THE SCIENCE OF POLYMERS : PAST, PRESENT AND FUTURE

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DR. S. SIVARAM

A 201, Polymers & 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
Visit us at : http://www.ncl-india.org

1950-2010
Celebrating Sixty Years of Science

THE SCIENCE OF POLYMERS : PAST, PRESENT AND FUTURE

- The origins and the history
- How relevant is polymer material science today ?
- Where is technology leading ? What are the barriers and opportunities ?
- Where is science leading ? What are the new frontiers in polymer science ?

THE AGES OF HUMAN KIND

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

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

- *Polymer Materials Age (Carbon based 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

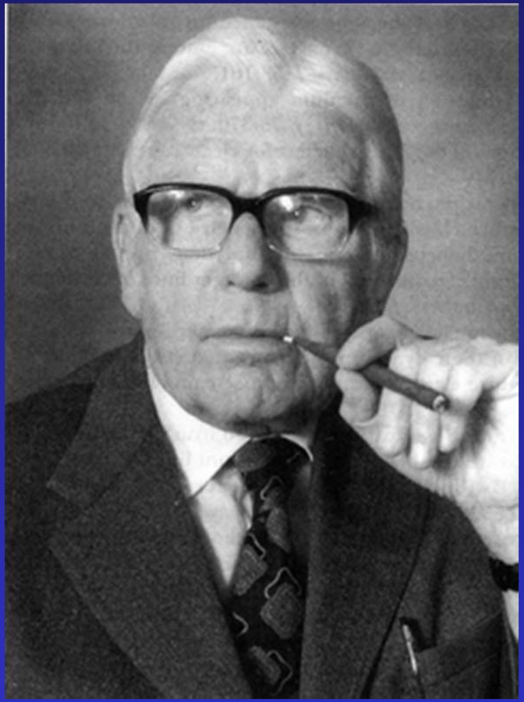
(1827- 1907)

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

WHAT IS THE ORIGIN OF THE TERM POLYMER ?

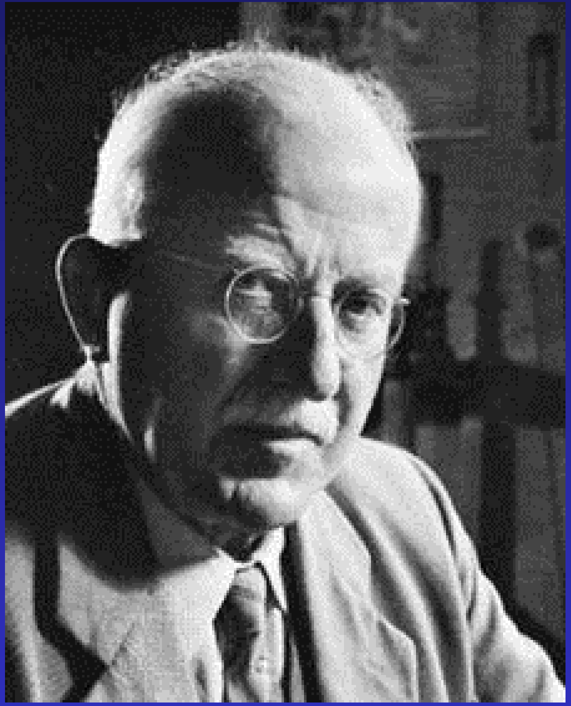
- **Faraday in 1826 was puzzled by the fact that ethylene and butene differed in their gas density , but had the same elemental composition**
- **Berzelius was astounded by Faraday`s observation and suggested that butene be referred to as a “polymer” of ethylene (1827, 1832). All through the nineteenth century, there are references to styrene being a polymer of acetylene and lactic acid as a polymer of formaldehyde**
- **Staudinger adopted this definition of Berzelius. For Staudinger, polystyrene was a polymer of styrene. However, he objected to the use of this term for products of polycondensation**
- **It was Carothers in 1929 who gave a general definition of the term. He defined them as substances” whose structures may be represented by R-R-R- where -R- are bivalent radicals which in general are not capable of independent existence” *(J.Am.Chem.Soc., 51, 2548 , 1929)***

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

- 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)

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**

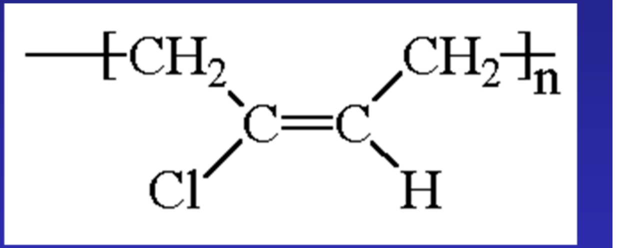
- **One of the materials chosen was cellulose fiber. They found that cellulose fiber upon stretching leads to increase in modulus**

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"

WALLACE CAROTHERS AND THE BIRTH OF RATIONAL POLYMER SYNTHESIS

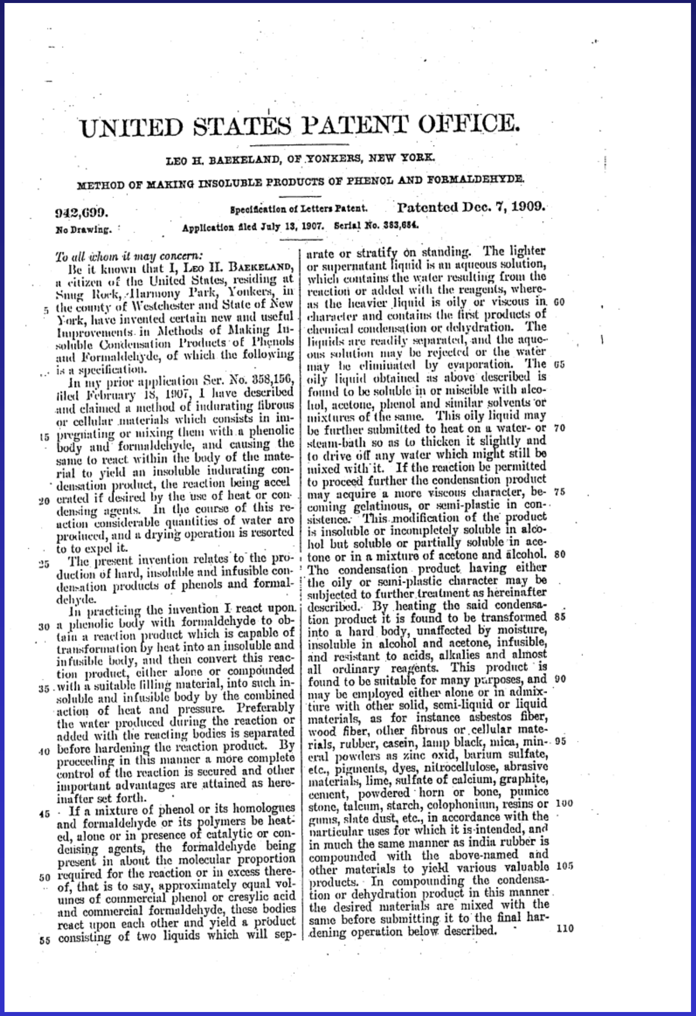
1896-1937

- 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 papers in JACS in 1929 where in he establishes the equivalence of organic and polymer forming reactions, namely esterification and polyesterification



Poly(chloroprene)

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.

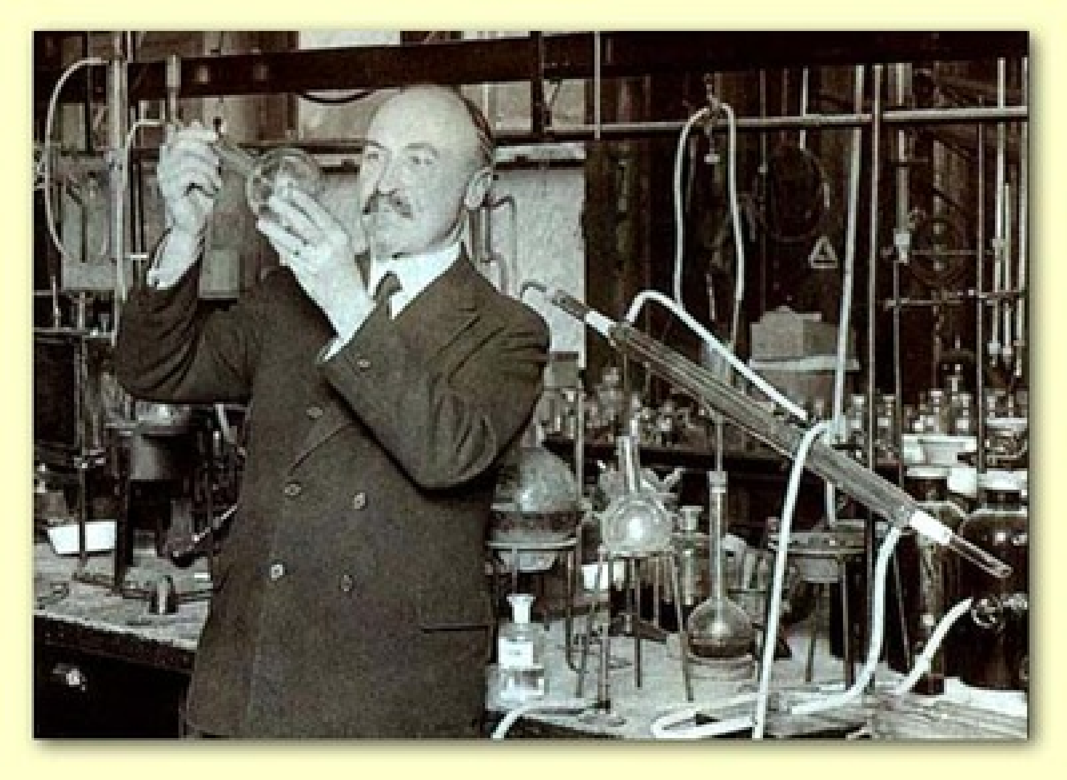
In practicing the invention I react upon a phenolic body with formaldehyde to obtain a reaction product which is capable of transformation by heat into an insoluble and infusible body, and then convert this reaction product, either alone or compounded with a suitable filling material, into such insoluble 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"

POLYMER SCIENCE : THREE PHASES OF EVOLUTION

- Post Industrial Revolution (1760-1900)
- World War I and II (1900-1950)
- The Era of Inexpensive Petroleum (1950- 2000)

- The beginnings of chemistry as a science (1800-1900)
- Atoms and molecules; understanding structure and the nature of the chemical bond (1900-1940)
- Understanding reactive intermediates in chemistry: The birth of physical organic chemistry (1940-60)

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):**
- **Poly(tetrafluoroethylene) (1946) : Teflon by DuPont**
- **Epoxy Resins(1947) : Araldite by CIBA**

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 !**

1967

Mr. McGuire: Come with me for a minute. I want to talk to you. I just want to say one word to you. Just one word

Ben: Yes, sir

Mr. McGuire: Are you listening ?

Ben: Yes sir, I am

Mr.McGuire: PLASTICS

Ben: Exactly how do you mean ?

Mr. McGuire: There is a great future in plastics. Think about it. Will you think about it?

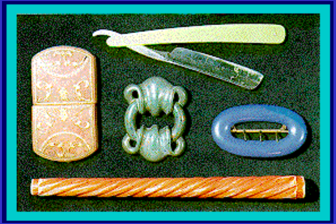
POLYMERS FULFILLING MATERIAL NEEDS OF SOCIETY…
(Global consumption exceeds 250 million tons)

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

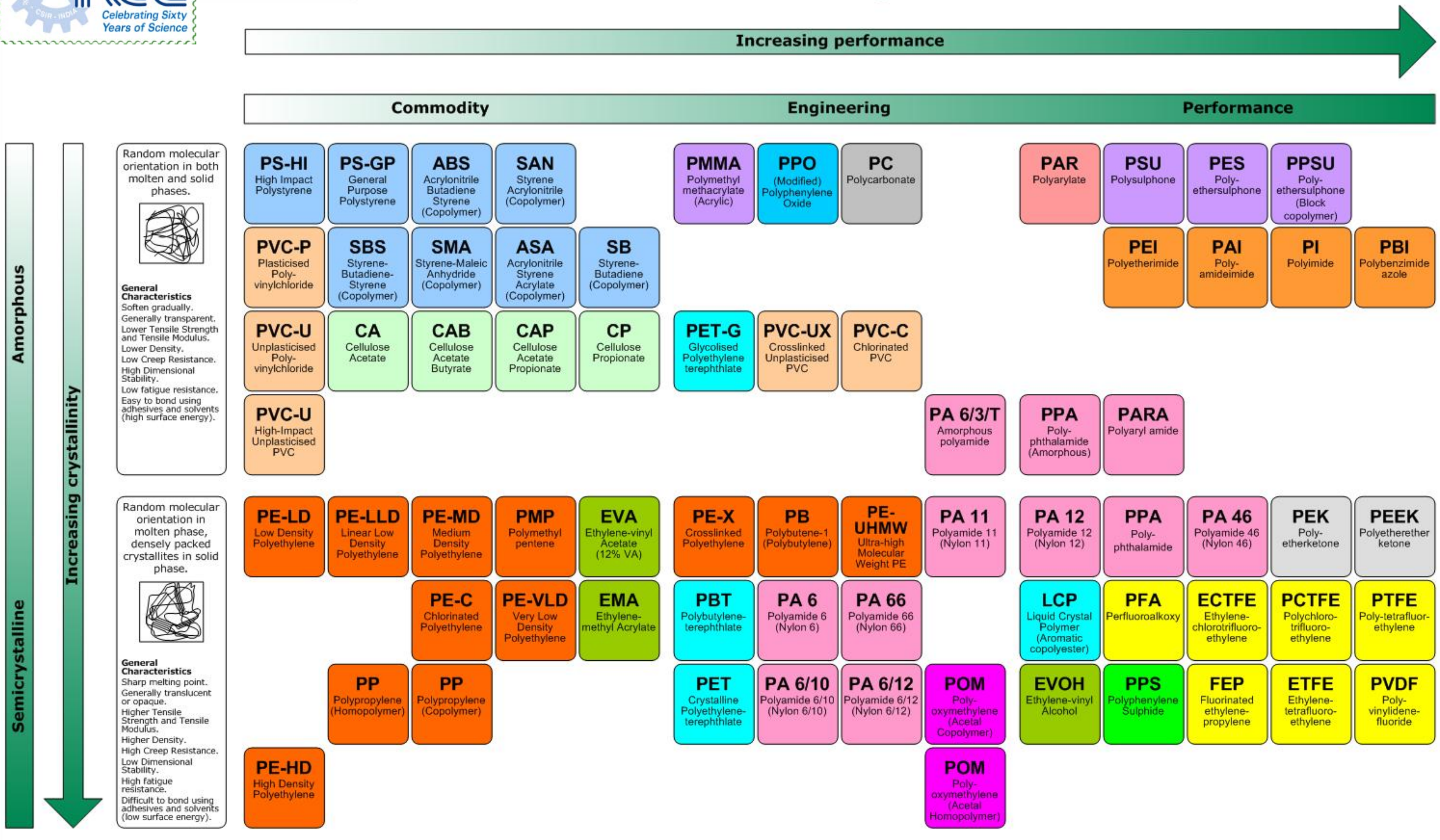
v was a historic achievement in
tionship between structure and

en structure and properties and this
provide a simple codification of the

ible to include all of the variations in
e most common polymers.

Tangram Technology
Periodic Table of Thermoplastics

TANGRAM TECHNOLOGY | Consulting Engineers



Increasing performance

Commodity **Engineering** **Performance**

Amorphous

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).

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** Polybenzimidazole
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			

Semicrystalline

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

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

POLYMER MATERIALS : FROM VISIBLE TO INVISIBLE

NEW POLYMER INTRODUCTION : ENTRY BARRIERS

- No new polymers has entered the market since the early nineties. The last ones were poly(propylene terephthalate) by DuPont (PTT), poly(ethylene naphthalate) by Teijin (PEN) and Nature Works Poly (Lactic Acid)s by Cargill.

- Several new polymers developed in the last fifteen years have been abandoned after market introductions. Example, Carilon (ethylene-carbon monoxide copolymers) by Shell and Questra (syndiotactic polystyrene), PCHE (hydrogenated polystyrene) and Index (ethylene –styrene copolymers) by Dow.

- The rate of growth of markets for the new polymers introduced after the nineties have been painfully slow.

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)

FUTURE OF POLYMER SCIENCE

- **Systems, not molecules**
- **Functions, not molecular structure**

No longer "What is it?" but "What does it do?"

POLYMER MATERIALS : SUSTAINABILITY CHALLENGE

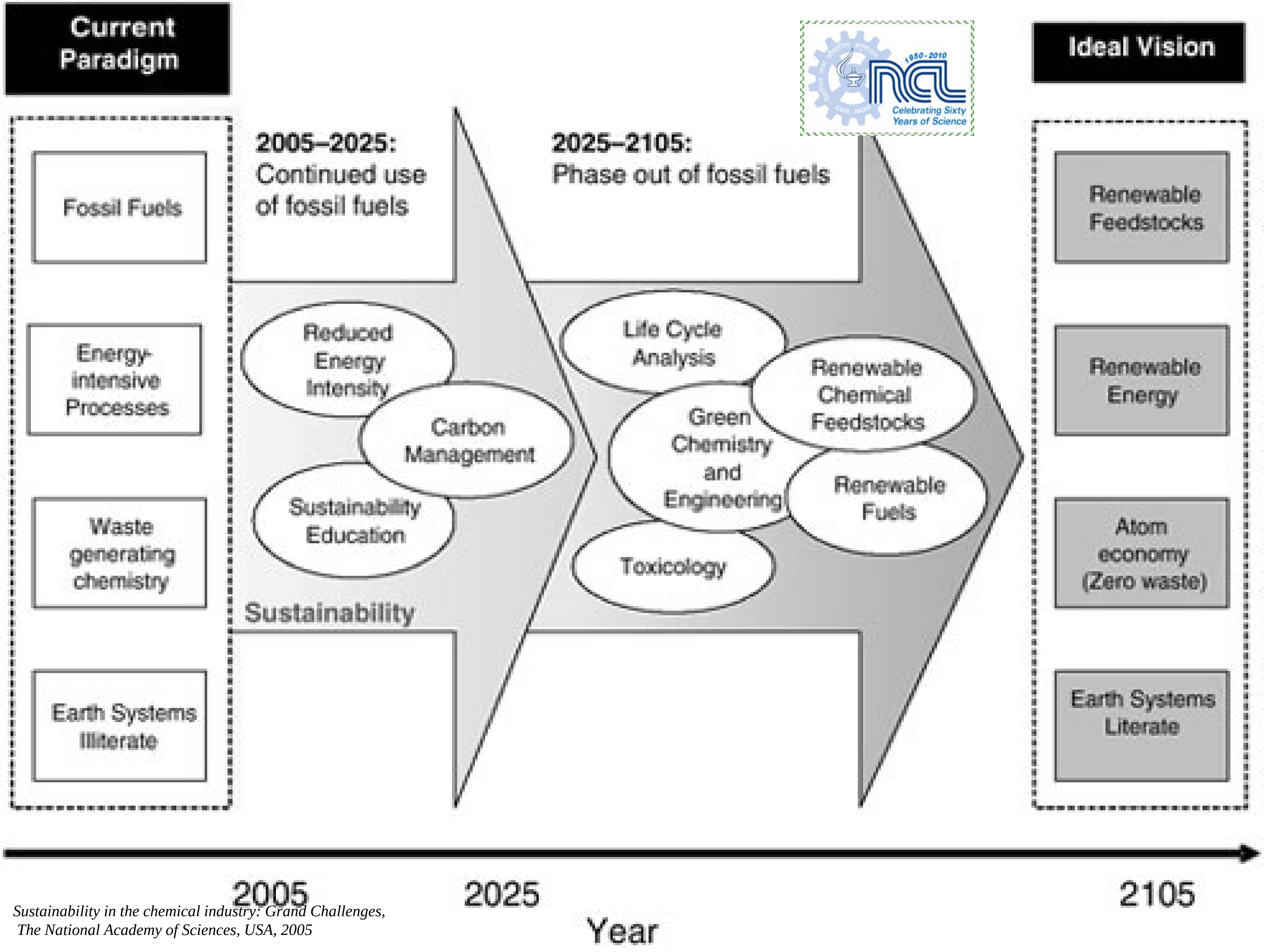
- **Excessive dependence on fossil fuel ; a finite natural resource**

- **Persist in the environment**

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



Current Paradigm

- Fossil Fuels
- Energy-intensive Processes
- Waste generating chemistry
- Earth Systems Illiterate

2005–2025: Continued use of fossil fuels

- Reduced Energy Intensity
- Carbon Management
- Sustainability Education

Sustainability

2025–2105: Phase out of fossil fuels

- Life Cycle Analysis
- Green Chemistry and Engineering
- Renewable Chemical Feedstocks
- Renewable Fuels
- Toxicology

Ideal Vision

- Renewable Feedstocks
- Renewable Energy
- Atom economy (Zero waste)
- Earth Systems Literate

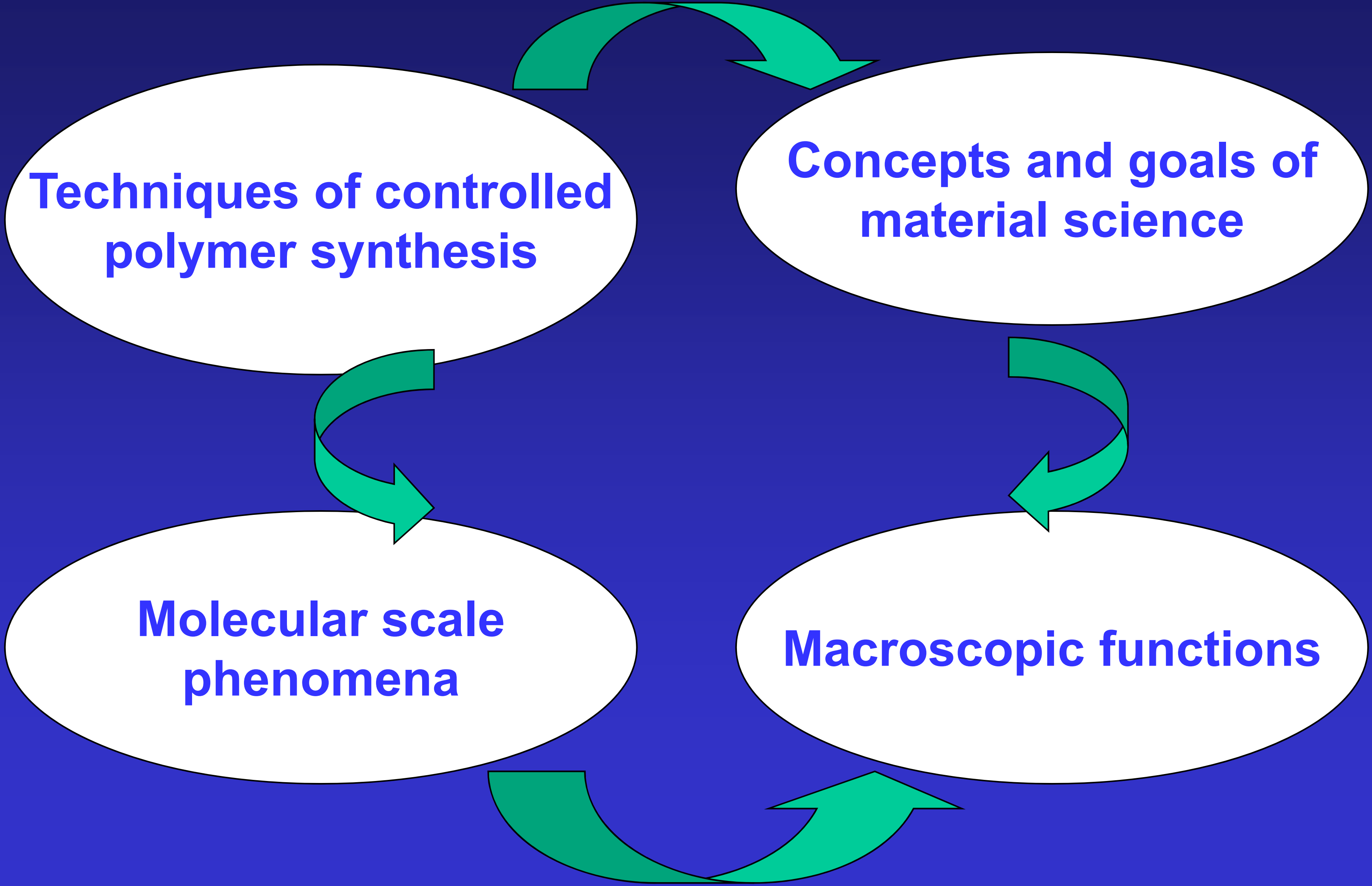
2005 2025 2105

Year

1950 - 2010 Celebrating Sixty Years of Science

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

GOALS OF POLYMER SCIENCE



Techniques of controlled polymer synthesis

Concepts and goals of material science

Molecular scale phenomena

Macroscopic functions

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 absolutely 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 …….

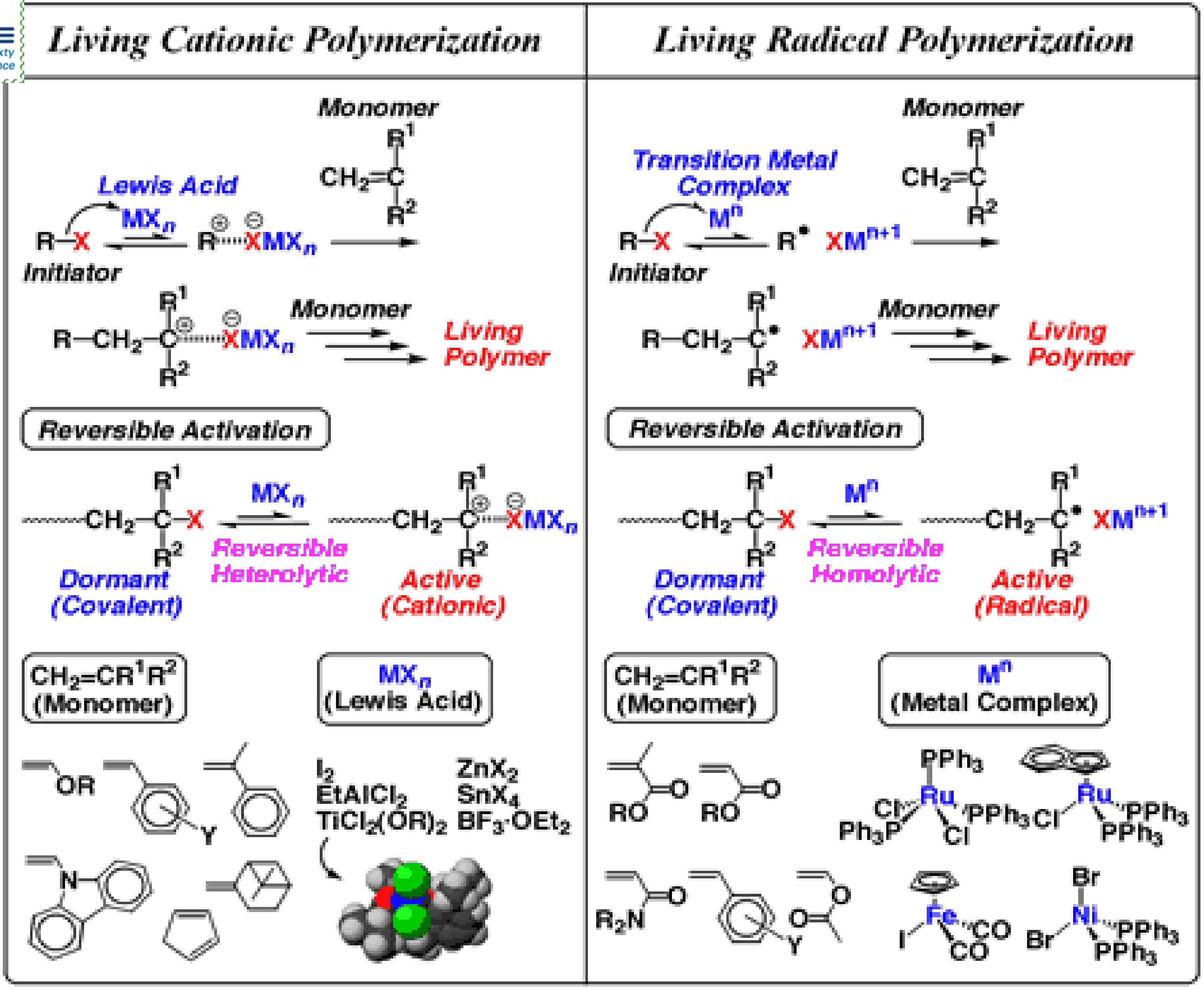
- Crystalline properties, solubility and rheological behavior

Diversity of polymer architectures

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

Challenge…..

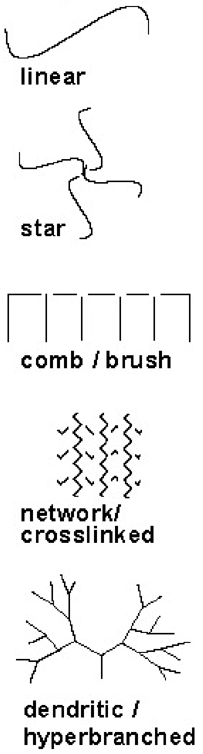
- To provide control of both topology and molecular geometry over large length scales in real space


Living Cationic Polymerization
Living Radical Polymerization
Monomer
Lewis Acid
MX$_n$
R–X
R–X···MX$_n$
Initiator
Living Polymer
Reversible Activation
Dormant (Covalent)
Reversible Heterolytic
Active (Cationic)
CH$_2$=CR^{1}R^2 (Monomer)
MX$_n$ (Lewis Acid)
I$_2$
EtAlCl$_2$
TiCl$_2$(OR)$_2$
ZnX$_2$
SnX$_4$
BF$_3$·OEt$_2$
Transition Metal Complex
M^n
XM^{n+1}
Reversible Homolytic
Active (Radical)
M^n (Metal Complex)
PPh$_3$
Ru
Fe
Ni
CO
Br
Cl
I
RO
R$_2$N
OR
Y

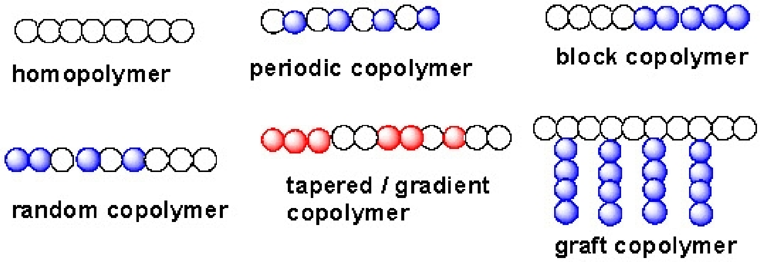
What Can Controlled/ Living Polymerizations Do ?

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

Topologies:

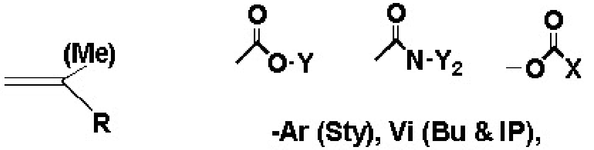


Compositions:



Monomers:

Vinyl:



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

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

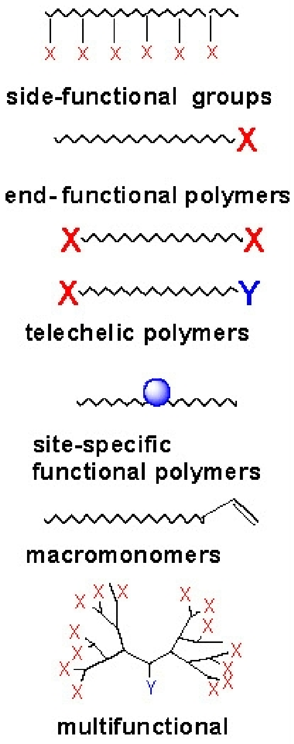
Transformations:

⊕ → ⊙
⊖ → ⊙
⊙ → ⊕

Z-N → ⊙
ROMP → ⊙
PCond. → ⊙

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

Functionalities:



1950 - 2010
NCL
Celebrating Sixty Years of Science

Polymer Chemistry, 3,1677 (2012)

Polymer Chemistry

www.rsc.org/polymers

Volume 1 | Number 10 | December 2010 | Pages 1521–1708

ISSN 1759-9954

RSC Publishing

PAPER
Xi Zhang *et al.*
Selenium-containing block copolymers and their oxidation-responsive aggregates

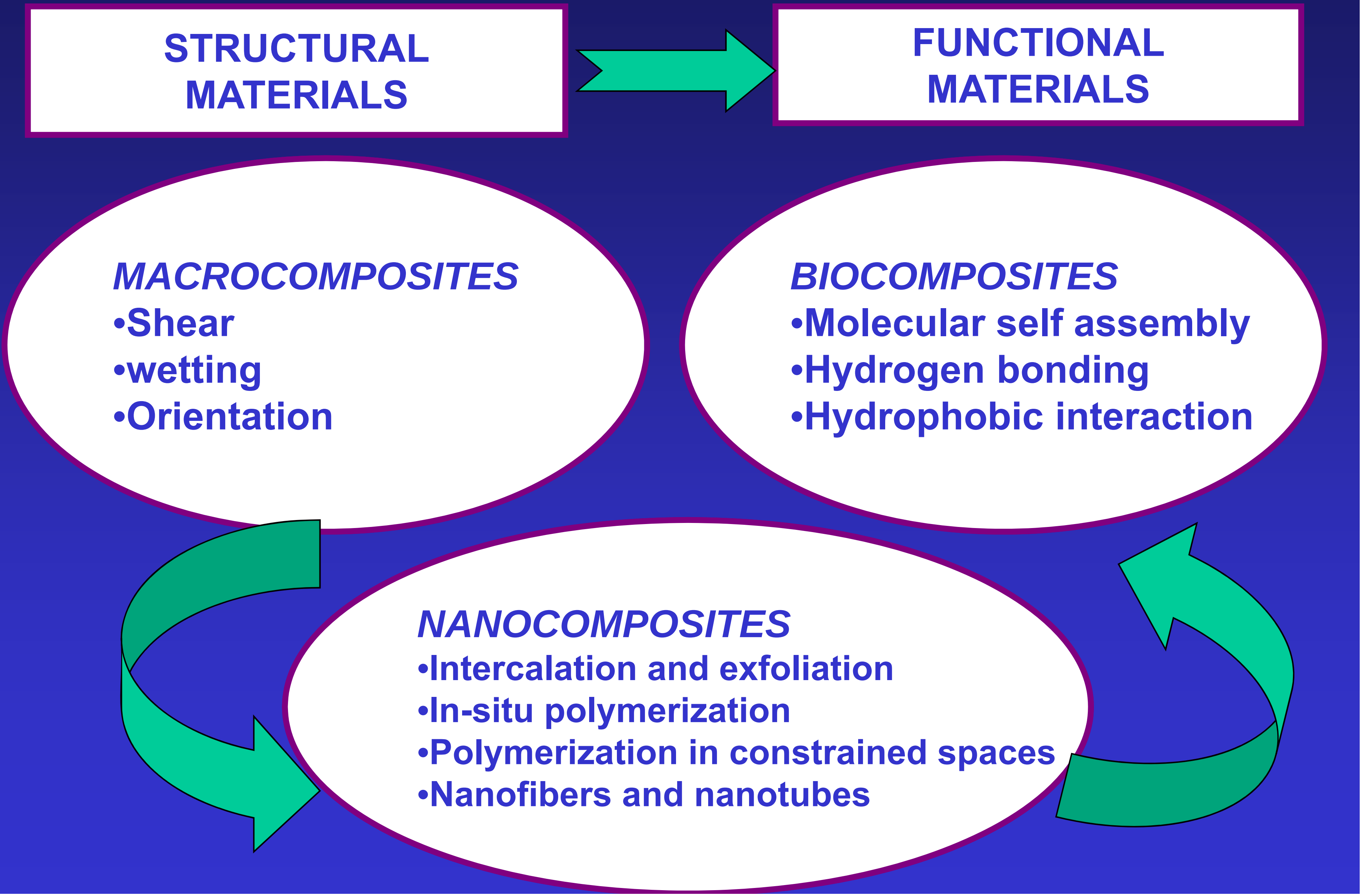
1759-9954(2010)1:10;1-4

New Methods of Polymer Synthesis

ROMP
Conjugated Polymers
RAFT
Click Chemistry
Bis orthogonal ligation

Control of structure, function, tcticity, monomer sequence, topology and precision end group control

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**

BIO INSPIRED MATERIALS

- Spider Silk : High Modulus Fiber
- Abalone / Mollusk Shell : Balancing impact resistance with strength
- Gekko Feet : Adhesion in wet conditions
- Mantis Shrimp : Light weight, stiff and impact resistance

POLYMER 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**

THE NEW DIMENSIONS OF MATERIAL SCIENCE

MATERIALS SCIENCE

- Nanostructured Materials
- Electronic Materials
- Ceramic Materials
- Composite Materials
- Materials for Energy Storage and Conversion
- Soft Materials
- Smart Materials
- Biomaterials

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

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

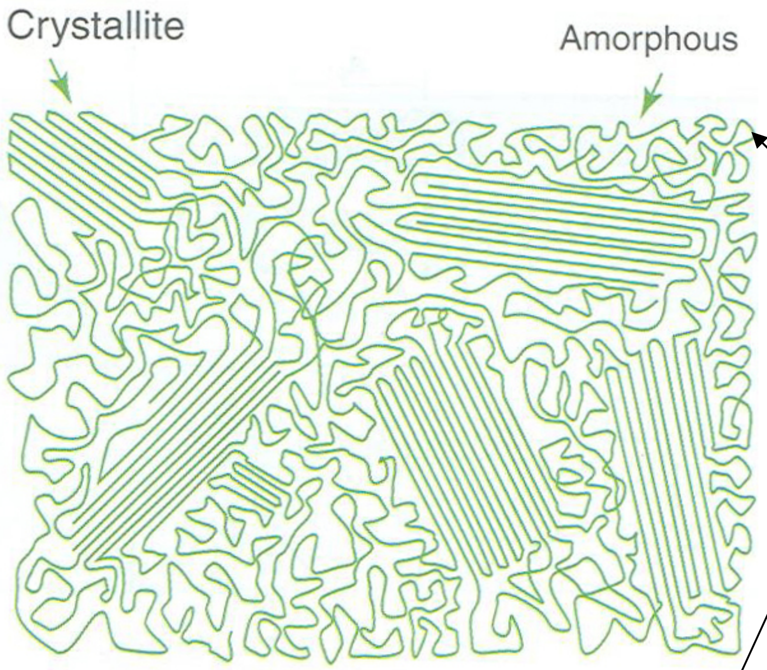
- Key fundamental scientific challenges :

  - 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

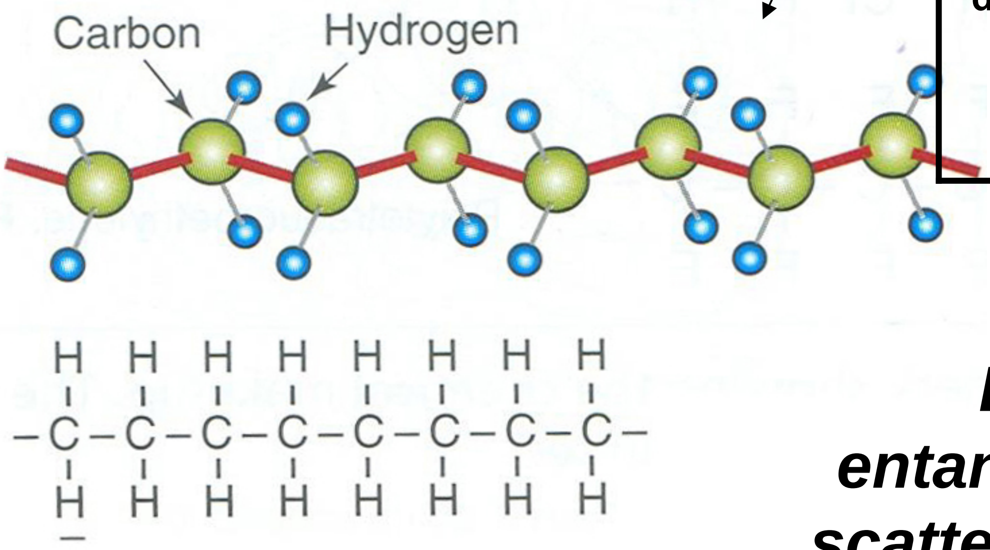
SOME UNSOLVED PROBLEMS :
THE CHALLENGE OF THE OPPOSITE

- **High molecular weight polymers without chain entanglement**
- **High glass transition temperature with high ductility; Polymers having Tg between 110 and 150 degrees celsius**
- **High impact with high modulus**
- **Chain stiffening through conventional processing**
- **High optical clarity with high electrical conductivity**

INFLUENCE OF C-C BOND ON YOUNG'S MODULUS



bulk polyethylene



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cold drawn polythylene

bulk polyethylene **E : 0.2GPa**
cold drawn polyethylene **E: 300 GPa**
dc diamond **K : 440 GPa,**
fcc diamond **σ >> 450 GPa**
diamond nanorods from (111) **K : 490 GPa**

Disentangled Polyethylenes

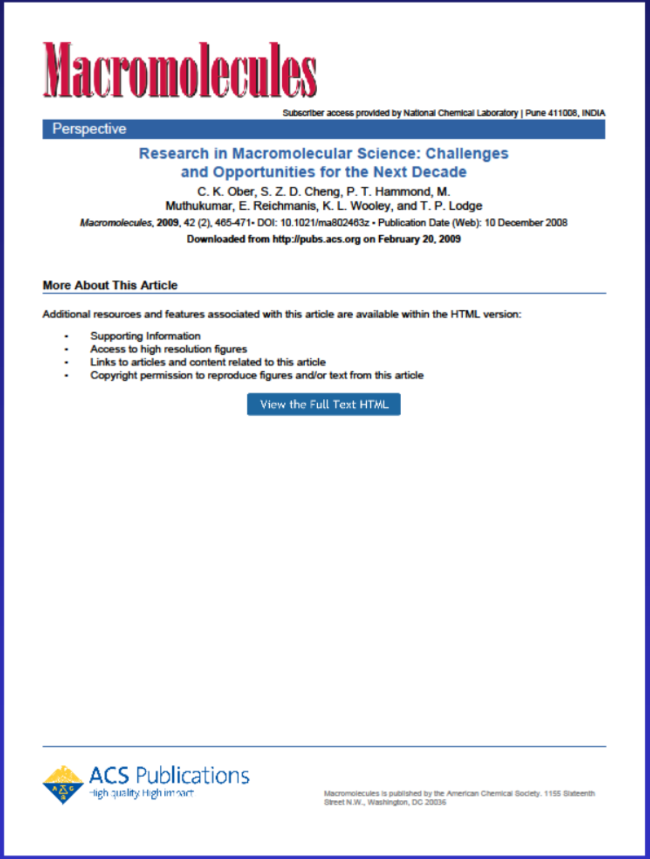
High Thermal Conductivities, >100 W/m/K; Theoretical Value, ~350 W/m/K

Defects (chain ends, entanglements) act as phonon scattering sites for heat transfer

NOVEL MATERIALS

- Self Healing
- Phase Change
- Porous Polymers
- 2-D Polymers
- Polymer Nano particles
- Polymer Surface Modification
- Polymers with barrier to moisture and oxygen

POLYMER SCIENCE : QUO VADIS



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Perspective

Research in Macromolecular Science: Challenges and Opportunities for the Next Decade

C. K. Ober, S. Z. D. Cheng, P. T. Hammond, M.
Muthukumar, E. Reichmanis, K. L. Wooley, and T. P. Lodge

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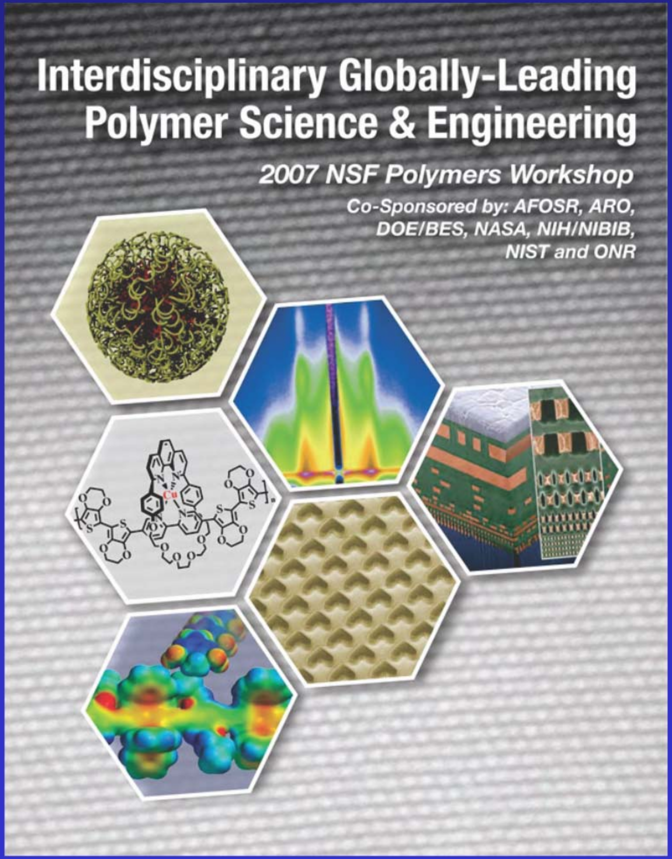

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