POLYMER SCIENCE : CHALLENGES AND OPPORTUNITIES

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INTERNATIONAL YEAR OF CHEMISTRY

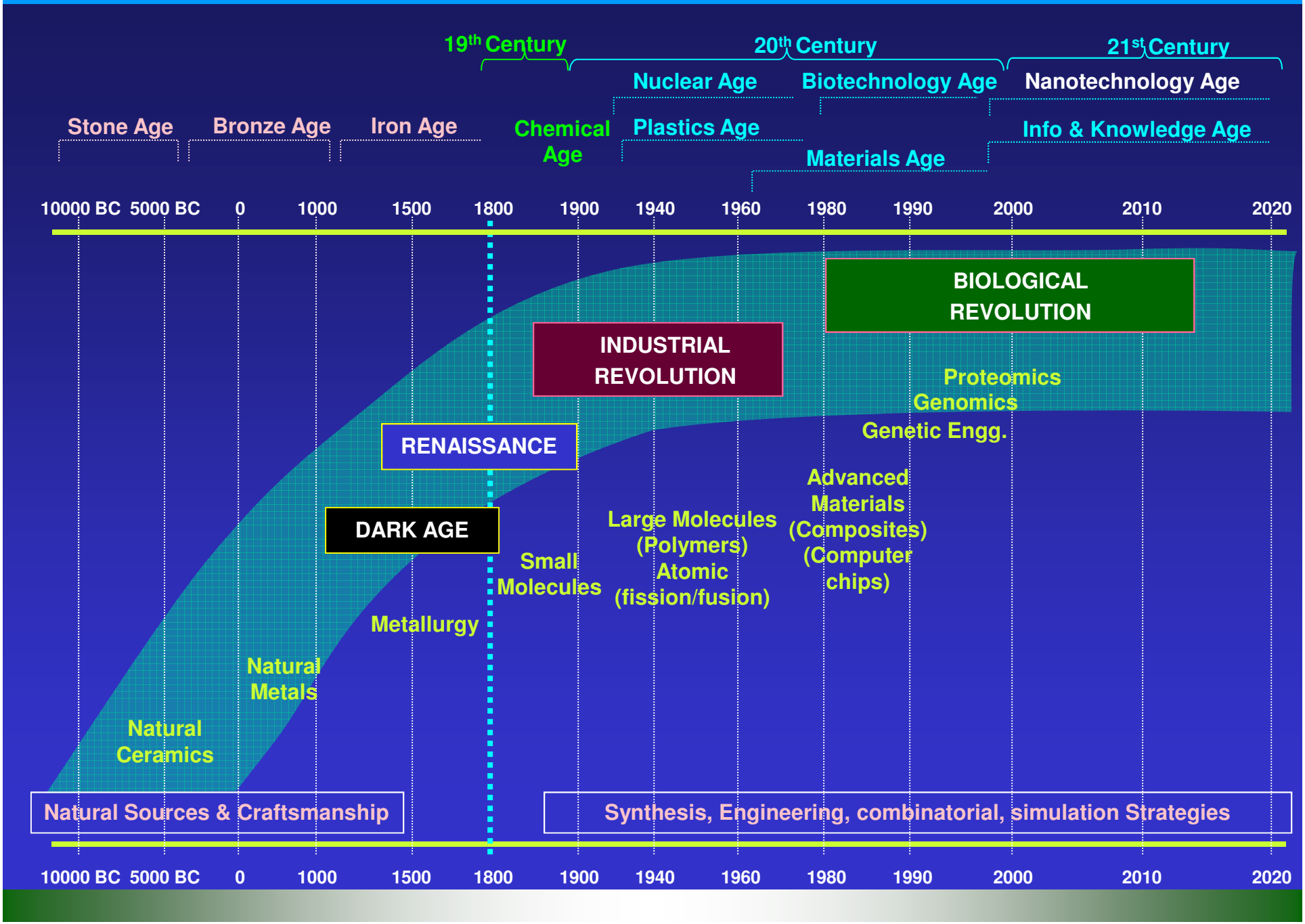
- Celebrate the achievements of chemistry
- Improve public understanding of chemistry
- Champion the role of chemistry in addressing the critical challenges of our society
  - Food and nutrition
  - Clean water
  - Sustainable energy
  - Climate change
- Broader outreach and engagement
- Get younger people more interested in chemistry

Madame Curie, Nobel Prize in Chemistry , 1911

OUTLINE

- How relevant is Polymer Science? How will this science address some of the most pressing problems of our society ?
- Where is technology leading ? What are the barriers and opportunities ?
- What are the new frontiers of research ?

TECHNOLOGY THROUGH AGES



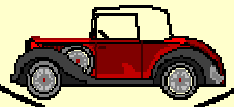
POLYMER SCIENCE : HISTORY

- **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 !**

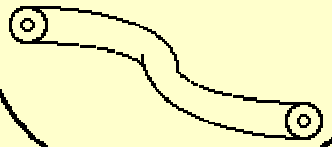
HISTORY OF POLYMERS

1500's
British explorers discover the ancient Mayan civilization in Central America. The Mayans are assumed to be among the first to find an application for polymers; as their children were fond of playing with balls made from local **rubber** trees.

1839
Charles Goodyear discovers **vulcanization**, by combining natural rubber with sulfur and heating it to 270 degrees Fahrenheit. Vulcanized rubber is a polymeric substances that is much more durable than its natural counter part. Its most common use today is in automobile tires.



1907
The oldest recorded synthetic plastic is fabricated by Leo Bakeland. **Bakelite**'s hardness and high heat resistivity made it an excellent choice as an electrical insulator.



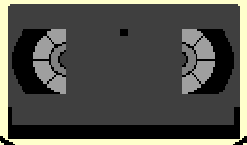
1917
X-ray crystallography is invented as a method of analyzing crystal structures. Eight years later, this method is used by M. Polanyi to discover the chemical structure of **cellulose**. This establishes the fact that polymer unit cells contain sections of long chain molecules rather than small molecular species.

1500-PRESENT

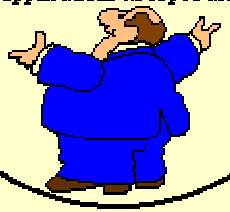
1920
Staudinger published his classic paper entitled "Uber **Polymerization**." Publication of this paper heralded a decade of intense research and presented to the world the development of modern polymer theory.

1927
Large scale production of **vinyl-chloride** resins begins. This polymeric compound continues to be widely used today to make plumbing (PVC) pipe, Buttery tile, and bottles.

1930
Polystyrene is invented. This polymeric material is used in videocasettes and other packaging. Expanded polystyrene (commonly called Styrofoam) is used in cups, packaging, and thermally insulated containers.



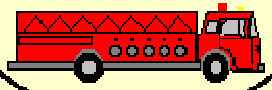
1938
Wallace Carothers of the Dupont company produces another well known polymeric product, nylon. **Nylon** is a common material used today for such applications as ropes and clothes.



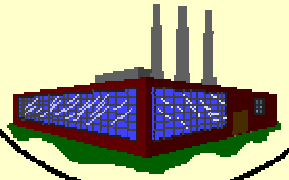
1941
Polyethylene is developed. Billions of pounds of both high and low density versions of this material are produced annually for everything from packaging film to piping to toys.

1970
James Economy develops one of the pioneer moldable high temperature polymers (**Ekonol**). This polymeric material paved the way for the development of liquid crystal polymers one year later. Ekonol's most common applications occur in electronic devices and aircraft engines.

1971
S. Kwolek, who has been awarded more than 37 patents in polymer science, develops **kevlar**. Kevlar is a high strength material that can withstand temperatures up to 300°C, and is used in applications such as bullet proof vests, and fire proof garments for firefighting and auto racing.



1976
The polymer/plastics industry outstripped steel as the nation's most widely used **material** per unit volume. We now use more plastic than steel, aluminum and copper combined.



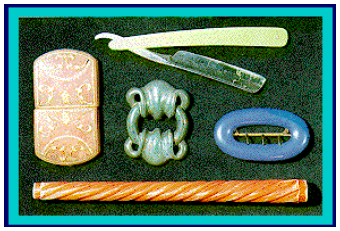
POLYMERS FULFILLING MATERIAL NEEDS OF SOCIETY…

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

Hi Tech Plastics

Sourc[illegible]lastic Federation Website

NEW PRODUCTS INTRODUCTIONS IN POLYMERS

- **Polymer Light Emitting Diodes (DuPont)**
- **SILK Dielectric Resins (Dow)**
- **Enhanced PU Tire System (Michelin)**
- **Strand Foam – PP Foam (Dow)**
- **Dendrimers (DSM)**
- **Smart Coatings (BASF)**
- **Materials for Fuel Cells (Celanese, DuPont)**
- **Polyester carbonate for body panels (Sollx / W-4, GE)**

Recent new product introductions have been predominantly small volume specialty materials

POLYMER SCENCE : 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 ~ 175 million tons of polymers.**

- **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 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 by Shell, Questra (syndiotactic polystyrene), PCHE (hydrogenated polystyrene), Index (ethylene –styrene copolymers by Dow).**

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

GLOBAL ISSUES THAT IMPACT THE POLYMER INDUSTRY

- **Energy consumption , driven by demands of emerging economies, is increasing exponentially**
- **Greater than 85 % of global energy demand is met by non renewable fossil fuels**
- **It is generally recognized that fossil fuel production has reached its peak and the era of "cheap oil" is over. Price of oil will be demand not supply driven**
- **Increase in oil prices will spiral into increase in the cost of feedstocks and polymer costs which cannot be passed on to consumers**
- **Polymers consume only 7 % of the fossil fuel; yet human addiction to oil as an energy resource will take precedence , making the cost of feedstock for polymers derived from oil unsustainable**

- **Difficulties in creating value and high entry barriers for new product introductions**

POLYMER MATERIALS : SUSTAINABILITY CHALLENGE

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

‘The future is in plastics, son’

Advise to Ben in

The Graduate (1967)

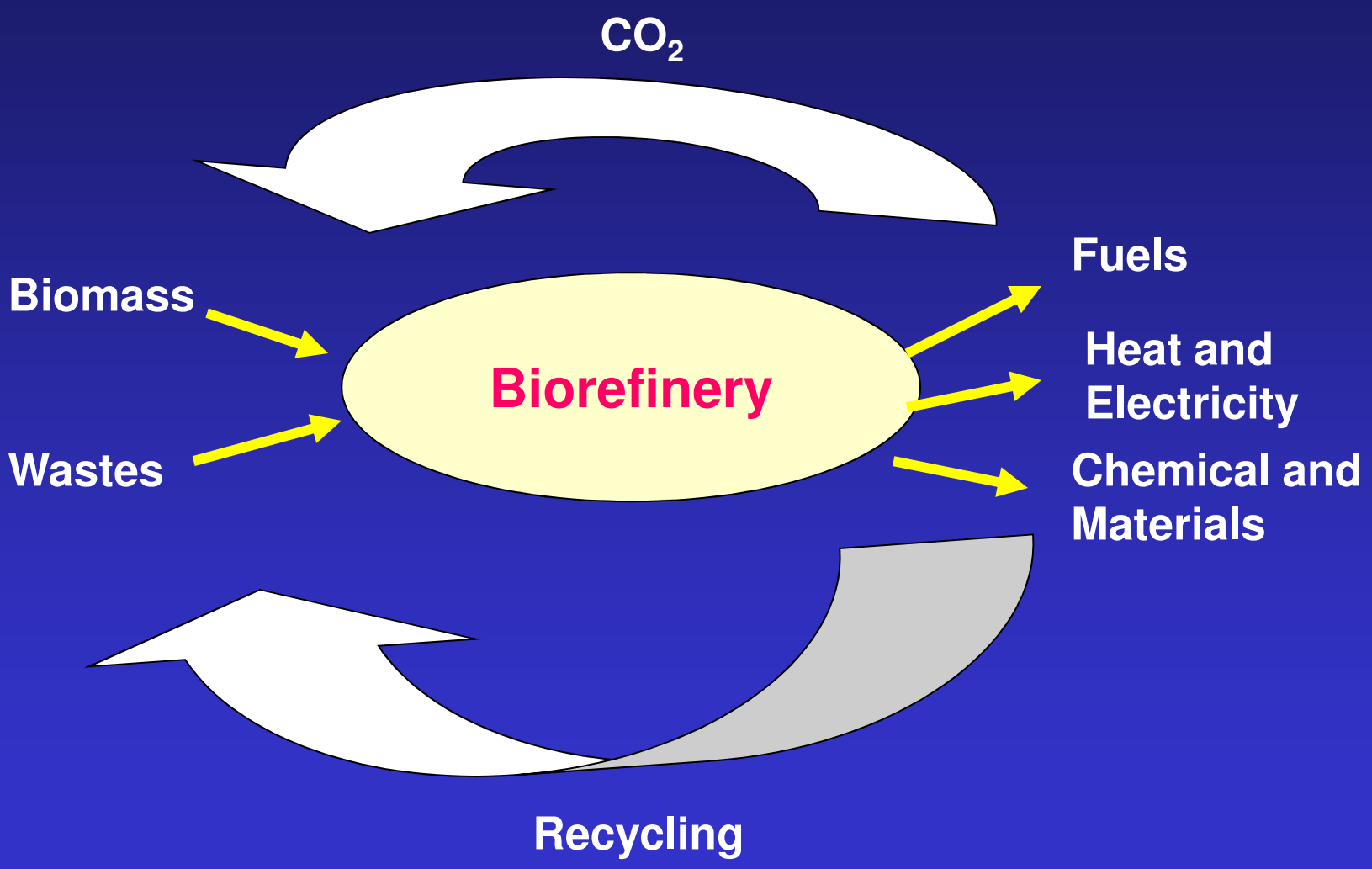
IS THIS STILL TRUE ?

FROM HYDROCARBONS TO CARBOHYDRATES REAPING THE BENEFIT OF RENEWABLE RESOURCES

- **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

FROM PETROLEUM TO BIOREFINERIES



ALIGNING POLYMER SCIENCE TO LARGER SOCIETAL NEEDS

Polymer Science

Areas of coalescence

- Energy
- Food
- Water
- Environment
- Functional materials
- Information Technology
- Health and human wellness
- Sustainable processes

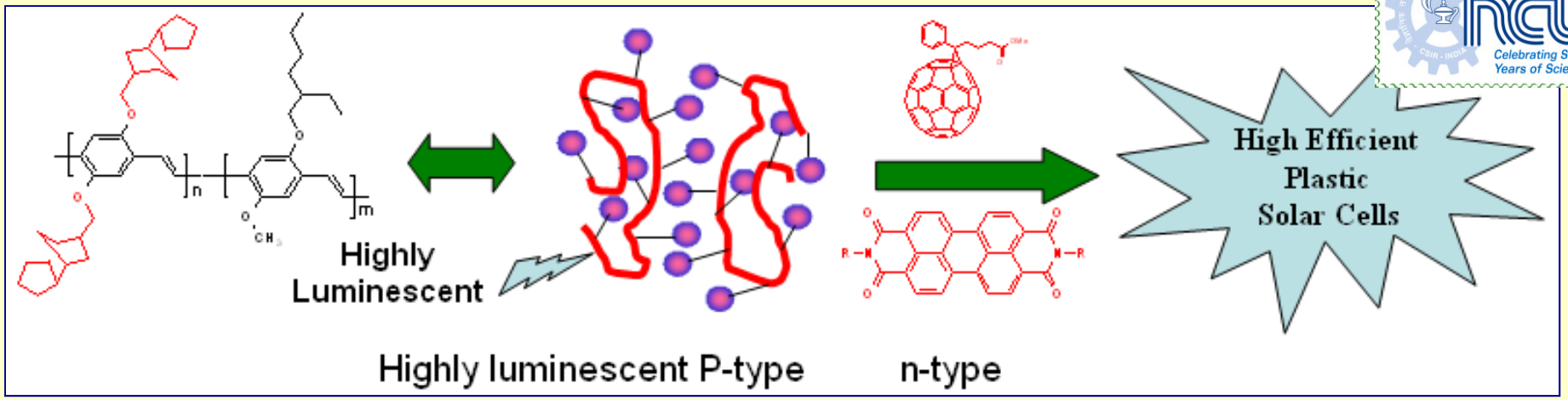
ADVANCED MATERIALS : EMERGING OPPORTUNITIES

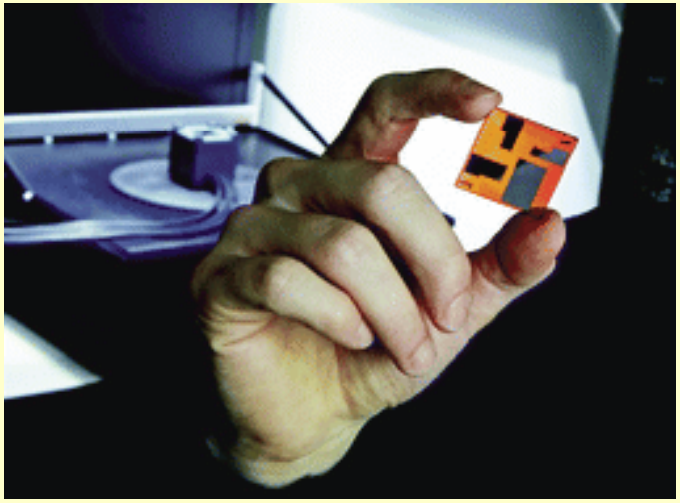
- ENERGY SYSTEMS

  - Flexible photovoltaics
  - Fuel cell materials

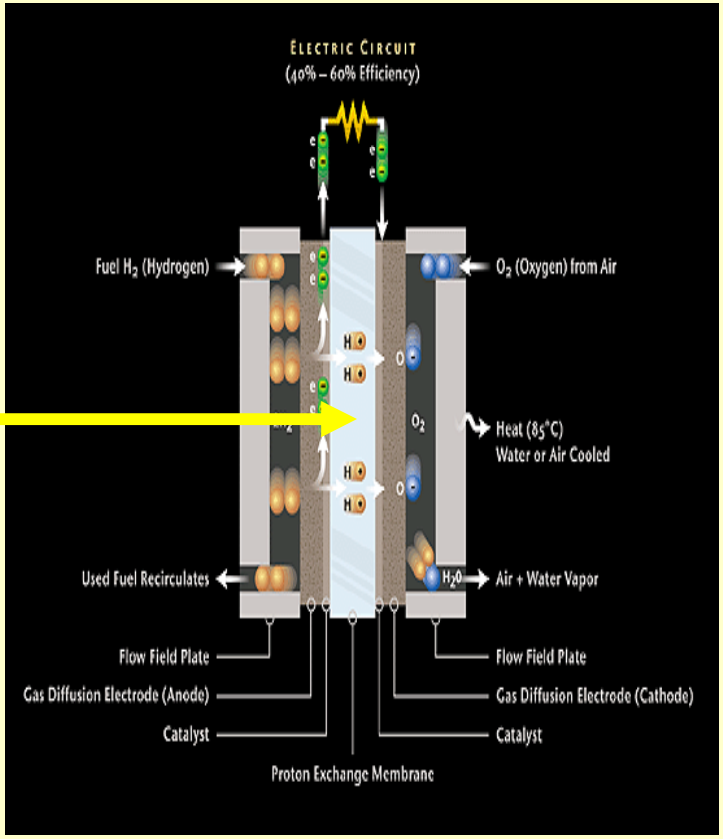
- SEPARATION TECHNOLOGIES

  - Nano-filtration using polymer membranes
  - Control of porosity
  - Polymers with tuned cavities
  - Porous Polymers by synthesis (HIPE)





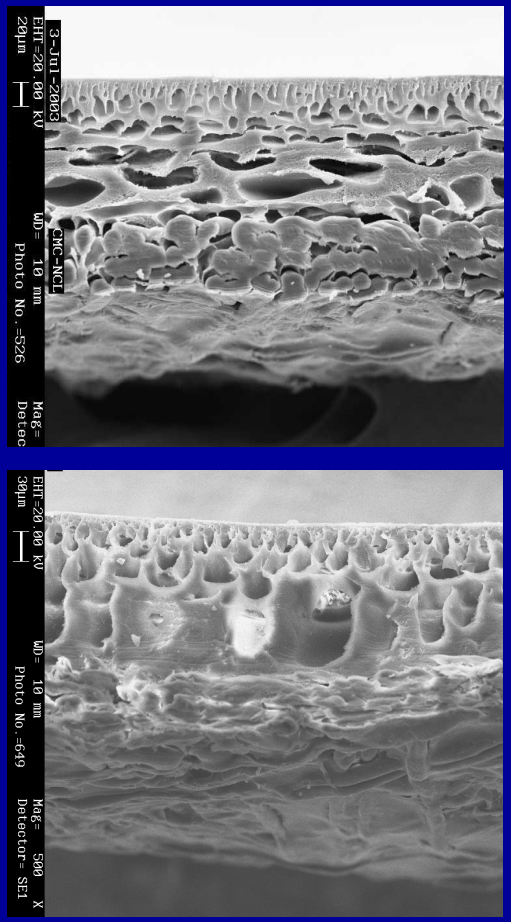
Polymer Membranes Sulfonated Fluoropolymer ionomers or Poly(benz-Imidazole)s



Conjugated polymer ZnO Nanoparticle hybrids

POROUS ULTRAFILTRATION MEMBRANE

- Membrane preparation: By phase inversion of a soluble complex of metal halides (salts of bivalent alkali metals) with poly(acrylonitrile) followed by washing the cast membrane with water
- Average water flux: 50 lmh at 0.5 bar
- 5 log reduction for viruses
- 7-9 log reduction for bacteria
- Molecular Weight Cut Off : ~ 60 k Dalton
- BSA rejection > 90 %
- Total membrane thickness : 9 - 11 mil



Membrane Cross Section (SEM)

UF MEMBRANE TECHNOLOGY : FROM CONCEPT TO MARKET

- **Discovery of a unique process to control membrane porosity**

  - Reject smallest known pathogenic species (virus);

  - Still be able to operate at tap water pressure (0.4 bar)

- **Prototype preparation, demonstration & performance evaluation**

  - Designed various easy to use prototypes

  - Demonstration & rigorous performance evaluation

- **Technology transfer**

  - Technology licensed to Membrane Filters India Ltd., Pune, a start up enterprise incubated at NCL

  - Product in the market since 2007; Current sales turnover of the company ~ US$ 15 million

THE DIMENSIONS OF MATERIAL SCIENCE

MATERIALS SCIENCE

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

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

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 multicomponent 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

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

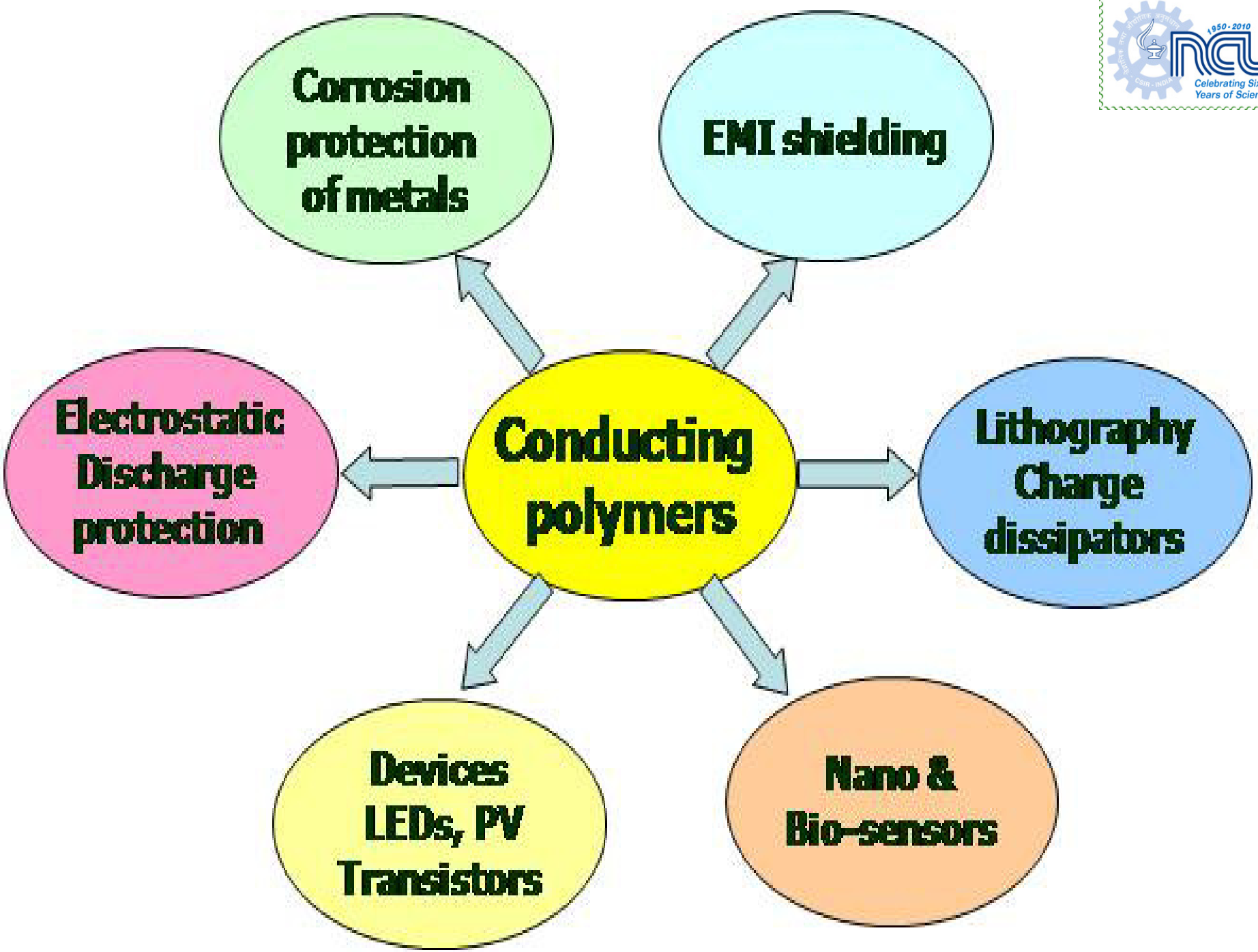
ADCVANCED AND FUNCTIONAL MATERIALS

- 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, molecular biology and physics

POLYMER NANO TECHNOLOGY

- **The creation and use of materials and processes on the nanometer scale with atomic precision**
  - **Semiconductor devices**
  - **Molecular wires**
  - **Molecular machines**
  - **Molecular switches/transistors**
  - **Molecular scale logic devices**


Corrosion protection of metals
EMI shielding
Electrostatic Discharge protection
Conducting polymers
Lithography Charge dissipators
Devices LEDs, PV Transistors
Nano & Bio-sensors

LIGHT EMITTING POLYMERS - THE SHAPE OF THINGS TO COME

- Use of polymers in light emitting diodes (LED's) exploits its semiconducting electronic properties
- LED's are conjugated polymers with delocalized π electrons. Electrons can be added, removed or transported easily along the chains. The extent of electron delocalization determines luminescence
- Forms the basis of emerging new display technologies (flexible electronics)
- High efficiencies (number of photons emitted per charge), high life times and a range of colors
- Major applications
  - Small monochromatic passively addressed displays (mobile phones/calculators)
  - Flat screen large area displays (TV/Laptop screens)
  - Flexible electronic newspapers
  - Custom signs
  - Wall paper that glows

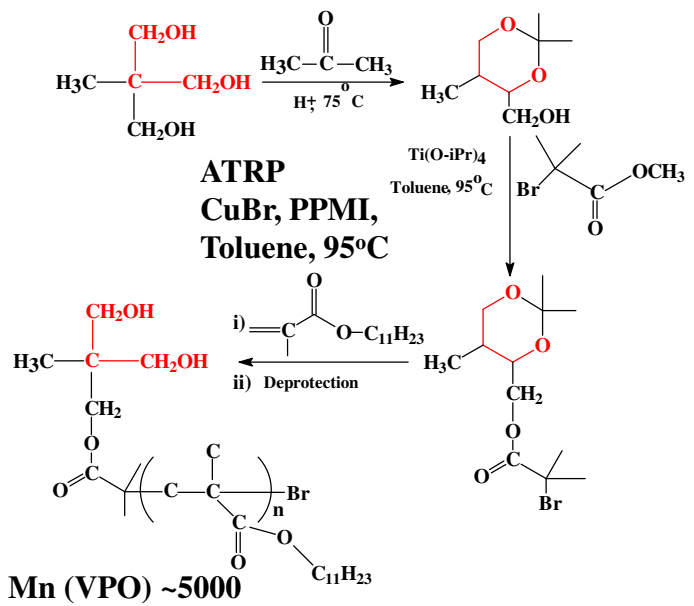
FUTURE CHALLENGES IN LED MATERIALS

- **Improved efficiencies, life time, purer color and fabrication of pixelated color displays**
- **Influence of chemical structure and supramolecular organization on material properties**
- **Understand interplay between morphology, mobility and light emission**

POLYMER NANOPARTICLES WITH UNIFORM SIZE AND SHAPE

- **Versatile applications**
  - **Calibration standards**
  - **Surface coatings**
  - **Pharmaceutical reagents**
  - **Medical diagnostics**
  - **Drug delivery systems**
  - **Supports for solid phase synthesis**
  - **Media for chromatographic separations**
  - **Carriers for toners in reprography / digital printing**
  - **Templating and nano- patterning using self assembled monolayers**

NEARLY MONODISPERSE POLYURETHANE NANOPARTICLES - FUNCTIONAL POLY(LMA) AS STERIC SURFACTANTS



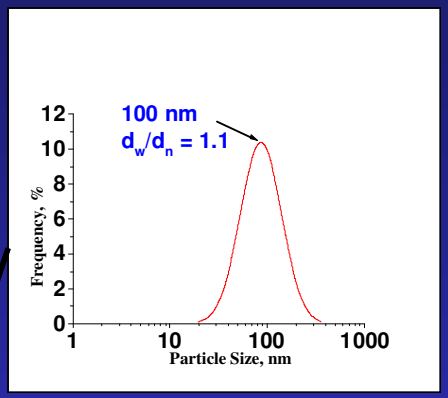
Mn (VPO) ~5000
Mw/Mn = 1.18

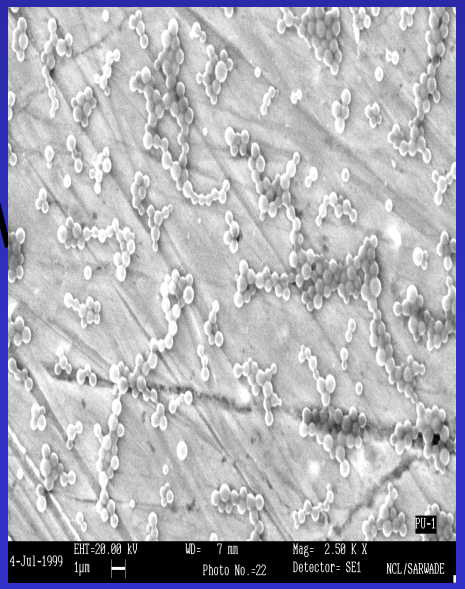
Stabilizer 5 wt %
DBTL 0.005%
Cyclohexane 20 parts

↓

TDI
60°C, 4 h
EHG
60°C, 4 h

PU particles





POLYMER SCIENCE R&D : NEW PARADIGMS

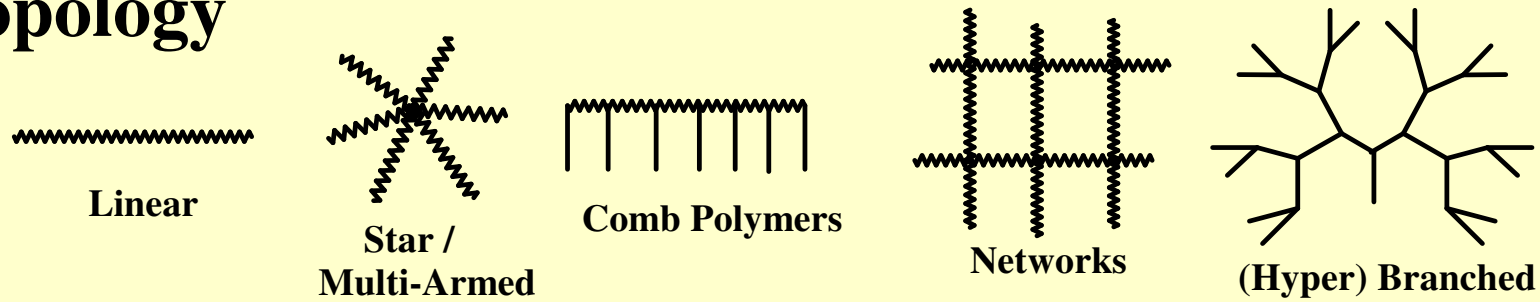
- **Research in polymer science began about sixty years ago as a discipline borne out of disciplines of chemistry , physics and engineering**
- **For over half a century the discipline flourished as an independent discipline – in education and research**
- **Explosive developments in the emergence of 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**

PLATFORM TECHNOLOGIES FOR THE 21st CENTURY

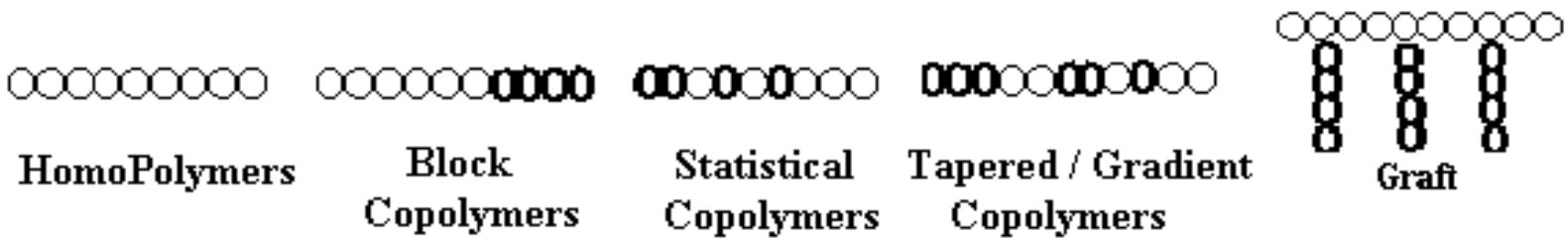
- **Information and communication technology**
- **Life Sciences and Biotechnology**
- **New Materials including Nanotechnology**

Structures accessible *via* techniques of controlled polymer synthesis

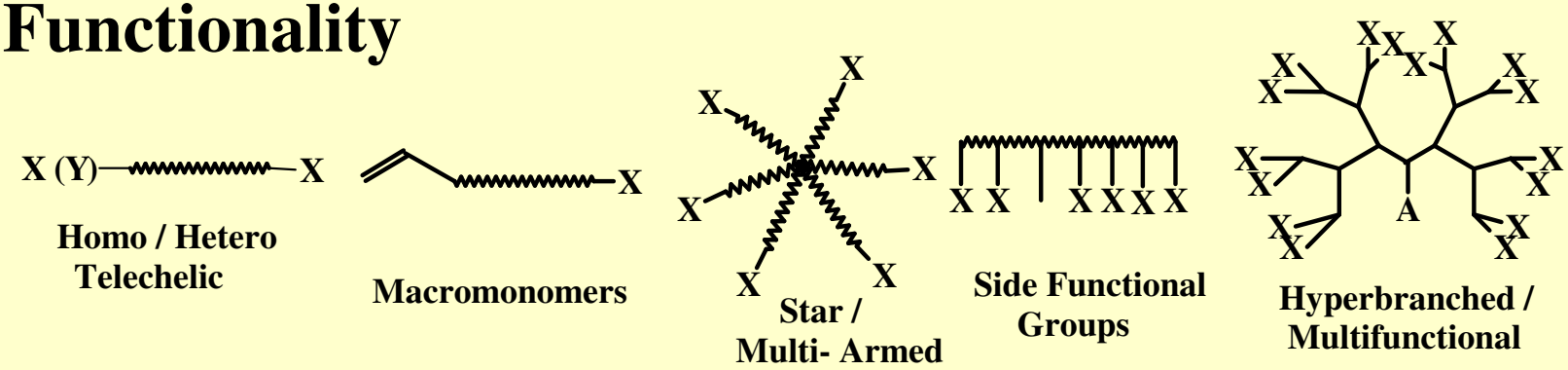
Topology



Composition



Functionality



CHAIN LENGTHS

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 …….

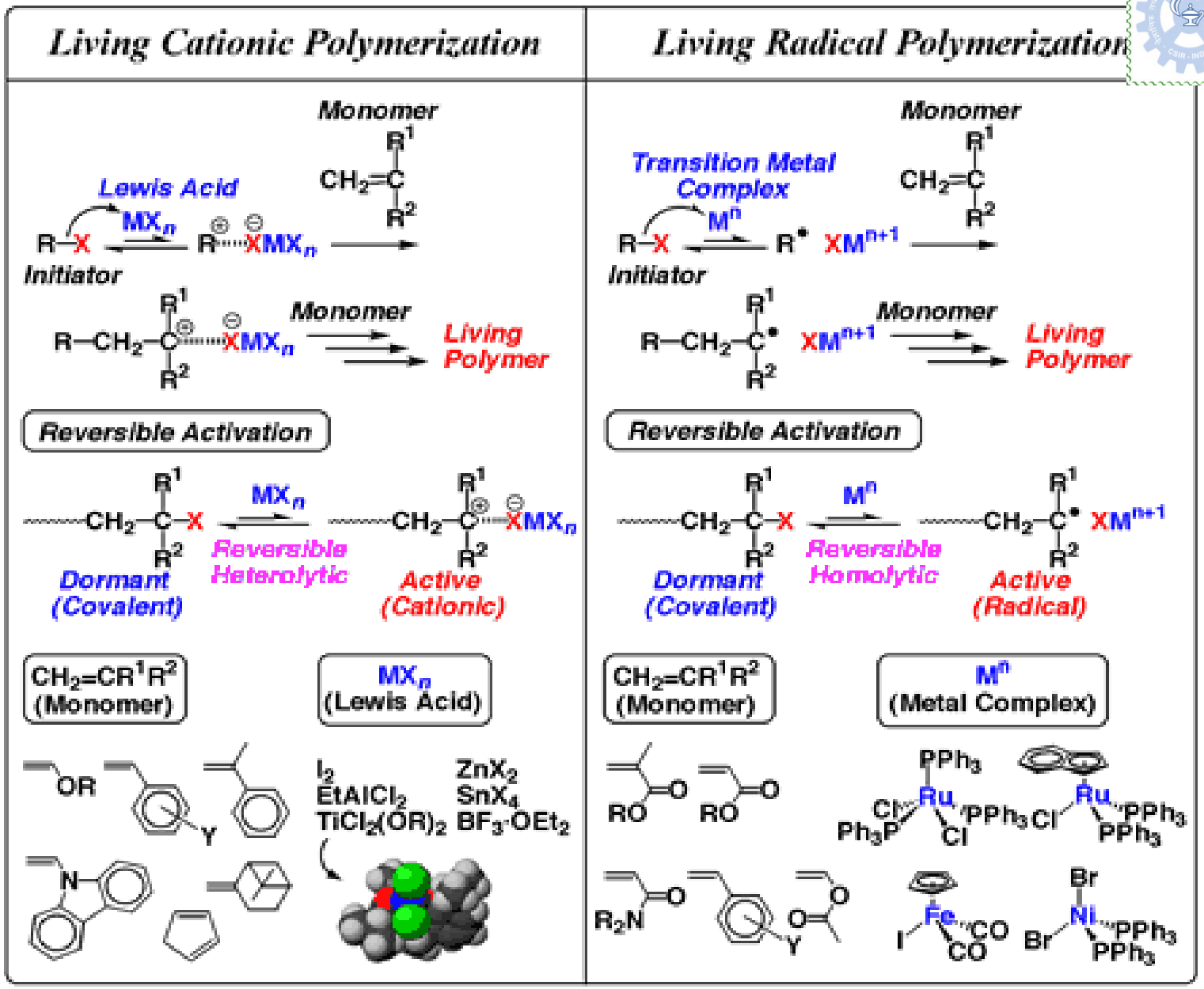
- Crystalline properties, solubility and rheological behavior

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
Monomer
Living Polymer
Transition Metal Complex
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

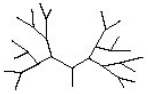
Topologies:


linear


star

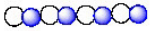

comb / brush

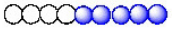

network/ crosslinked

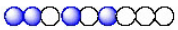

dendritic / hyperbranched

Compositions:

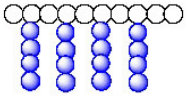

homopolymer


periodic copolymer


block copolymer

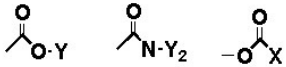

random copolymer


tapered / gradient copolymer


graft copolymer

Monomers:

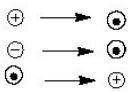
Vinyl:



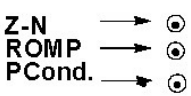
-Ar (Sty), Vi (Bu & IP), Pyr, CN, Cl, Br, Me, H

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

Transformations:



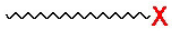
Z-N
ROMP
PCond.

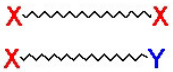


Hybrids:
synthetic/natural
organic/inorganic
surfaces; IPN; etc.

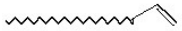
Functionalities:

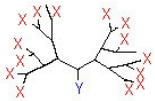

side-functional groups


end-functional polymers

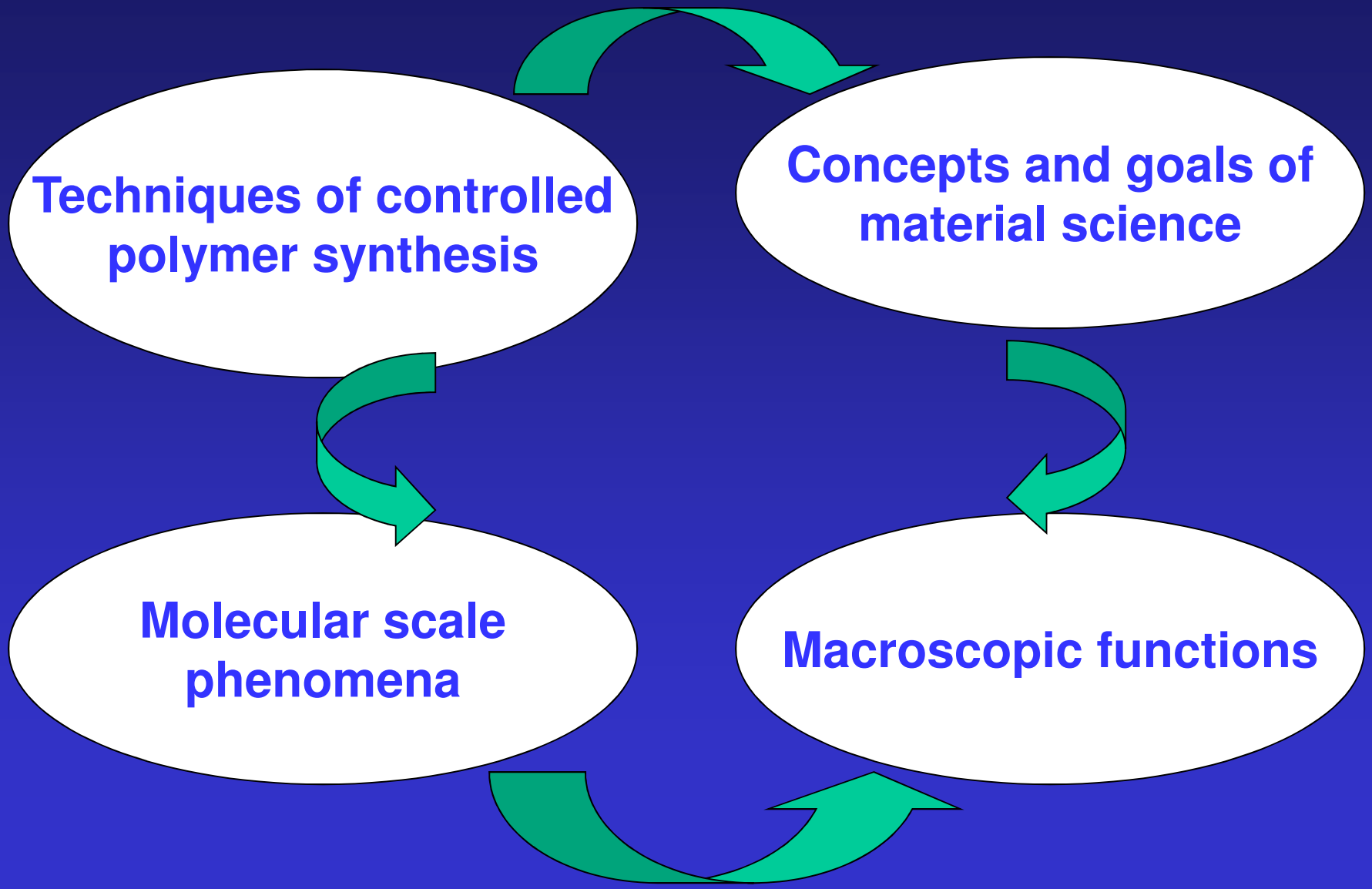

telechelic polymers


site-specific functional polymers


macromonomers


multifunctional

GOALS OF POLYMER SCIENCE



FUTURE OF POLYMER SCIENCE

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

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

LANGUAGE OF CHEMISTRY

Letters	Atoms
Words	Molecules
Sentences	Assembly of molecules
Paragraphs	Sets of molecular assemblies
Chapter	Expression of information by assemblies
Book	Transmission of information
Story	?

Nature has created the "story" of life millions of years ago through biological processes; chemists have just learnt to write sentences

THANK YOU