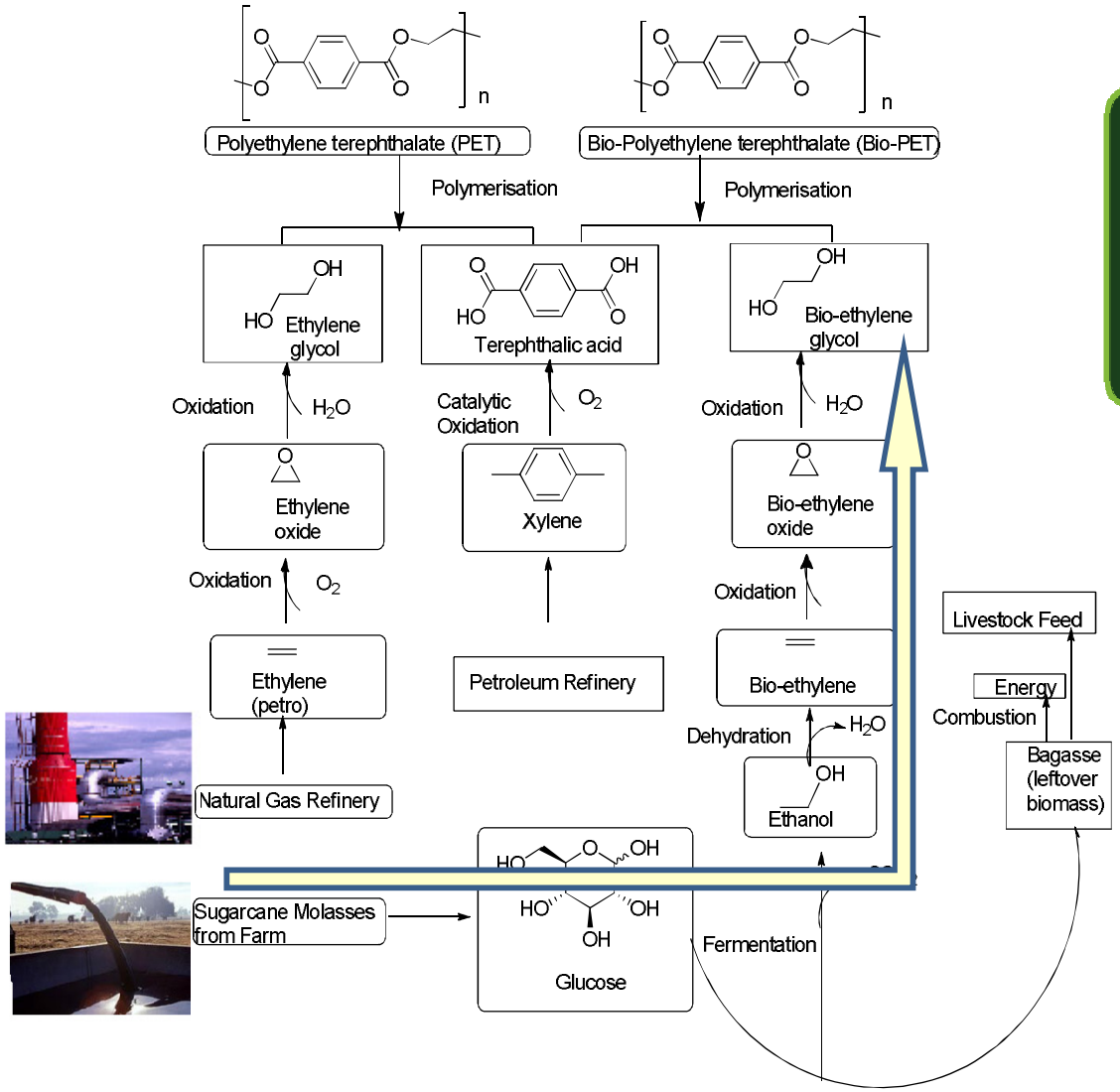
(a)


Xylitol
Sorbitol
Lactic acid
Levulinic acid
Glycerol
Hemicellulose
Cellulose
Furans
Ethanol
Succinic acid
3-Hydroxypropionic acid
Bio-hydrocarbons

(b)

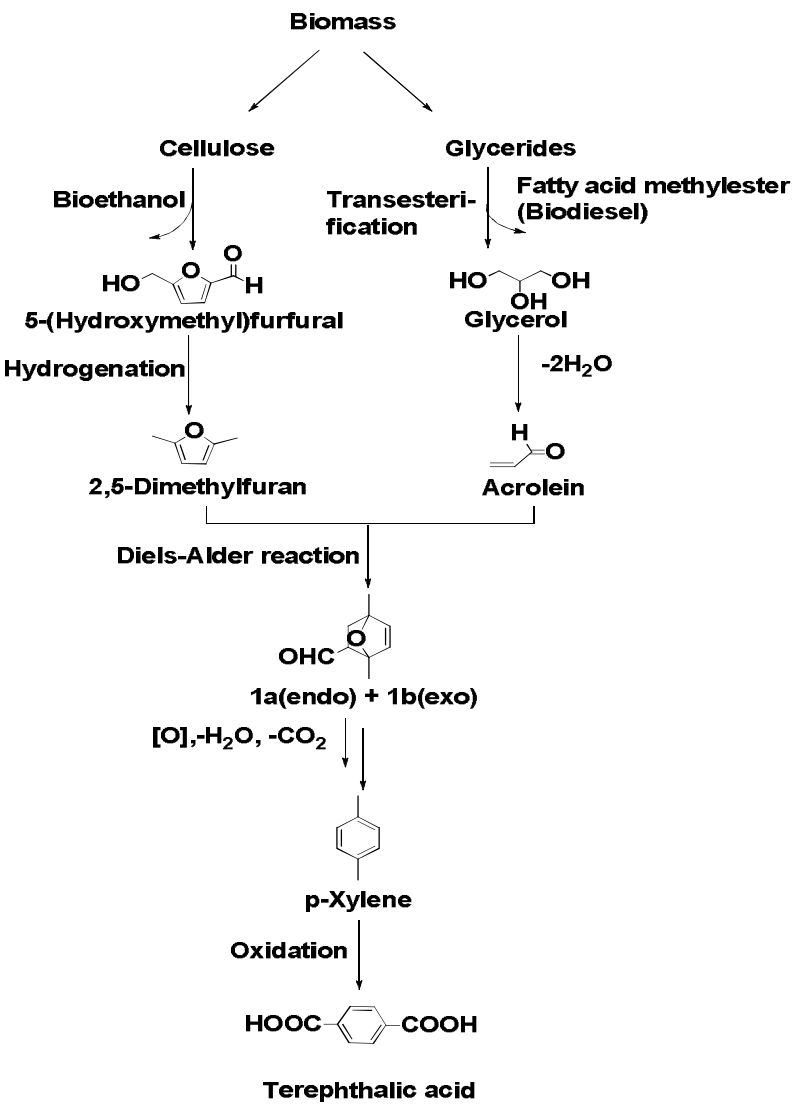

2,5-DFF
Antifungal agent
Macrocyclic ligands
Conductive polymers
2,5-DMF
Blending agent
5-HMF
Levulinic acid
Resins
Plasticizers
Textiles
"Emerging strategy"
2,5-DM-THF
Solvent
Formic acid
Antibacterial agent
Rubber production
Leather industry
2,5-FDCA
Polyamides
Polyesters
Polyurethanes
2,5-DHMF
Polyurethanes foams
Polyesters

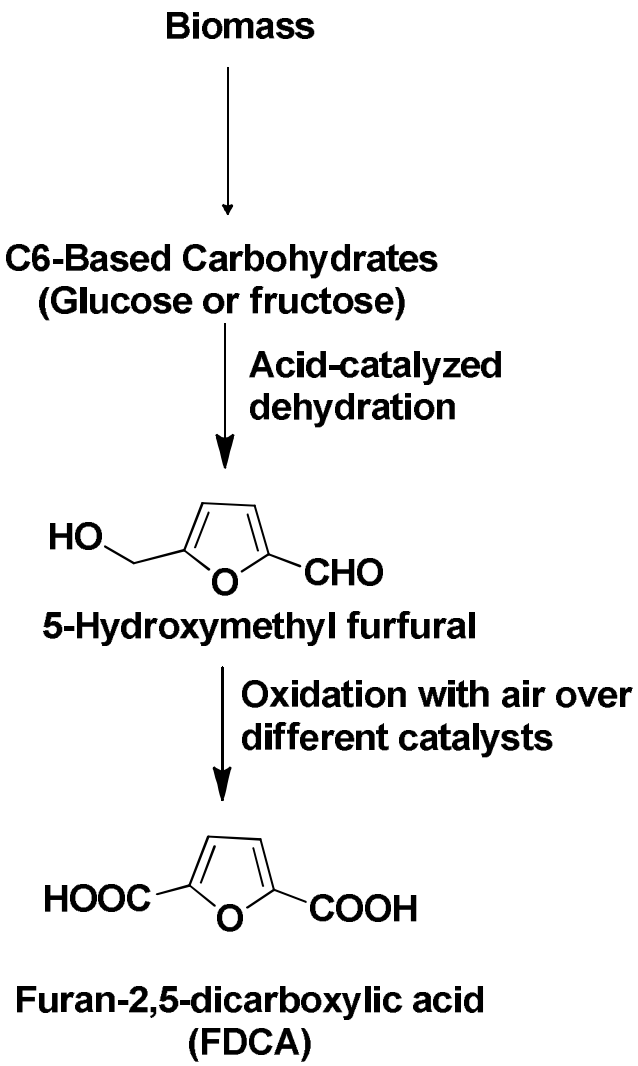
PET MANUFACTURE: PETRO- AND BIO-BASED

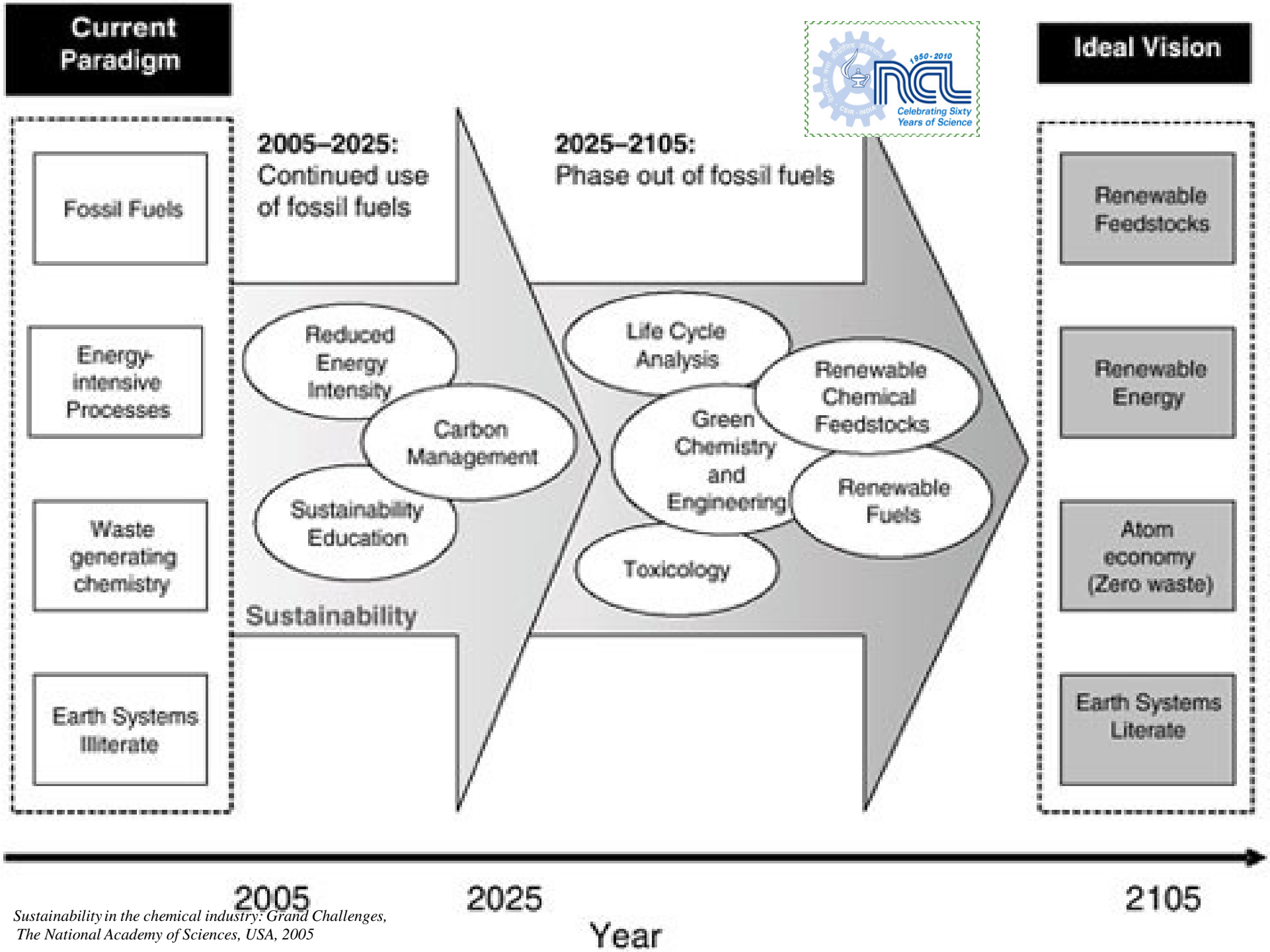


Adapted from Environ. Sci. Technol., 44, 8264 (2010)

BIOMASS DERIVED DICARBOXYLIC ACIDS FOR PET







Sustainability in the chemical industry: Grand Challenges, The National Academy of Sciences, USA, 2005

NEW DESIGN PARADIGMS IN POLYMER SYNTHESIS

Controlled Polymer synthesis

- **Polymerization through rational catalyst / initiator design**
- **Mono-disperse step growth polymers through iterative synthetic methods**
- **Molecular self assembly methods applied to synthesis of polymers with novel topologies**

CHAIN LENGTH

Determines …….

- **Mechanical strength**
- **Thermal behavior**
- **Processability**
- **Adsorption at interfaces**

Control of chain length

- **Still difficult and is determined largely by statistics**

Challenge…..

- **Synthesis of polymers with <u>absolutely</u> uniform length for a wide range of polymers**

CHAIN SEQUENCE

Determines …….

- Thermal behavior
- Crystalline properties

Copolymer sequence

- Random
- Alternating
- Block
- Graft

Challenge…..

- Synthesis of macromolecules with precisely defined sequences

CHAIN ISOMERISM

Determines …….

- Thermal behavior
- Morphology
- Crystallinity

Polymer stereochemistry

- Geometrical isomerism
- Regioisomerism
- Stereoisomerism

Challenge…..

- Control polymer stereochemistry through rational design of catalysts

CHAIN TOPOLOGY

Determines …….

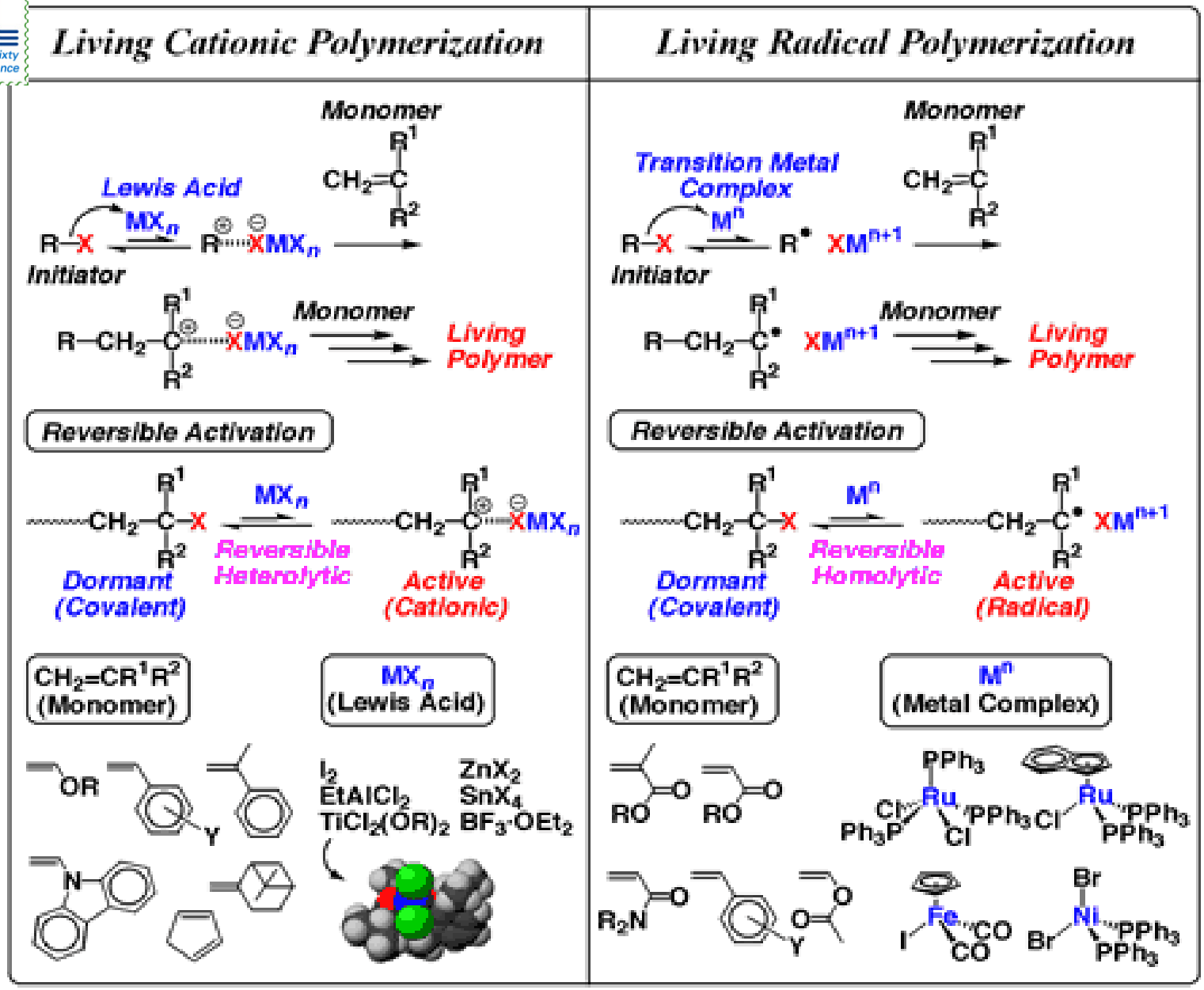
- Crystalline properties, solubility and rheological behavior

Diversity of polymer architectures

- Linear, Branched, Hyper-branched
- Stars, Dendrimers
- Catenanes , Rotaxanes
- Ribbons , Wires

Challenge…..

- To provide control of both topology and molecular geometry over large length scales in real space

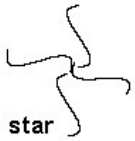

Living Cationic Polymerization
Living Radical Polymerization
Monomer
Lewis Acid
Initiator
Transition Metal Complex
Living Polymer
Reversible Activation
Dormant (Covalent)
Reversible Heterolytic
Active (Cationic)
Reversible Homolytic
Active (Radical)
CH2=CR1R2 (Monomer)
MXn (Lewis Acid)
Mn (Metal Complex)
I2
EtAlCl2
TiCl2(OR)2
ZnX2
SnX4
BF3·OEt2

What Can Controlled/ Living Polymerizations Do ?

$DP_n = \Delta[M]/[I]_o$; $200<M_n<10^6$ (or more?); $1.01<M_w/M_n < 1.5$ & designed MWD; tacticity

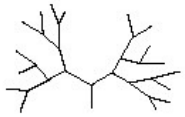
Topologies:


linear


star


comb / brush


network/ crosslinked

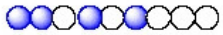

dendritic / hyperbranched

Compositions:

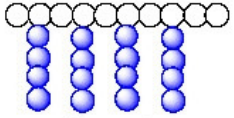

homopolymer


periodic copolymer


block copolymer

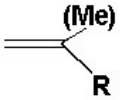

random copolymer

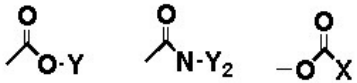

tapered / gradient copolymer


graft copolymer

Monomers:

Vinyl:

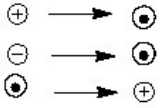




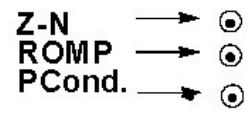
-Ar (Sty), Vi (Bu & IP), Pyr, CN, Cl, Br, Me, H

Systems: bulk, solution (org., H_2O, CO_2), suspension, emulsion, ...

Transformations:

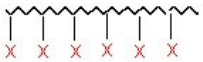


Z-N
ROMP
PCond.

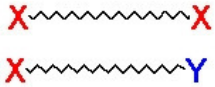


Hybrids:
synthetic/natural
organic/inorganic
surfaces; IPN; etc.

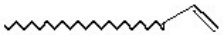
Functionalities:

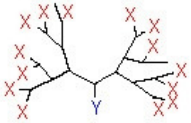

side-functional groups


end-functional polymers


telechelic polymers


site-specific functional polymers

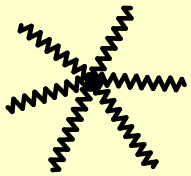

macromonomers


multifunctional

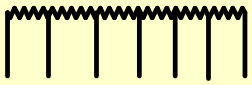
STRUCTURES ACCESSIBLE VIA TECHNIQUES CONTROLLED POLYMER SYNTHESIS

Topology

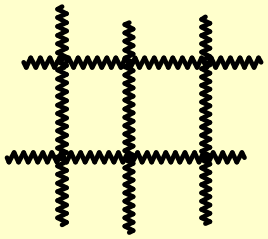
Linear



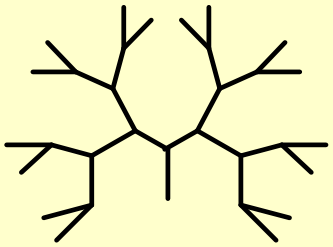
Star / Multi-Armed



Comb Polymers



Networks



(Hyper) Branched

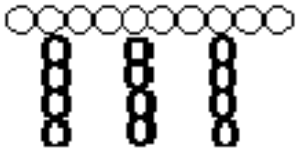
Composition

HomoPolymers

Block Copolymers

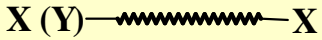
Statistical Copolymers

Tapered / Gradient Copolymers

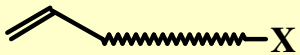


Graft

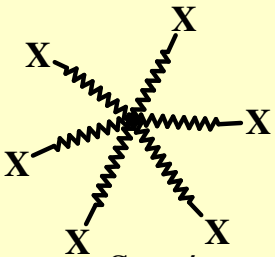
Functionality



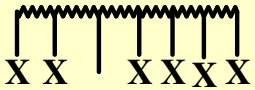
Homo / Hetero Telechelic



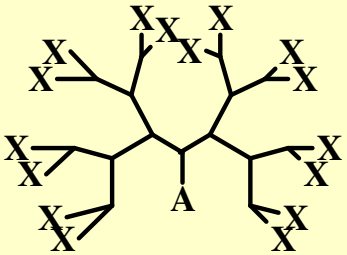
Macromonomers



Star / Multi- Armed

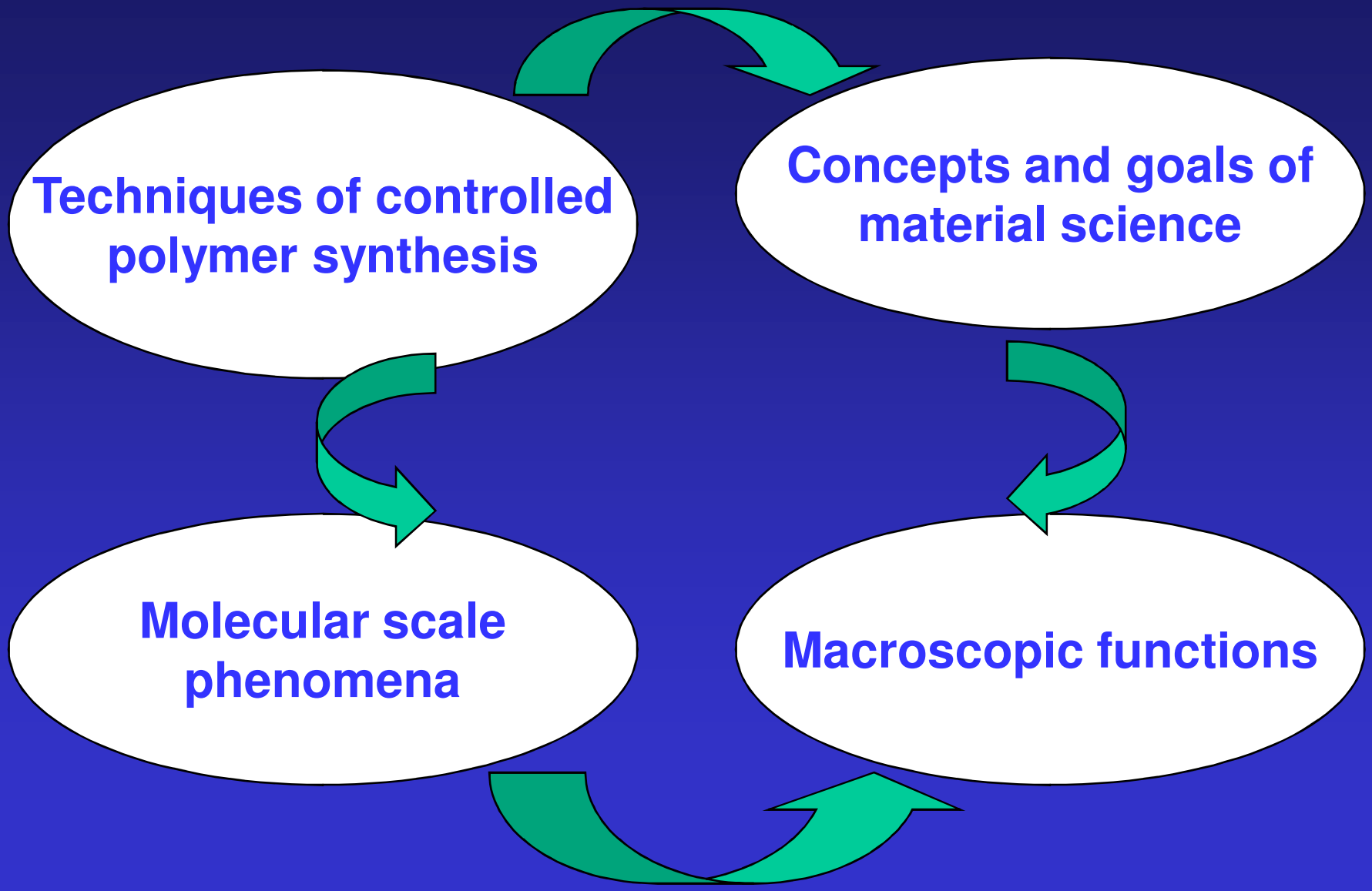


Side Functional Groups



Hyperbranched / Multifunctional

GOALS OF POLYMER SCIENCE



POLYMER MATERIAL SCIENCE : THE NEXT WAVE

- **Research in polymer science began about sixty years ago as a discipline borne out of disciplines of chemistry , physics and engineering**
- **For over half a century the discipline flourished as an independent discipline – in education and research**
- **Explosive developments in the emergence of new polymers and the birth and growth of the polymer industry paralleled the growth of polymer science as a discipline**
- **Polymer science as a stand alone discipline has probably now attained maturity. Most of the major challenges facing this discipline today are at the interface of polymer science with material science, biology, medicine or physics**
- **The next frontiers that await polymer scientist will need deep collaboration with multiple disciplines**

POLYMER SCIENCE AT CROSSROADS

- **Polymer science is at the end of one wave of development and struggling to begin another; perceptible shift in the centre of gravity of the discipline**
- **There are still many important opportunities in both fundamental and applied science**
- **The disciplines offers fewer puzzles to solve; What confronts are large number of problems**
- **Longer term curiosity driven research is more important than in the past, but harder to justify**

In the future, functions will be more important than molecules. Molecules are no longer enough (they never really were)

THANK YOU