SCIENCE OF POLYMERS : QUO VADIS ?

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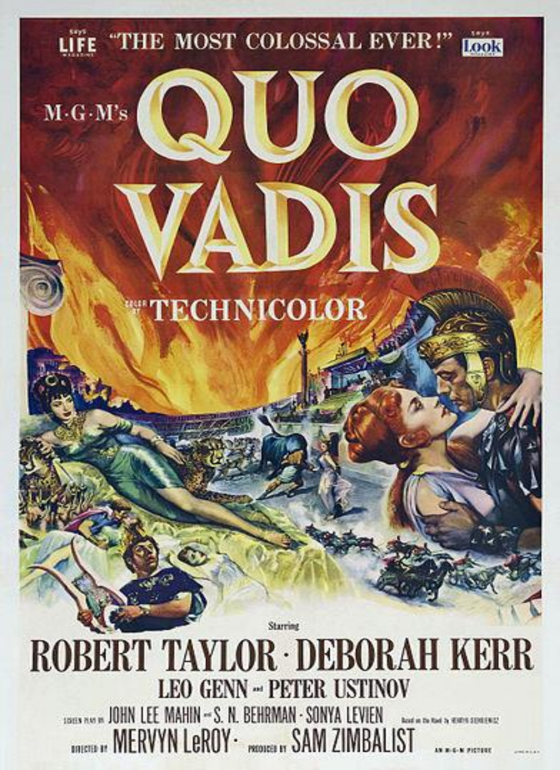
Quo Vadis ?

Peter asks Jesus "*Quo vadis?*" (pronounced [kʷo□ wadi□ s]), to which he replies, "*Romam vado iterum crucifigi*" ("I am going to Rome to be crucified again"). Peter thereby gains the courage to continue his ministry and returns to the city, to eventually be martyred by crucifying upside down

http://en.wikipedia.org/wiki/Quo_vadis%3F



A 1951 movie which won eight Academy Awards; considered a classic

OUTLINE

- Scientific frontiers and technology fronts
- Polymer science : History in perspective
- Polymers : Sustainability issues and learning from nature
- Polymer science : From the visible to the invisible
- Future of polymer science

TEMPTATIONS OF PREDICTING THE FUTURE: WHY DO IT?

- Choice of research area
- What should we teach the next generation?
- Curiosity
- Philosophy
- Expectations from society
- To ask if there is research that should not be done.

ANSWERS MUST BE SUBJECTIVE !

We are all like the blindfolded men who were asked to describe an elephant

And so these men of Hindoostan
Disputed loud and long
Each in his own opinion
Exceeding stiff and strong
Though each one was partly in right
But all were in the wrong

John Saxe (1872)

SCIENTIFIC FRONTIERS AND TECHNOLOGY FRONTS

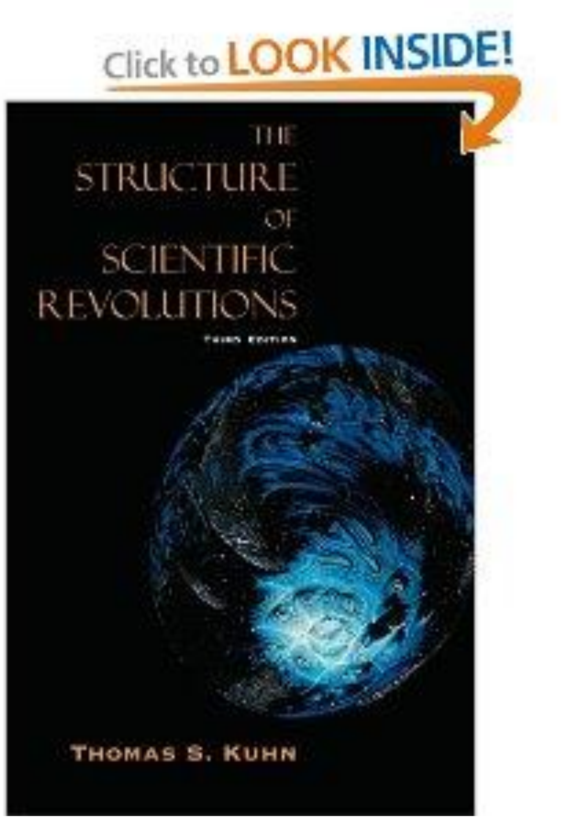
SCIENTIFIC FRONTIERS	:	**Frontiers, is a thought or knowledge not explored; difficult to predict frontiers; new science emerges rather unexpectedly**
TECHNOLOGY FRONTS	:	**Front, is a position directly ahead and can be forecast with some accuracy; it is often an extrapolation of the present**

New science can lead to technology; similarly emergence of technology can stimulate science

It is a two way street; science leads technology and technology leads science

THE NORMAL, DISCOVERY AND USE INSPIRED SCIENCE

- ***Normal Science*** : Develops existing and accepted ideas or scientific paradigms; solution of puzzles; answer is not important, but elegance of solution is more important
- ***Discovery Science***: Fundamental change in thought; solutions to problems; answer is important
- ***Use inspired science :*** It means using basic science for a purpose and practical problems as stimulus to curiosity driven research (G. W. Whitesides and J, Deutch, Nature 460, 21 (2011); D. E. Stokes, Pasteur's Quadrant, Brookings Institution, 1996)



The Structure of Scientific Revolution, T .S. Kuhn , University of Chicago Press, 1962

SCIENCE AND TECHNOLOGY

Technology: predictable (somewhat)

Science : unpredictable (totally)

To succeed in technology : pick robust science

To succeed in science : pick fragile assumptions

G. W. Whitesides, Assumptions: Taking Chemistry in New Directions, Angew. Chem., 43,3632 (2004)

PERILS OF PREDICTION

Those who have knowledge do not predict; Those who predict do not have knowledge
Lao Tzu

When a distinguished but elderly scientist states that something is possible, he is almost certainly right. When he states that something is impossible, he is very probably wrong

Arthur C. Clarke

Fools predict the future; smart people create it

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 !

POLYMER SCIENCE : THREE PHASES OF EVOLUTION

- Post Industrial Revolution (1760-1900)
- World War I and II (1900-1950)
- The era of Inexpensive Petroleum (1950- 1980)

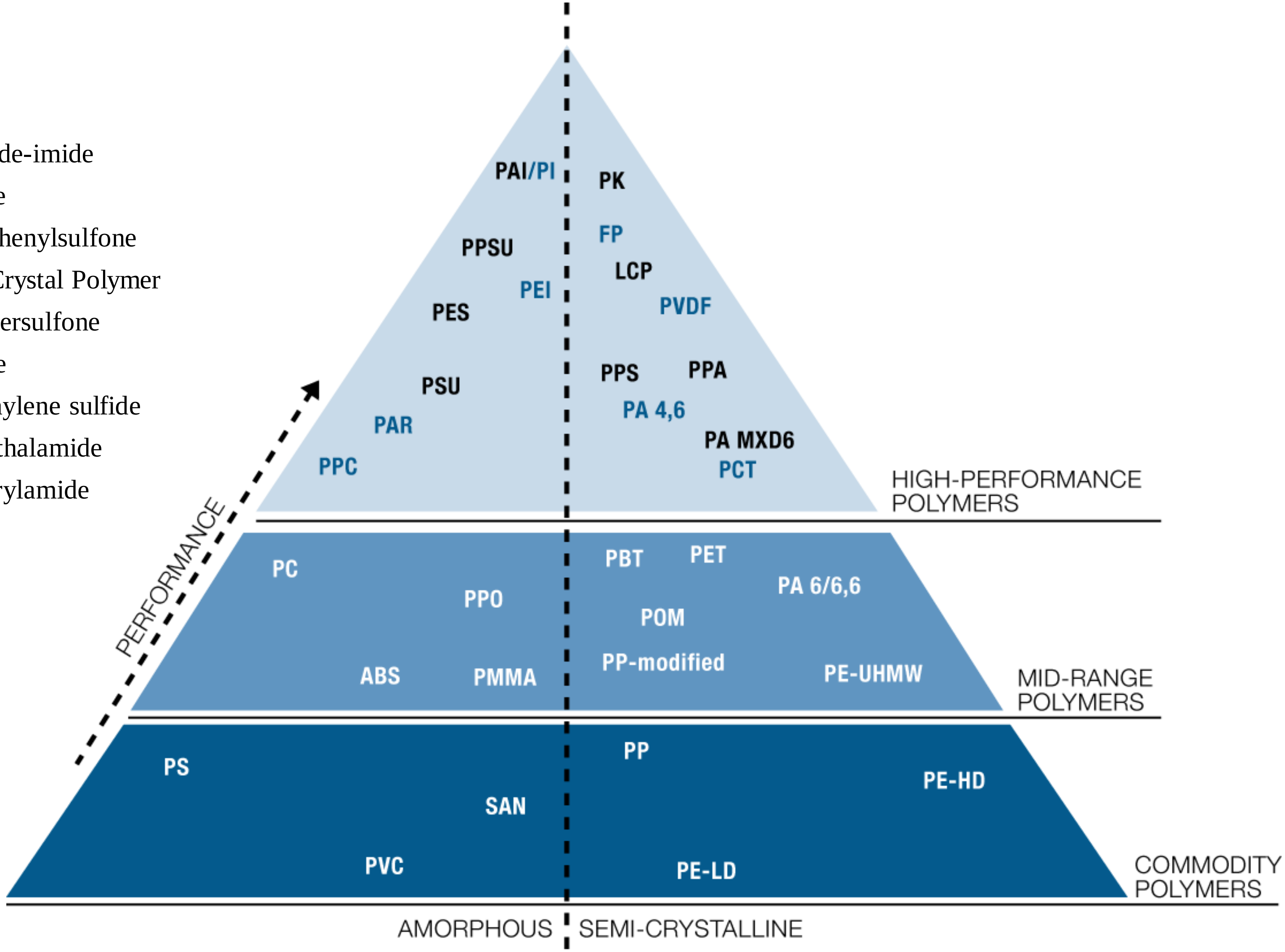
- The beginnings of chemistry as a science (1800-1900)
- Atoms and molecules; understanding structure and the nature of the chemical bond (1900-1940)
- Understanding reactive intermediates in chemistry: The birth of physical organic chemistry (1940-60)

THE GOLDEN ERA IN POLYMER SCIENCE (1930-1960)

- PVC (**1927**) : Replaces natural rubber as cable insulation/ sheathing
- Polystyrene (**1930**) : First commercial production by IG Farben
- Poly(chloroprene (**1931**) by DuPont , the first man made elastomer
- LDPE (**1935**) by ICI for radar, telecommunication cables
- PMMA (**1936**) : Canopies and cockpit covers for airplanes
- Nylon **(1938**) by DuPont, 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**) by GE
- Poly(tetrafluoroethylene) **(1946**) : Teflon by DuPont
- Epoxy Resins(**1947**) : Araldite by CIBA
- Linear polyethylene (**1954)** and polypropylene (**1955)**
- High *cis* polybutadiene and *cis* polyisoprene (**1954**)
- Polycarbonate (**1960**) by GE and Bayer
- Polyacetal, polysulfones, polyetherketones and polyetherimides (**1960-65**)

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



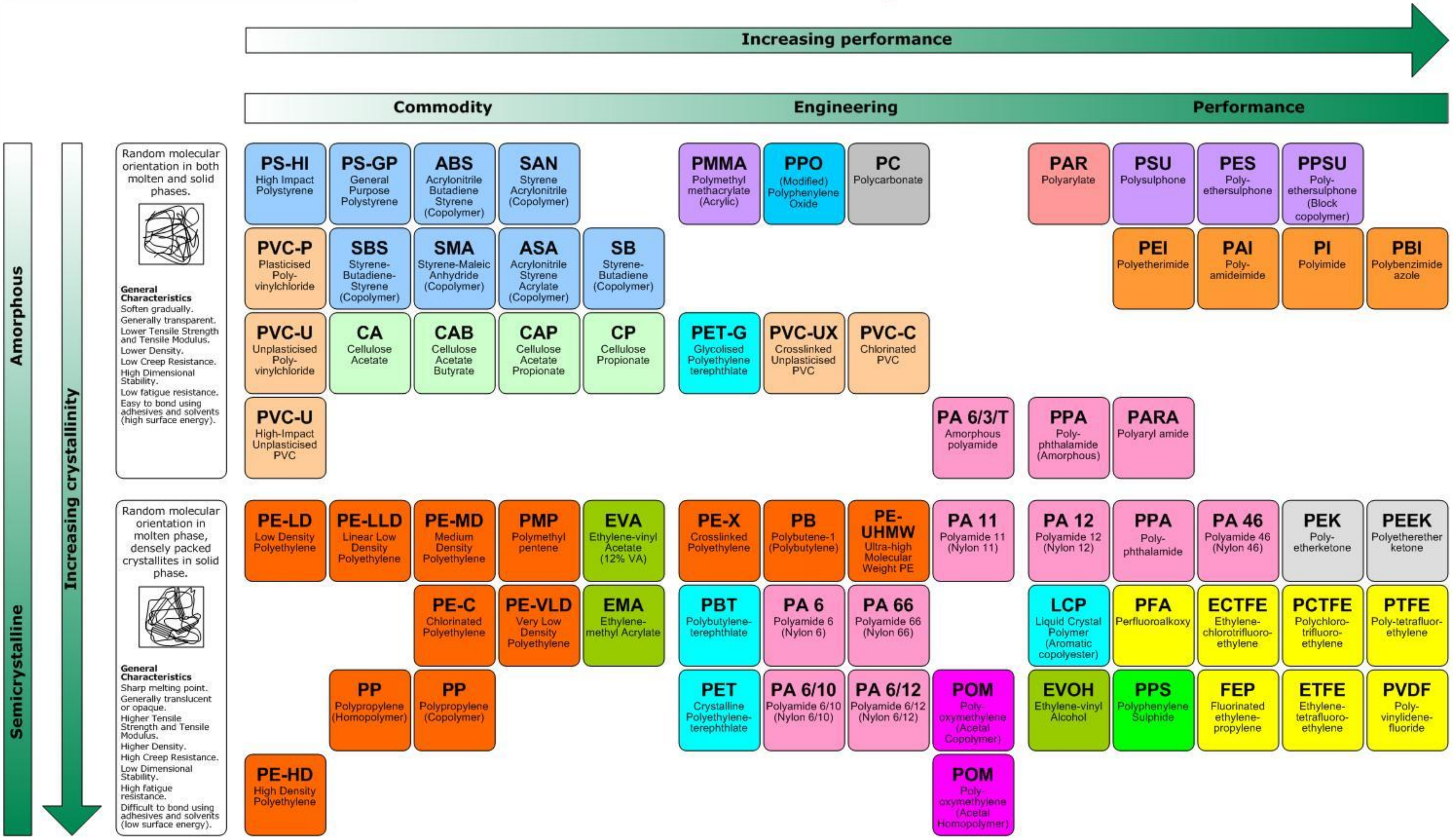
…nts by Medvedev was a historic achievement in … to see the relationship between structure and …

…ationship 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



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).

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).

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			
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

POLYMER MATERIALS

- Global production : 270 million tons
- Employment : 60 million jobs
- Global consumption : 30 kg per capita
- Business value : US $ 1200 billion per annum
- Consume less than 10% of fossil hydrocarbons
- India’s production : 15 million tons by 2015

Industry grew from zero to present capacities in about fifty years, the fastest ever growth of any industry in the post industrialized world

NEW POLYMER INTRODUCTION : ENTRY BARRIERS

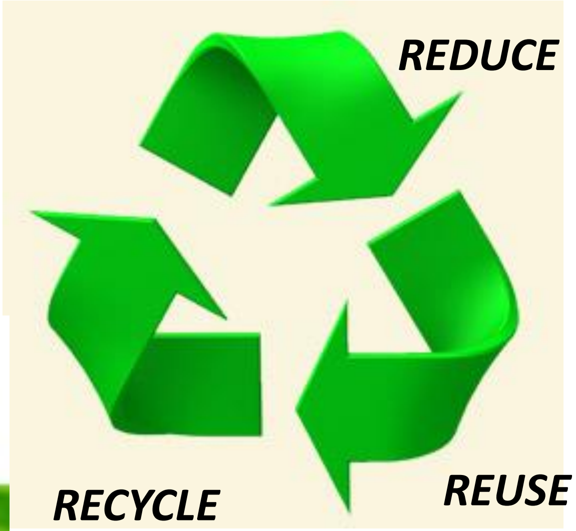
- No new polymers has entered the market since the early nineties. The last ones were poly(propylene terephthalate) by DuPont (PTT) , poly(ethylene naphthalate) by Teijin (PEN) and Nature Works poly (Lactic Acid)s by Cargill.

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

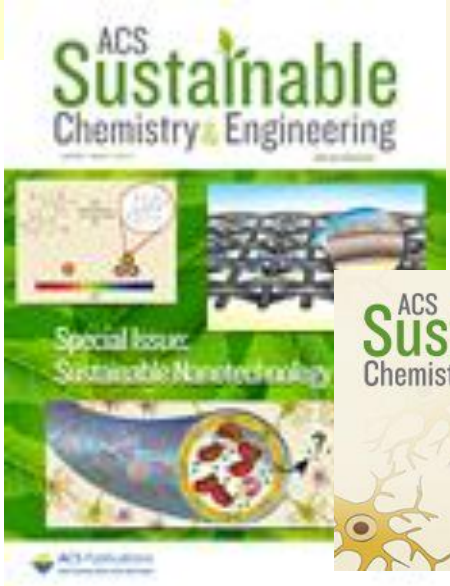
- The rate of growth of markets of the new polymers introduced after the nineties have been painfully slow.

ORGANIC POLYMERS : SUSTAINABILITY ISSUES

- **Exclusive dependence on fossil fuel based resources**
- **Generation of wastes that need disposal**



Sustainability is the key concern of science, technology, industry and society today


ACS Sustainable Chemistry & Engineering

Special Issue: Sustainable Nanotechnology


ACS Sustainable Chemistry & Engineering

Special Issue: Sustainable Nanotechnology

Can the materials needs of humankind be based on the concept of sustainability of both resources and environment?

Poly(ethylene terephthalate)

Over 30 billion liters of bottled water is consumed annually

Every second we throw away about 1500 bottles

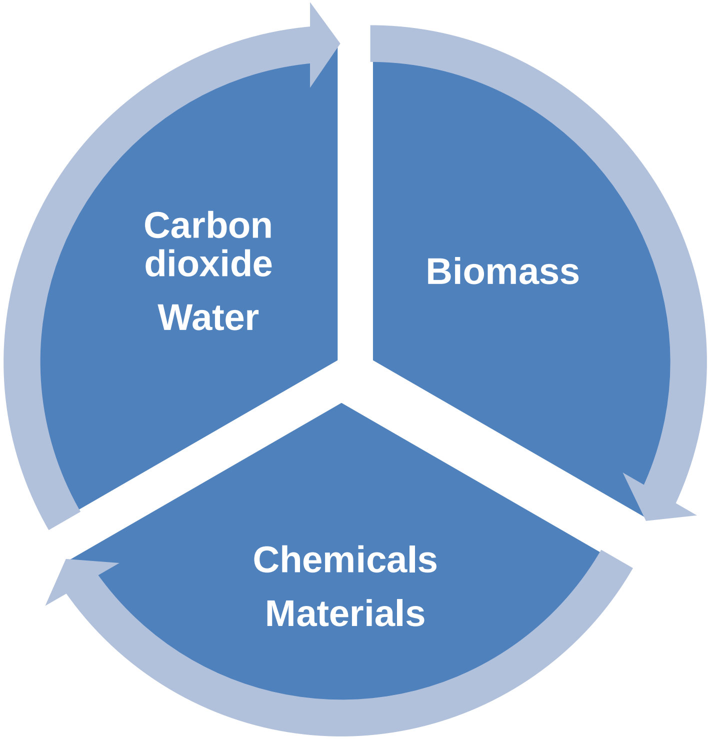
What is the solution ?

OUR INSATIABLE DESIRE TO CONSUME

- W. Europe consumes an average of 16 tons of materials per person per year, of which 6 tons ends up as waste, including 3 tons of landfill
- We consume 30 kg of packaging material per person per year, all of which ends up as waste
- We discard about one trillion single use plastic bags each year; generate 2 billion tons per annum of municipal waste; 13 billion plastic bottles thrown away annually; 5 million tons of plastics find their way into our oceans
- Global recycling rate is only about 10 % of the materials consumed
- Delhi generates 10,000 tons per day of solid municipal waste; By 2020 Delhi will need 28 sq km of land for landfill, equivalent to the area of New Delhi !
- Using resources at the current rate we will need " the equivalent of more than two planets to sustain us " by 2050 !

Unsustainable consumption of finite resources requires resource innovation

FROM HYDROCARBONS TO CARBOHYDRATES : FROM NON RENEWABLES TO RENEWABLES



Can a part of the chemicals / materials manufacturing progressively shift to renewable carbohydrate resources (biomass) ?

Is such a virtuous cycle just a dream ?

POLY(LACTIC ACID)S : AN ALIPHATIC POLYESTERS FROM A SIMPLE AB MONOMER

- Monomer Lactic acid (R or S) is produced by fermentation of sugars
- PLLA is hydrophobic, impermeable to water, hydrocarbon resistant
- Biodegradable and compostable
- Clarity and physical properties similar to PET
- Requires ~ 49 % less fossil fuel to produce PLLA compared to PET
- 0.75 kg of CO2 emitted per kg of PLLA produced versus 3.4 kg of CO2 per kg of PET

If PLLA is so attractive from a sustainability point of view, why is it still not a part of our every day life ?

“DROP- IN” BIOPOLYMERS : DOES IT MAKE SENSE ?

- Bio PE, Bio PP, Bio PET, Bio PVC , Bio Butyl, Bio butadiene !
- All monomers derived from sugar ethanol
- Apart from competition from food large scale fermentation processes are not carbon neutral; every Kg of ethanol by fermentation results in 1 Kg of carbon dioxide
- Poor atom efficiency; starch to ethylene has an overall carbon atom efficiency of 65%; A cracker converts ethane to ethylene in > 90 % carbon atom efficiency
- Selling price of PE is $ 34 per million Btu; ethanol from corn sells at $35 per million Btu
- We will need 400 sq miles of land planted with sugar cane to set up one world scale plant of PE of 350,000 tpa

Are we managing sustainability or mere perceptions ?

NATURE'S APPROACH TO SUSTAINABLE MATERIALS

Nature designs material with great care and attention to details

- Economy in the use of raw materials
- Minimum use of energy
- Easy to recycle under ambient conditions

Nature achieves this sophistication through highly organized fabrication methods and hierarchies of structures

WHICH COMPANY IN THE WORLD PRODUCES …………

- Biodegradable fibers stronger than steel
- Biodegradable photo-detectors more sensitive than the most advanced photonics technology
- Biodegradable super-hydrophobic surfaces
- Toughest ceramic biodegradable nano-composites
- Biodegradable data storage media that carry one bit of information for every three molecules

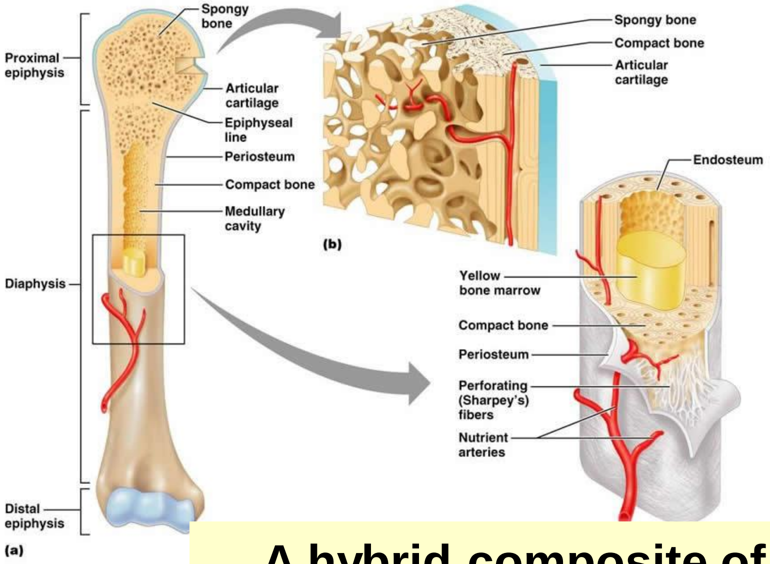
Superhydrophobic surface

Abalone shell

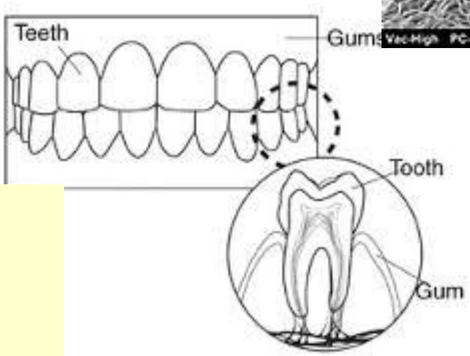
Surface Photonic Gratings

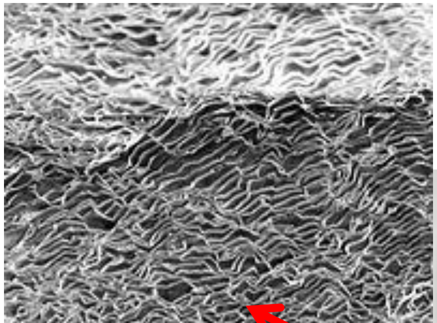
This company is called Life Inc.,

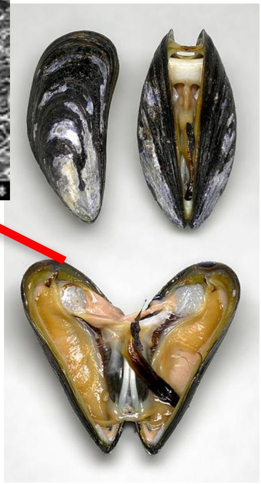
Its materials are the most advanced on this planet



A hybrid composite of Hydroxyapatite and Collagen Type II







Aragonite layers in the nacre of a blue mussel

MATERIAL SYNTHESIS : NATURE'S PRINCIPLES

- Optimal use of energy and raw materials
- Minimal energy consumption – most synthesis occurs at <45^{o}C
- Molecular control leading to flawless materials: Self healing and self-correcting principles
- Use of compatible chemistries
  - Ceramics : $CaCO_3$, SiO_2
  - Non-ceramics : Proteins, polysaccharides
  - Water : Plasticizer
  - Partitioning and separations : Lipid (Bilayer membranes)
  - Hydrophobic interaction : Orientation
  - Liquid crystallinity : Processing of materials

Will the twenty first century be the age of
bio-inspired materials ?

ADVANTAGES OF MATERIALS MADE BY NATURE

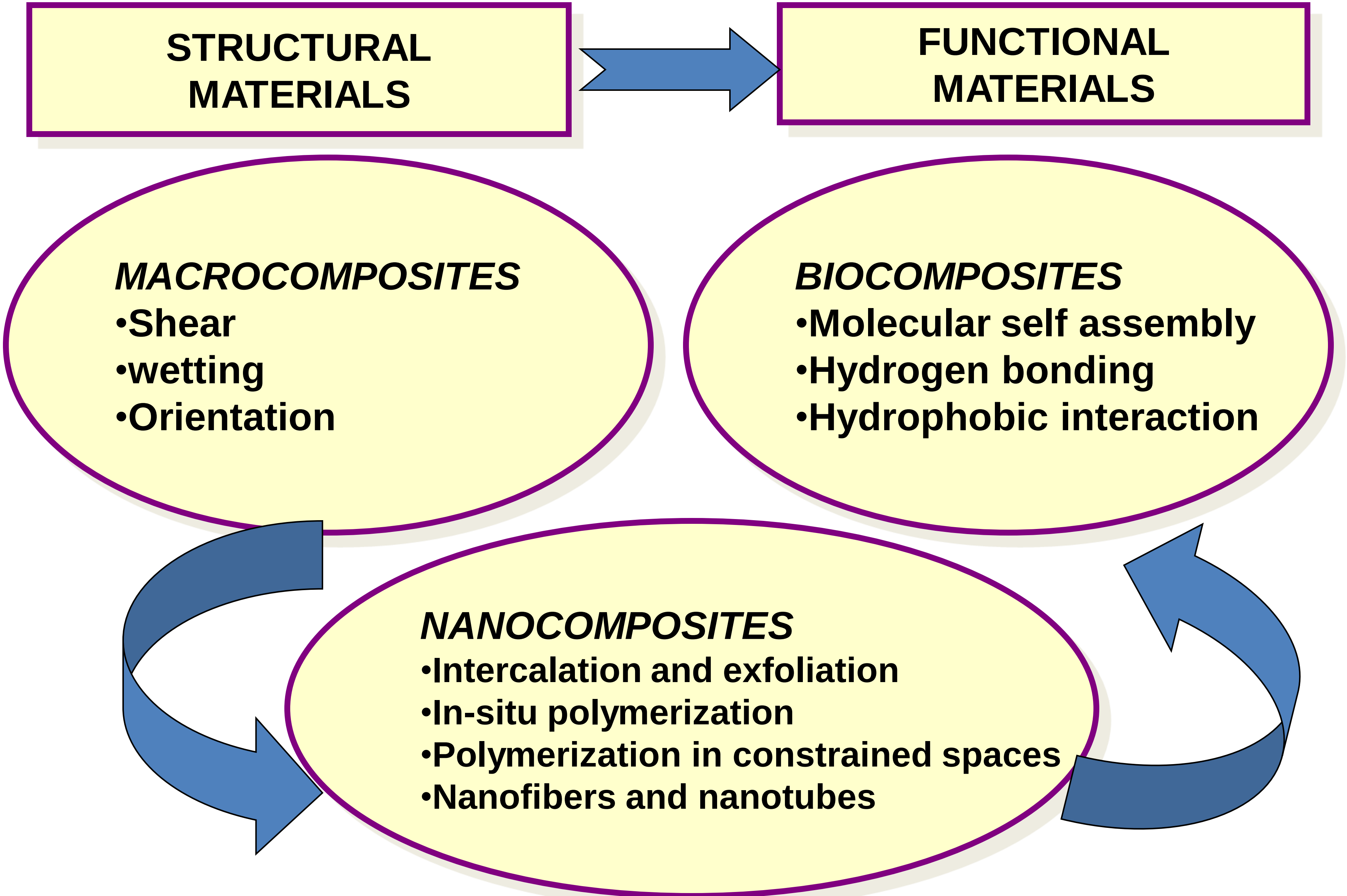
- Efficient synthesis, if you are prepared to wait long enough
  - Fastest rate of bone growth : 1 μm/day
  - Growth of egg shells : 5 g/day
- Recycling
  - Animals/Plant continuously recycle/ repair their constituent materials
  - Choice : make materials that are strong/ tough with finite probability of catastrophic failure (man)

    or

    make materials that are relatively weaker, but have self healing or repair capabilities (nature)

Self-healing structures and tough materials are emerging from an understanding of nature's processes

FROM STRUCTURAL TO FUNCTIONAL MATERIALS



STRUCTURAL MATERIALS

FUNCTIONAL MATERIALS

MACROCOMPOSITES

- **Shear**
- **wetting**
- **Orientation**

BIOCOMPOSITES

- **Molecular self assembly**
- **Hydrogen bonding**
- **Hydrophobic interaction**

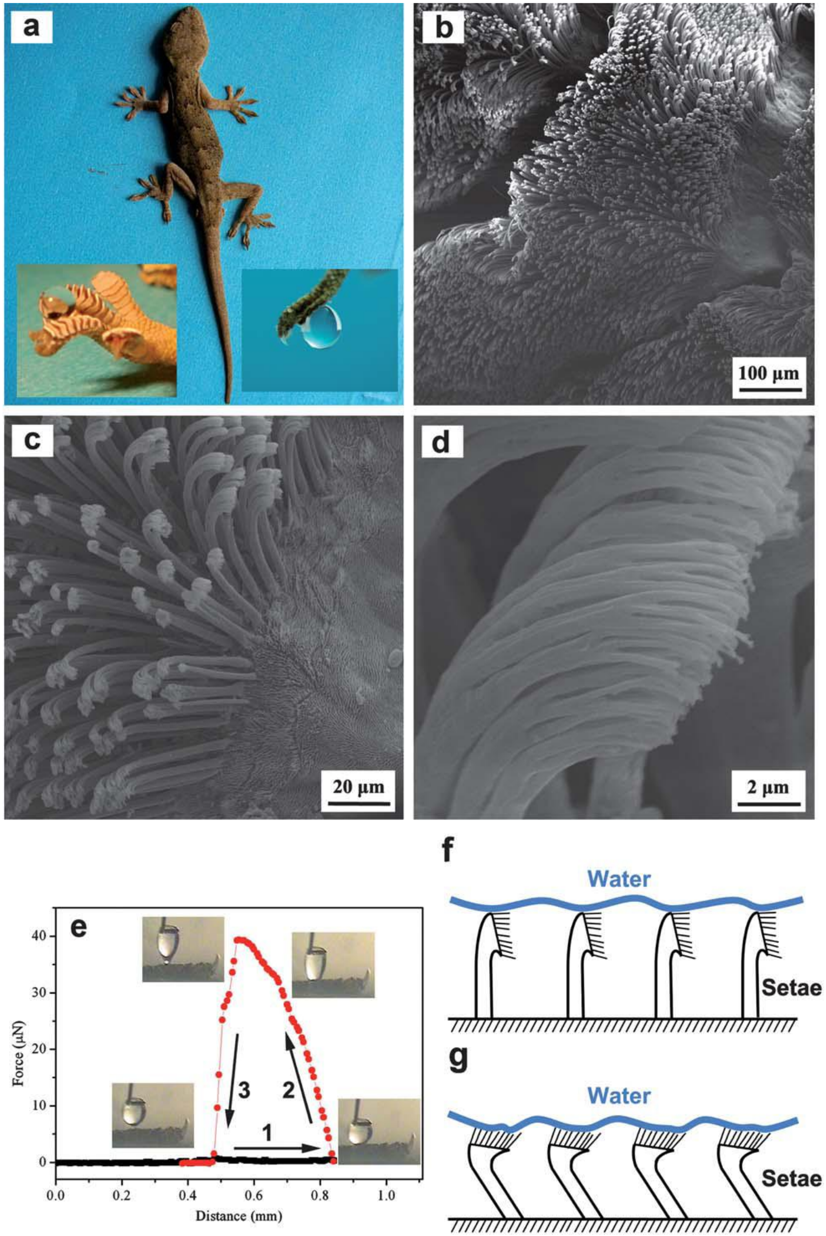
NANOCOMPOSITES

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

SUPER HYDROPHOBIC GECKO FEET WITH HIGH ADHESIVE FORCE TOWARDS WATER

An illustration of functional integration of multiscale structures in biological materials

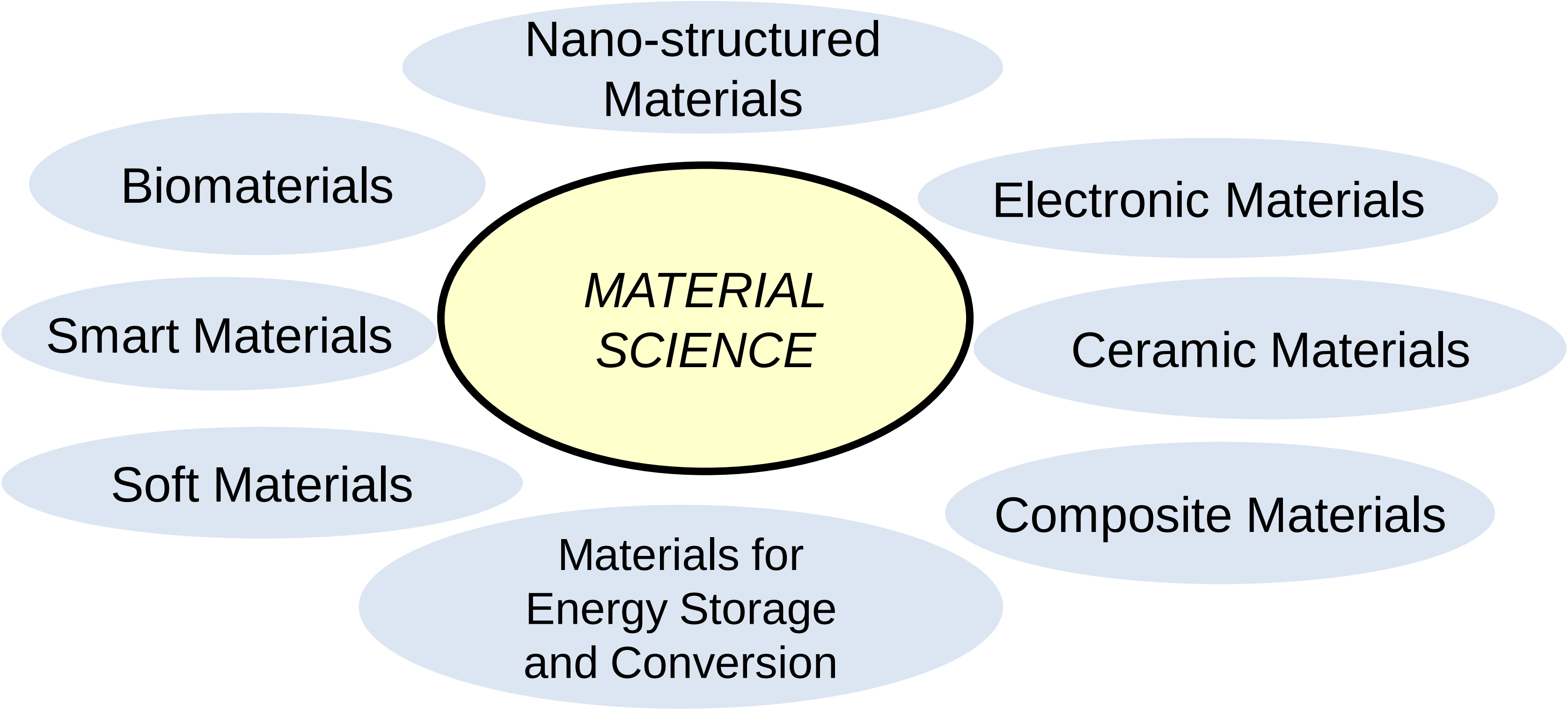
K. Liu et al.,Nanoscale, 4, 768 (2012)



POLYMER SCIENCE: FROM A VISIBLE TO AN INVISIBLE SCIENCE

- In the early years, advances in polymer science led to objects that you could see, touch and feel
- However, increasingly polymer science is becoming invisible.
  - Energy harvesting, conversion and storage devices
  - Micro-electronics
  - Medicine / therapeutics / diagnostics
  - Information technology
  - Clean air and water
  - Formulated products(adhesives, coatings, lubricants, cosmetics, personal care products, construction chemicals etc)

THE NEW DIMENSIONS OF MATERIAL SCIENCE



MATERIAL SCIENCE

Nano-structured Materials

Biomaterials

Electronic Materials

Smart Materials

Ceramic Materials

Soft Materials

Composite Materials

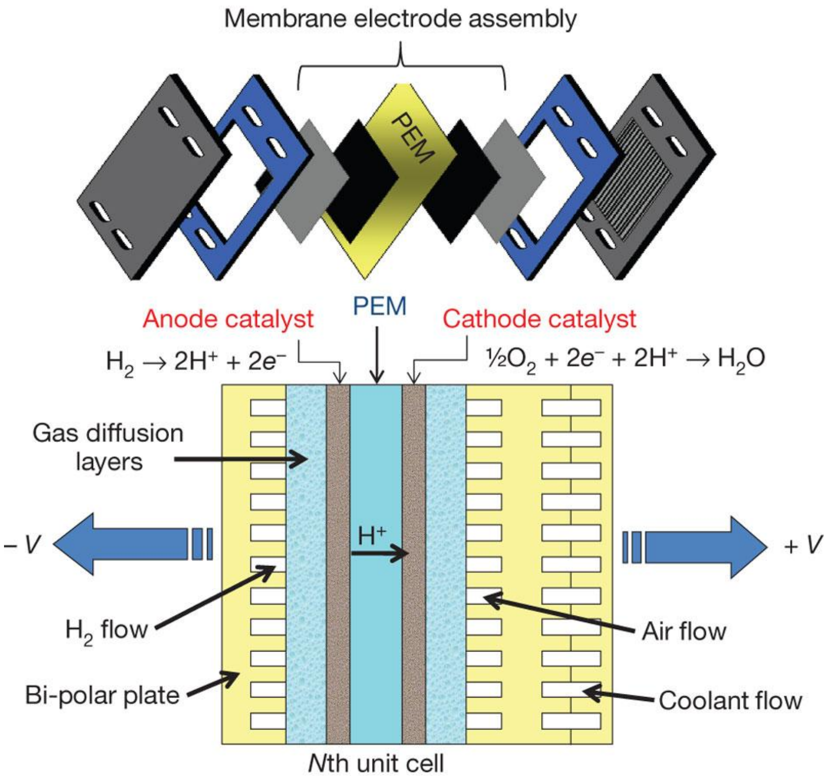
Materials for Energy Storage and Conversion

Increasingly polymer science will be an enabling science ; to create advanced materials with useful functions in combination with other materials

ADVANCED MATERIALS : EMERGING OPPORTUNITIES

- **ENERGY SYSTEMS**
  - Flexible photovoltaics
  - Fuel cell materials
- **SEPARATION TECHNOLOGIES**
  - Nano-filtration using polymer membranes
  - Porous polymers
  - Polymers with tuned cavities

COMPONENTS OF A FUEL CELL



- ➢ Produces electricity from the electrochemical oxidation of hydrogen
- ➢ A fuel cell stack comprises of identical repeating unit of cells, called Membrane Electrode Assembly (MEA)
- ➢ The MEA electrodes are attached to a solid polymer proton conducting membrane that conducts protons, not electrons
- ➢ Hydrogen is oxidized at the anode and oxygen is reduced at the cathode
- ➢ The entire assembly is compressed by bipolar plates that introduce gaseous reactants and coolants to the MEA

M K. Debe Nature, 486, 43-51 (2012)

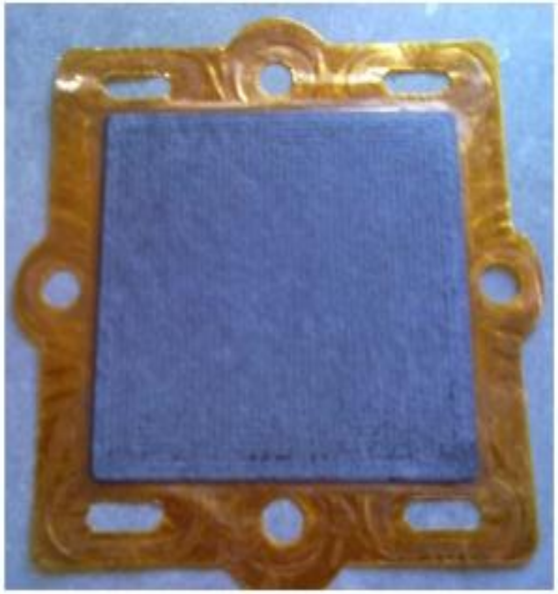
POLYMER STRUCTURE

- Ring substitution electronic/ steric
- Co-monomers flelxible / rigid
- Porosity
- Crosslinking

POROSITY

PROPERTY

- Molecular weight
- Tg / free volume
- Crystalline/amorphous
- Acid binding sites
- Water retention
- Tensile strength and elongation

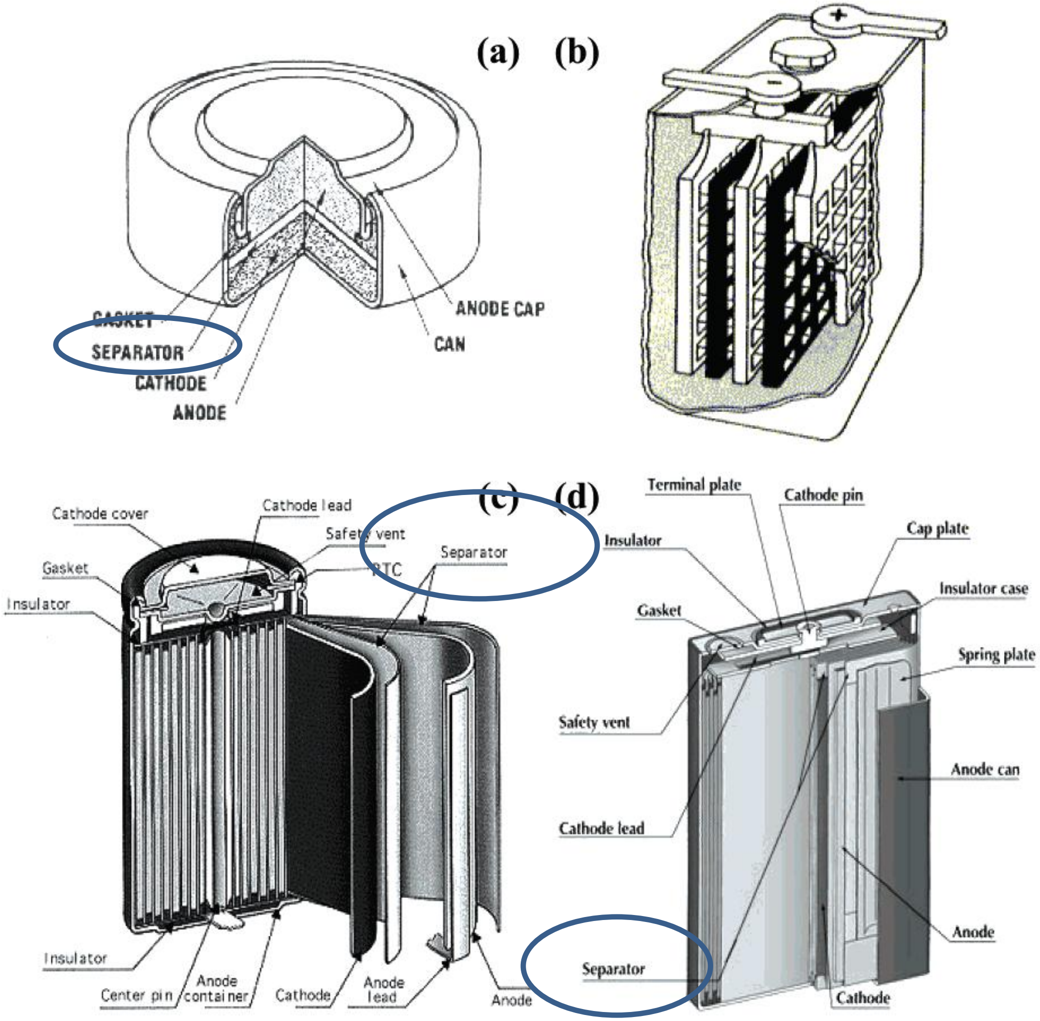


PERFORMANCE

- Chemical stability
- Thermal stability
- Proton conductivity
- Gas permeability

STRUCTURE – PROPERTY – PERFORMANCE MATRIX FOR FUEL CELL MEMBRANES

POROUS POLYMERS FOR SELECTIVE TRANSPORT OF LITHIUM IONS



- ➢ Current material of choice : Polyolefins (PO)
- ➢ Polyolefins are hydrophobic and, hence, intrinsically less compatible with liquid electrolytes ; have low retention capacity to hold organic solvents with high dielectric constant
- ➢ PO separators have poor wettability characteristics in polar electrolytes, such as, ethylene carbonate (EC), propylene carbonate (PC), and γ-butyrolactone (GBL) owing to their low polarity.
- ➢ Polyolefins have a Tm ~ 150 to 160° C ; Pores tend to collapse near Tm, causing shrinkages and shorting
- ➢ Polyolefins are also flammable

POROUS POLYMERS FOR SELECTIVE TRANSPORT OF LITHIUM IONS

Need : A porous polymer material for selective transport of lithium ions

Desirable Features

- Retention of porosity at high temperature
- Amorphous polymers to prevent shrinkage at high temperatures and provide high dimensional stability
- High surface wettability for polar electrolytes; ability to form hydrogen bonds with electrolytes
- Ability to bind Lithium ions for facilitated ionic conduction

IS POLYMER SCIENCE LOSING ITS FOCUS?

- Are we repacking a discipline ?
  - Nanomaterials
  - Supramolecular chemistry
  - Self assembly
  - Soft matter / complex fluids
  - Advanced materials, etc.

- Motivation: Fashion, Funding and Factors (I, H etc.)

FUTURE OF POLYMER SCIENCE

- Systems, not molecules
- Functions, not molecular structure

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

Is the focus on "molecules" obsolete ? G. M.Whitesides, Annu. Rev. Anal. Chem., 6, 1 (2013)

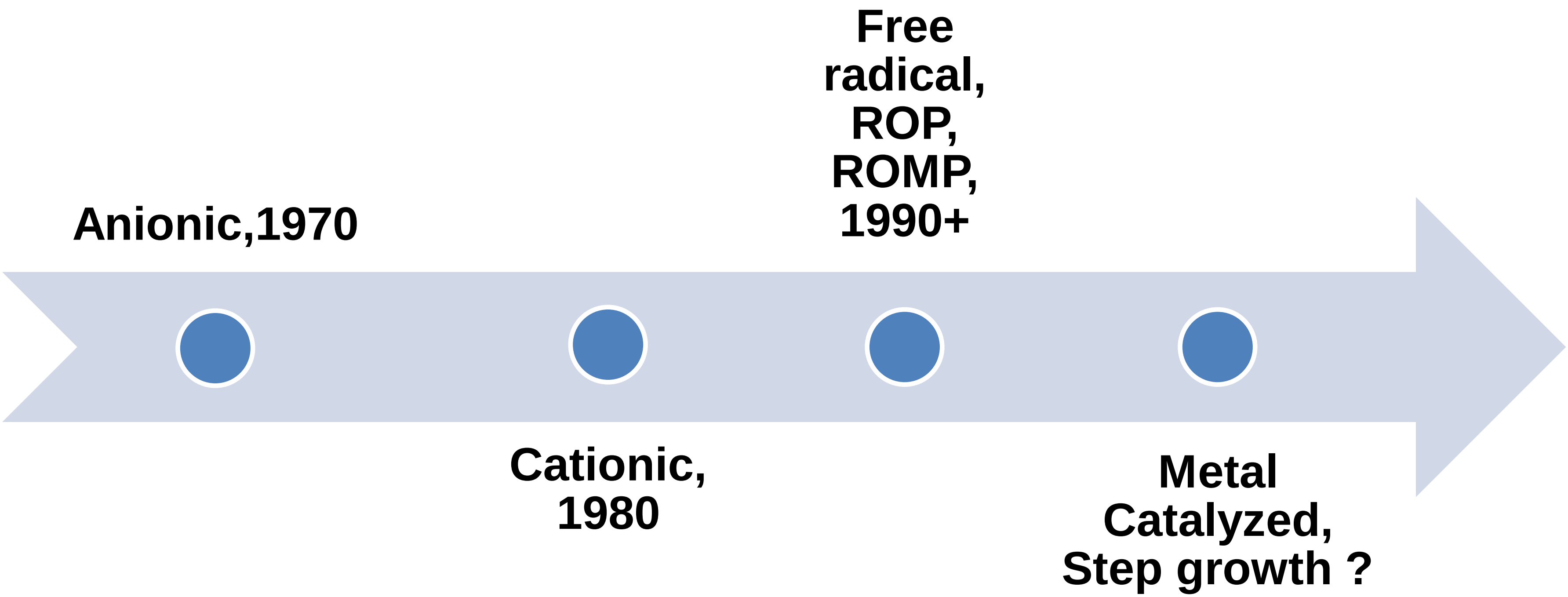
EVOLUTION OF RESEARCH TOPIC IN POLYMER SCIENCE, 1990-2013

January 1990	January 2000	2014
Radical Solution polymerization Cyclo-polymerization Radiation polymerization Poly-esterification	Metal catalyzed polymerization ROP ROMP Living Cationic and controlled free radical polymerization	Catalyst transfer poly-condensation RAFT ROP Functional Polymers Metal catalyzed polymerization
High resolution 13-C ESR Fluorescence FT IR ESCA	11-Boron and 13-C NMR Solid state NMR	STEM XPS SAXS Real time spectroscopy

EVOLUTION OF RESEARCH TOPIC IN POLYMER SCIENCE, 1990-2013

January 1990	January 2000	2014
Mean square radius of gyration and hydrodynamic radii Theta temperature Phase separation, thermodynamics and diffusivity in miscible blends	Second virial coefficient in miktoarm star polymers Order disorder transitions in diblock copolymers Morphology of stereoblock PP	Thermal, mechanical, solvent, photo-responsive soft matter Transport, thermal, phase and solution properties of brush, ring, networks and entangled polymers
Chiral polymers Conformation in glasses and gels Light induced phase transitions	Band gap modifications in polymers	Molecular dynamics, DFT and simulations Nano-templating and patterning Polymer thin films Polymer electrolytes

ARE THERE STILL OPPORTUNITIES IN POLYMER SYNTHESIS ?



Anionic,1970

Cationic, 1980

Free radical, ROP, ROMP, 1990+

Metal Catalyzed, Step growth ?

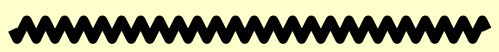
Perfect control of polymerization is only possible in anionic polymerization

Catalytic controlled polymerization is still not a general technique in metal catalyzed polymerization

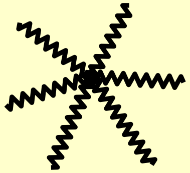
Step growth polymerization under equilibrium conditions has problems of control

STRUCTURES ACCESSIBLE VIA TECHNIQUES OF CONTROLLED POLYMER SYNTHESIS

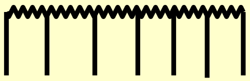
Topology



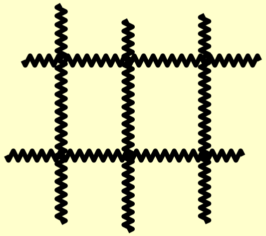
Linear



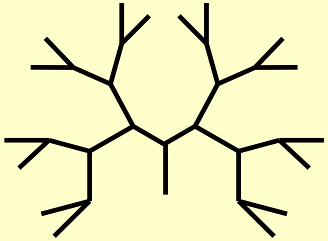
Star / Multi-Armed



Comb Polymers



Networks



(Hyper) Branched

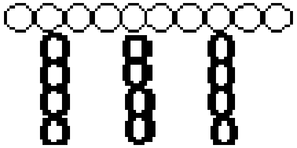
Composition

HomoPolymers

Block Copolymers

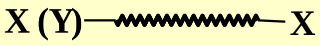
Statistical Copolymers

Tapered / Gradient Copolymers

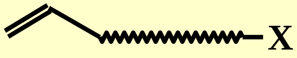


Graft

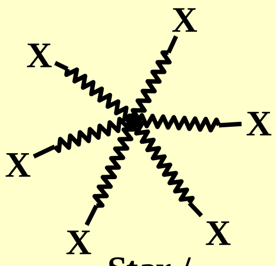
Functionality



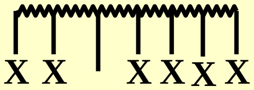
Homo / Hetero Telechelic



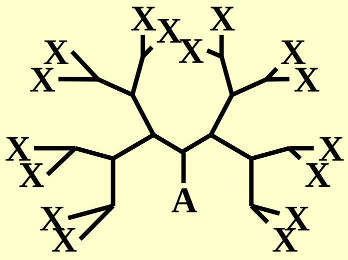
Macromonomers



Star / Multi- Armed



Side Functional Groups



Hyperbranched / Multifunctional

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 comonomer sequences**

CHAIN ISOMERISM

Determines …….

- Thermal behavior
- Morphology
- Crystallization

Polymer stereochemistry

- Geometrical isomerism
- Regio-isomerism
- Stereo-isomerism
- Tacticity

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, etc

Challenge…..

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

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 material

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

The beginning of the concept of *Emergent Properties : when whole becomes larger than the sum of the parts*

POLYMER SYNTHESIS: IS THERE ANYTHING LEFT TO DO?

- Increased synthetic precision
- Metal free catalysis for polymer synthesis
- Sequence controlled polymerization
- Orthogonal chemistries
- Iterative synthesis of mono-disperse step growth polymers
- Living , controlled chain growth π- conjugated polymers
- Synthesis of two dimensional polymers

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
- High thermal conductivity in virgin polymers through chain alignment
- Conducting or semiconducting polymers with inherent flexibility

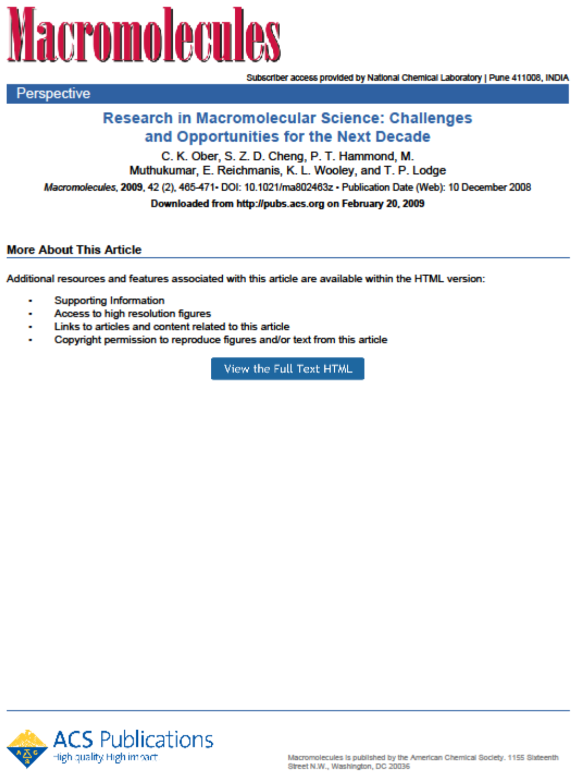
SOME UNSOLVED PROBLEMS :
ENDOW POLYMERS WITH NEW PROPERTIES

- Metamaterials : polymers with negative index of refraction or negative coefficient of expansion
- Self replenishing and self healing surfaces
- Photonic and piezoelectric properties in polymer nanocrystals
- Polymers with Tg in between PMMA and Polycarbonate
- Creation of co-ordinated multiple responses to one stimulus in sensing and actuating materials
- Polymers with reversible crosslinking
- Attaining theoretical limits of E modulus in synthetic fibers, e.g defect free (free of voids, entanglement, chain ends, metal residues) ordered fibers

POLYMER MATERIAL SCIENCE : THE NEXT WAVE

- Research in polymer science began about sixty years ago as a discipline borne out of 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 : QUO VADIS ?



Macromolecules

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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

Macromolecules, **2009**, 42 (2), 465-471• DOI: 10.1021/ma802463z • Publication Date (Web): 10 December 2008

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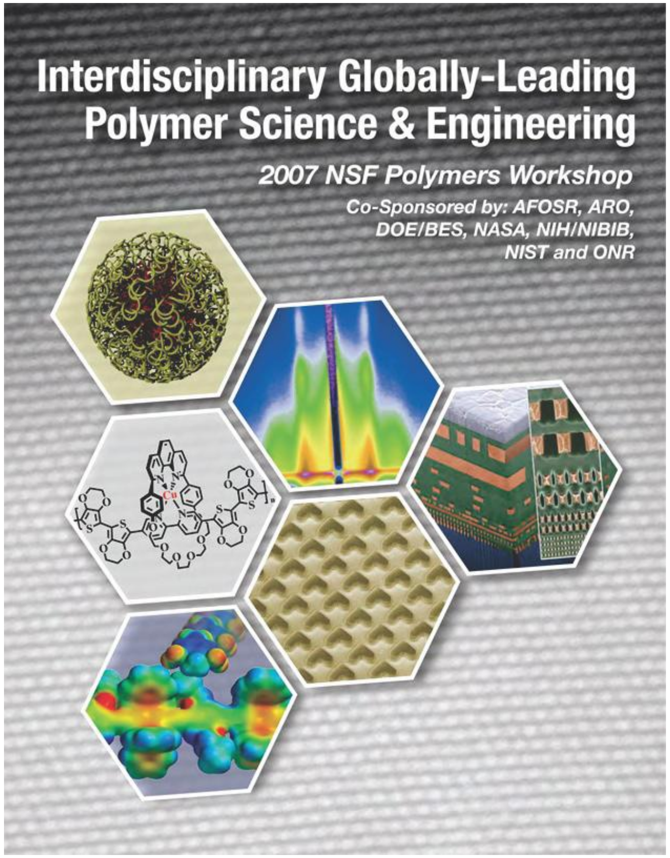

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