SCIENCE OF POLYMERS : QUO VADIS

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Quo Vadis ?

Peter asks Jesus "*Quo vadis?*" (pronounced [kʷoː wadiːs]), 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

- Nature of scientific research (or why do we perform research) ?
- Scientific frontiers and technology fronts
- Polymer Science : From the visible to the invisible
- What can we learn about the future from the past?
- What does the future beckon?

ANSWERS MUST BE SUBJECTIVE !

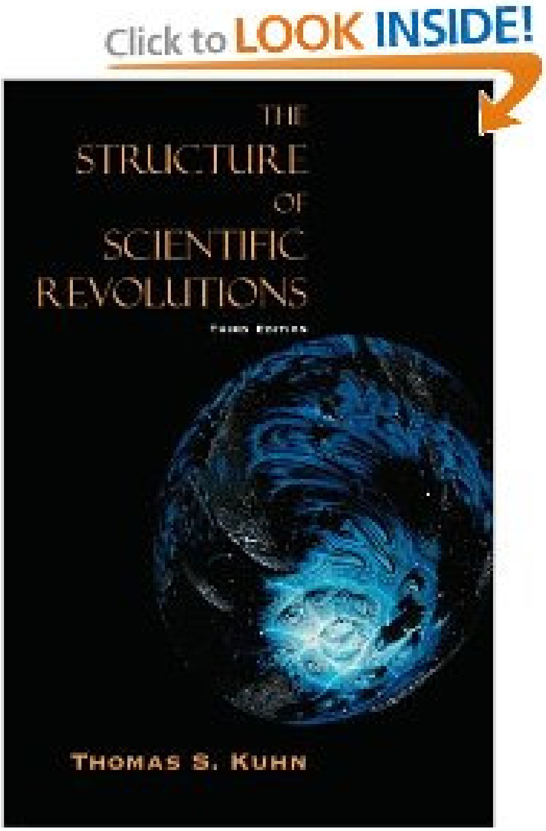
We are all like the blindfolded men who were asked to describe an elephant

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)

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

Sheltering and justifying curiosity driven discovery research ?

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

HOLY GRAILS IN SCIENCE

- Artificial photosynthesis
- Reforming carbon dioxide to methane
- Functionalisation and homologation of methane, e.g methane to methanol or methane to polyethylene
- Ammonia from nitrogen and hydrogen under mild conditions
- Room temperature superconductivity
- Building molecular complexity and diversity in the scale which nature does ; Nature takes ~20 amino acids and creates 10 billion molecular assemblies; polymer scientists take ~20 monomers and can make only 100 polymers !

How many of us will risk our career and reputation in science in pursuit of holy grails ?

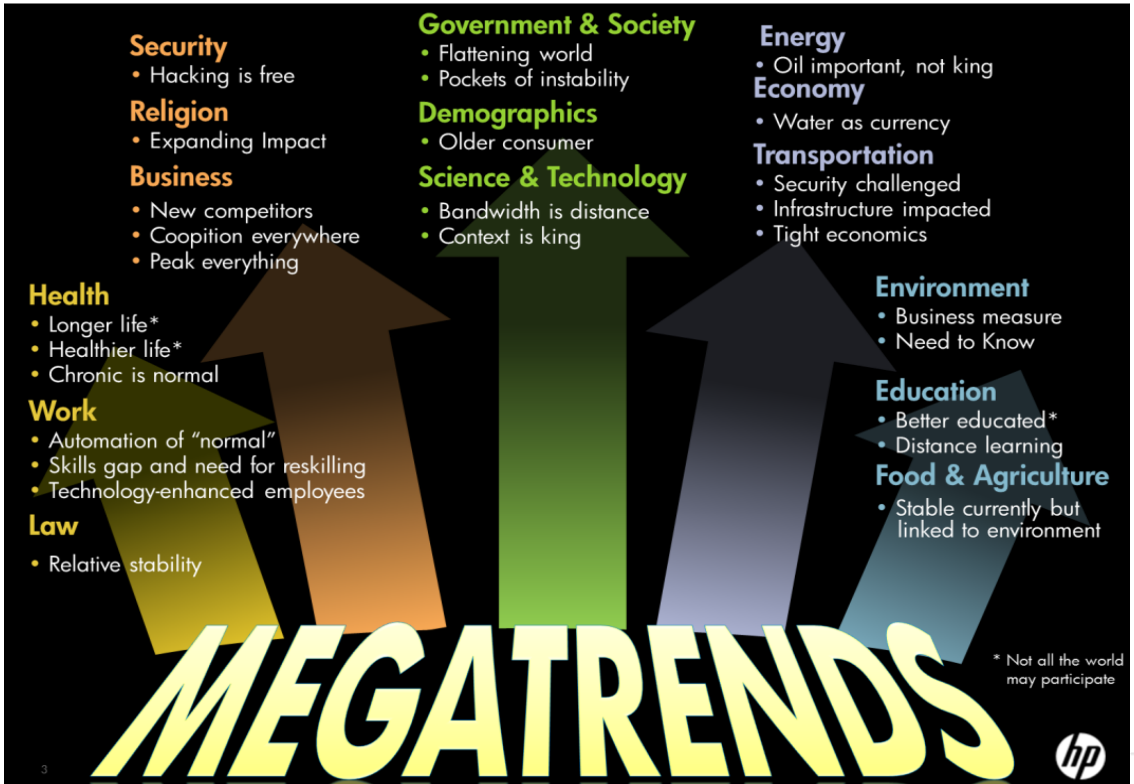
IS SCIENCE DRIVEN BY IDEAS OR TOOLS?

- Early Science, in the first half of 20th century was driven by ideas, largely abstract; quantum chemistry, theoretical physics, existence of large molecules, etc. Tools were primitive
- The latter half of the 20th century belonged to tools; tools defined new frontiers of science
- At the threshold of 21st century, both ideas and tools will compete in the world of science.

Freeman Dyson, Science, 338, 1426, 14 December 2012

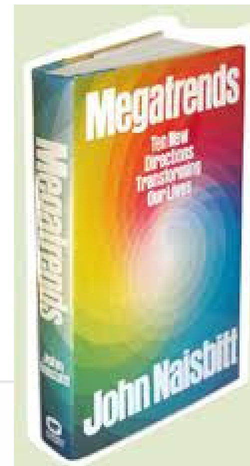
SCIENCE ENABLED BY TOOLS

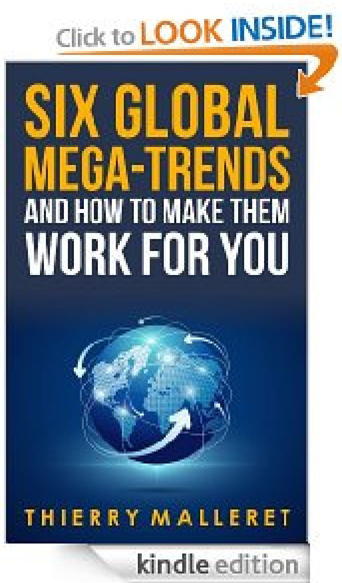
Tools	Science
NMR	Organic Synthesis
Laser	Spectroscopy
XRD	Protein structure
XPS/SIMS/EXFAS	Surface science
PCR	Genomics
Mass spectroscopy	Proteomics
Photolithography	Microelectronics
Ink jet printing	Flexible electronics
Hand held devices and connectivity	Sensors/actuators/diagnostics
3D printing	Advanced manufacturing
Computers/information technology	Big data / Fifth Paradigm

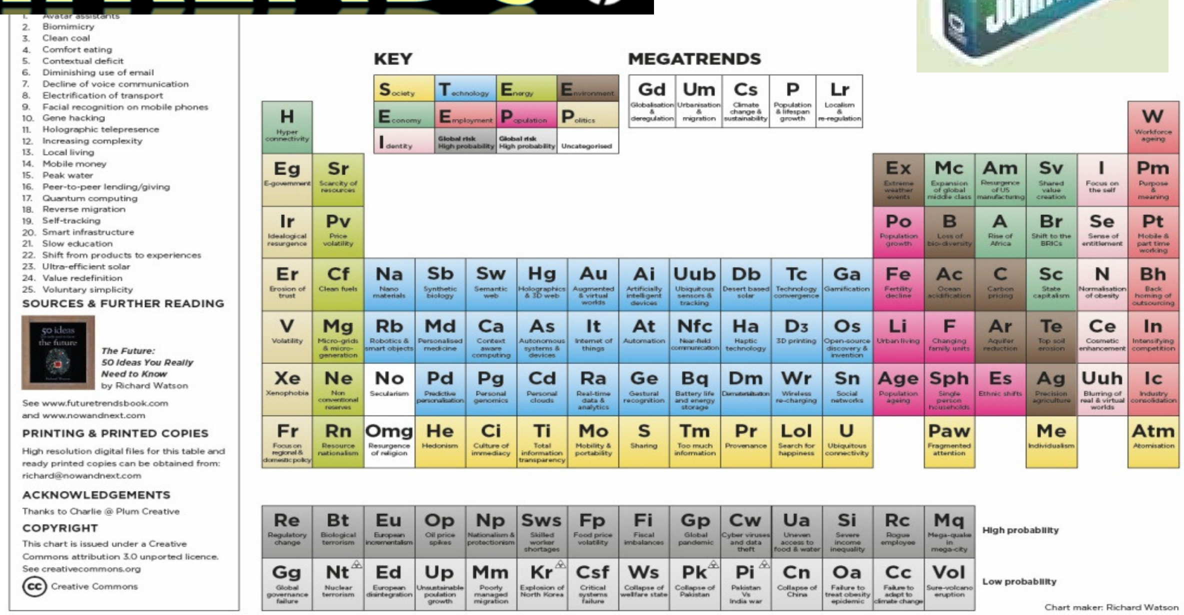


THE NEW BUZZWORD

MEGATRENDS !







MEGATRENDS USEFUL FOR PREDICTING THE FUTURE OF TECHNOLOGY

- Consumer habits & demands
- Demographics
- Population
- Climate Change
- Economic growth
- Disposable income
- Infrastructure
- Urbanization
- Constrained natural resources

- Food, nutrition &hygiene
- Energy
- Water
- Health
- Transportation
- Environment
- Sustainability
- Housing
- Education
- Job creation
- Safety and protection

S&T Solutions

- Precision agriculture
- Plant biotechnology
- Fortified food
- Renewable energy
- Green Chemistry and catalysis
- Light weight materials
- Lower water foot print
- Lower carbon footprint
- Materials based on renewable resources
- Affordable drugs and health care, etc.

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)

TEMPTATIONS OF PREDICTING THE FUTURE: WHY DO IT?

- Choice of research area
- Curiosity
- Philosophy
- Expectations from Society
- To ask if there is research that should not be done.

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 !

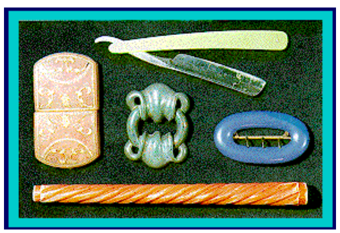
POLYMERS FULFILLING MATERIAL NEEDS OF SOCIETY…

Precursor 19th Century → Semi Synthetics

- 1839 : Natural Rubber
- 1843 : Gutta Percha
- 1856 : Shellac / Bois Durci
- 1862 : Parkesine
- 1863 : Celluloid
- 1894 : Viscose Rayon

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

Source : British Plastic Federation Website

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, COC by Ticona, Syndiotactic PP etc

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

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)

IS POLYMER SCIENCE LOSING ITS FOCUS?

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

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

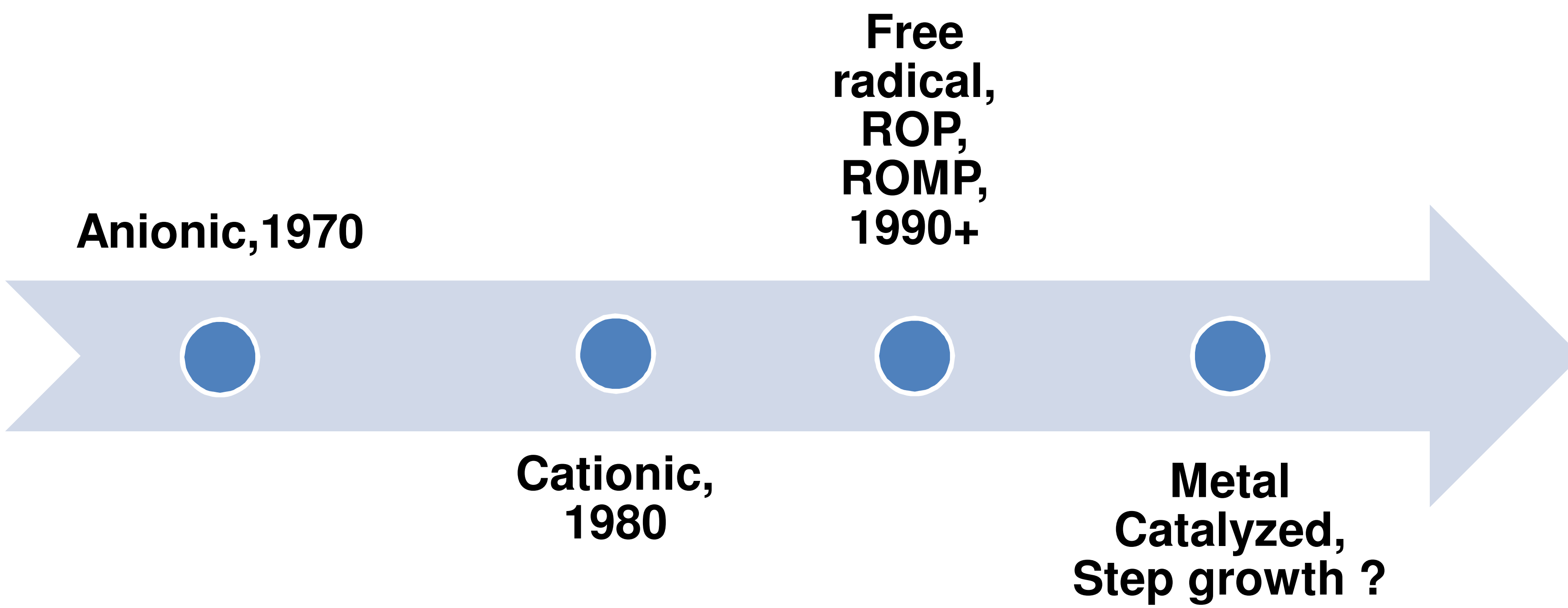
EVOLUTION OF RESEARCH TOPIC IN POLYMER SCIENCE, 1990-2013

January 1990	January 2000	November 12, 2013
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	November 12, 2013
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

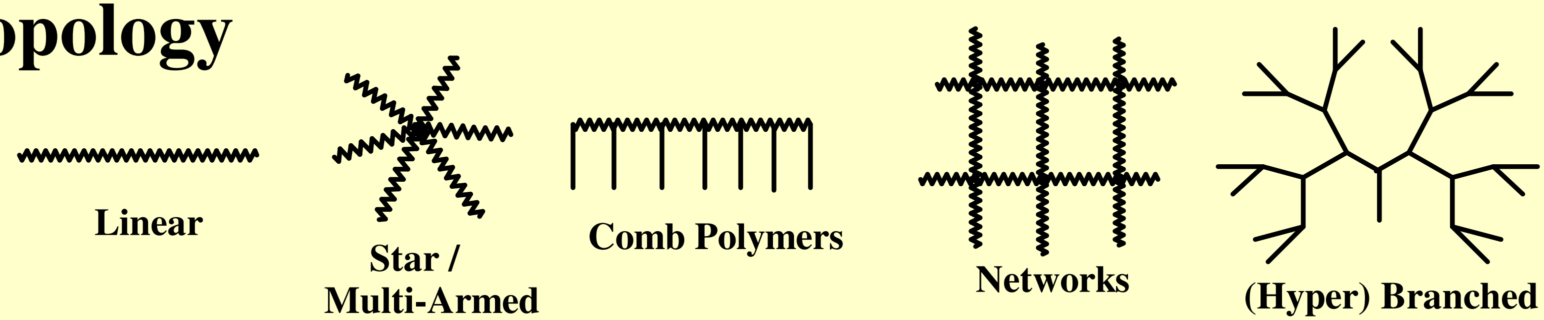
ARE THERE STILL OPPORTUNITIES IN POLYMER SYNTHESIS ?



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

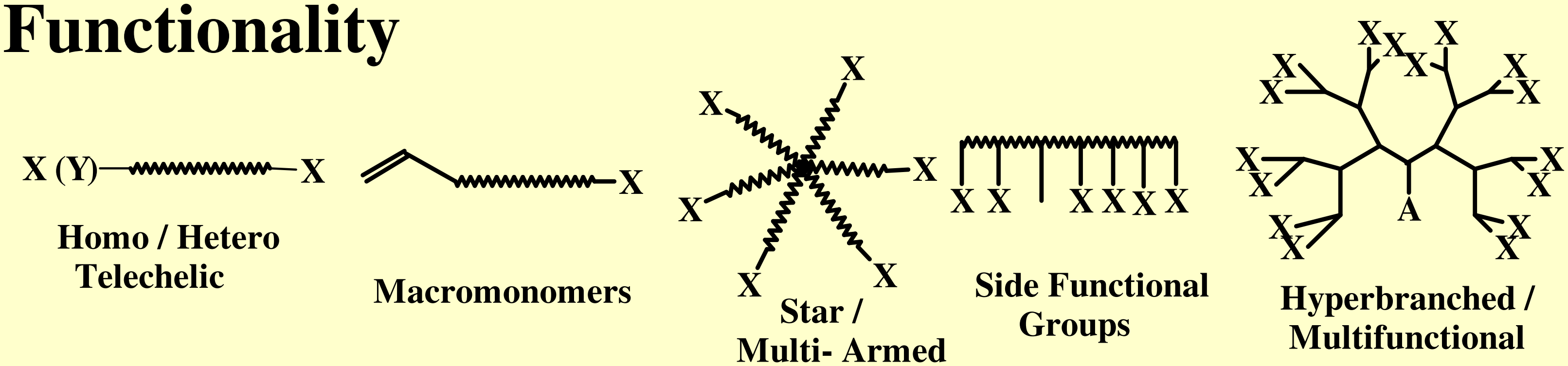
STRUCTURES ACCESSIBLE VIA TECHNIQUES OF CONTROLLED POLYMER SYNTHESIS

Topology



Composition

Functionality



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
- 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

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**

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)

POLYMER SCIENCE : 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

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