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
Quo Vadis?

Peter asks Jesus "Quo vadis?" (pronounced [kʷoː wədiːs]), 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.


*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 FRONTIERS | : 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
<table>
<thead>
<tr>
<th>Tools</th>
<th>Science</th>
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<tbody>
<tr>
<td>NMR</td>
<td>Organic Synthesis</td>
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<td>Laser</td>
<td>Spectroscopy</td>
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<td>XRD</td>
<td>Protein structure</td>
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<td>XPS/SIMS/EXFAS</td>
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<td>PCR</td>
<td>Genomics</td>
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<td>Mass spectroscopy</td>
<td>Proteomics</td>
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<td>Photolithography</td>
<td>Microelectronics</td>
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<tr>
<td>Ink jet printing</td>
<td>Flexible electronics</td>
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<td>Hand held devices and connectivity</td>
<td>Sensors/actuators/diagnostics</td>
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<td>3D printing</td>
<td>Advanced manufacturing</td>
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<tr>
<td>Computers/information technology</td>
<td>Big data / Fifth Paradigm</td>
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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

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…

<table>
<thead>
<tr>
<th>Precursor 19th Century</th>
<th>Natural Rubber</th>
<th>Gutta Percha</th>
<th>Shellac / Bois Durci</th>
<th>Parkesine</th>
<th>Celluloid</th>
<th>Viscose Rayon</th>
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<tr>
<td>1839</td>
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<tr>
<th>Semi Synthetics</th>
<th>Cellophane</th>
<th>Bakelite</th>
<th>Vinyl or PVC</th>
<th>Cellulose Acetate</th>
<th>Polyvinylidene chloride</th>
<th>Low density polyethylene</th>
<th>Polymethyl Methacrylate</th>
<th>Polyurethane</th>
<th>Polystyrene</th>
<th>Teflon</th>
<th>Nylon and Neoprene</th>
<th>PET</th>
<th>LDPE</th>
<th>Unsaturated Polyester</th>
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<tbody>
<tr>
<td>Thermoplastics</td>
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<tr>
<th>1950 onwards</th>
<th>Growth Phase</th>
<th>HDPE</th>
<th>PP</th>
<th>Styrofoam</th>
<th>PC, PPO</th>
<th>Polyamide</th>
<th>Thermoplastic Polyester</th>
<th>LLDPE</th>
<th>Liquid Crystal Polymers</th>
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<tbody>
<tr>
<td>1951</td>
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<tr>
<th>Hi Tech Plastics</th>
<th>Plastics in Packaging</th>
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<tr>
<td>Source: British Plastic Federation Website</td>
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</table>
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.
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

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Radical Solution polymerization</td>
<td>Metal catalyzed polymerization</td>
<td>Catalyst transfer poly-condensation</td>
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<td>Cyclo-polymerization</td>
<td>ROP</td>
<td>RAFT</td>
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<tr>
<td>Radiation polymerization</td>
<td>ROMP</td>
<td>ROP</td>
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<tr>
<td>Poly-esterification</td>
<td>Living Cationic and controlled free radical polymerization</td>
<td>Functional Polymers</td>
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<tr>
<td></td>
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<td>Metal catalyzed polymerization</td>
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<tr>
<td>High resolution 13-C ESR</td>
<td>11-Boron and 13-C NMR</td>
<td>STEM</td>
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<td>Fluorescence</td>
<td>Solid state NMR</td>
<td>XPS</td>
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<td>FT IR</td>
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<td>SAXS</td>
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<td>ESCA</td>
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<td>Real time spectroscopy</td>
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## EVOLUTION OF RESEARCH TOPIC IN POLYMER SCIENCE, 1990-2013

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

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

STRUCTURAL MATERIALS

FUNCTIONAL MATERIALS
FUTURE OF POLYMER SCIENCE

- Systems, not molecules
- Functions, not molecular structure

No longer “What is it?” but “What does it do?”

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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