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OUTLINE

• Polymer science: Historical Perspectives
• Scientific frontiers, technology fronts and megatrends
• Polymer science: Birth of an industry
• Polymers: Sustainability issues
• Polymer science: From the visible to the invisible
• Future of polymer science
POLYMER SCIENCE: THREE PHASES OF EVOLUTION

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

- The beginnings of chemistry as a science (1800-1900)
- Atoms and molecules; understanding structure and the nature of the chemical bond (1900-1940)
- Understanding reactive intermediates in chemistry: The birth of physical organic chemistry (1940-60)
Chemistry creates its own object. This creative power, similar to that of arts distinguishes it fundamentally from the other natural and historical sciences

Marcellin Bertholet, 1860
(1827-1907)

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

- Bertholet came to a remarkable understanding of the conversion of vinyl compounds into polymeric chain molecules. He reasoned that upon addition of an olefin to a chain with a terminal double bond, the unsaturation would be retained, so that there was no reason why long chains should not be produced. Bertholet isolated the dimer, trimer and tetramer of pentene.

- In 1853, Bertholet reported the thermal and catalytic polymerization of pinene; 1869 he published his results on polymerization of ethylene, propylene, pentene and pinene.

- His prescience is all the more remarkable, because the only techniques available to him were, density and boiling point measurement and softening temperature of solids.

- He presented his results in a long lecture titled “la polymerie” presented at the Chemical Society of Paris in 1863.
THREE EARLY EXPERIMENTS

1805, John Gough
Natural rubber heats up when stretched; a phenomena which took a century thereafter for formulating an understanding

1826, Michael Faraday
Determined the elemental composition of natural rubber. In his note book he also recorded, in passing, a reaction of rubber with sulfur

1839, E. Simon
First isolation of styrene from a natural resource and observed that upon distillation styrene left a residue
Concept of macromolecules as large molecules linked together by covalent bonds (1920)

Hermann Staudinger (1881-1965)
Nobel Laureate 1953
STAUDINGER AND THE ORIGIN OF MACROMOLECULES

• He propounded the revolutionary concept, that macromolecules can be formed by linking of a large number of small molecules by means of covalent bonds.

• Through sheer audacity of intuition and imagination, he proposed that polymers were composed of large number of base units linked together by covalent bonds. At that time he had no experimental evidence for his hypothesis.

• His ideas met with much resistance and criticism from eminent chemists of the period, notable amongst them, Emil Fischer.
WHAT IS THE ORIGIN OF THE TERM POLYMER?

• Faraday in 1826 was puzzled by the fact that ethylene and butene differed in their gas density, but had the same elemental composition.

• Berzelius was astounded by Faraday’s observation and suggested that butene be referred to as a “polymer” of ethylene (1827, 1832). All through the nineteenth century, there are references to styrene being a polymer of acetylene and lactic acid as a polymer of formaldehyde.

• Staudinger adopted this definition of Berzelius. For Staudinger, polystyrene was a polymer of styrene. However, he objected to the use of this term for products of poly-condensation.

• It was Carothers in 1929 who gave a general definition of the term. He defined them as substances” whose structures may be represented by R-R-R- where -R- are bivalent radicals which in general are not capable of independent existence” (J.Am.Chem.Soc., 51, 2548, 1929).
WALLACE CAROTHERS AND THE BIRTH OF RATIONAL POLYMER SYNTHESIS

• Trained as an organic chemist with Roger Adams, PhD, 1924; hired as a faculty at Harvard

• DuPont lured him to Wilmington Delaware to lead a fundamental research programme in organic chemistry and polymers

• By 1931, he had synthesized chloroprene and polymerized to a new synthetic rubber, called by DuPont as Neoprene

• Publishes his seminal papers in JACS in 1929 where in he establishes the equivalence of organic and polymer forming reactions, namely esterification and polyesterification
Baekland set out to discover a substitute for Shellac, then wholly supplied by India to the world.

In the process he made the first man made material, a product of chemical synthesis with no direct analog in nature.

Heat resistant and insulating, demand from the burgeoning electrical goods industry.

He founded a company called General Bakelite Corporation in 1910 to manufacture the product.
THE DAWN OF THE CHEMICAL INDUSTRY: THE MANUFACTURE OF BAKELITE

Leopoldo Baekeland (1863-1944)

When asked why he chose to work in the field of synthetic resins, he replied, “to make money”
Shellac, a natural resin secreted by the female lac bug on trees; Main constituent: Aleuritic acid; In the early part of twentieth century, India was the largest supplier of Shellac to the world.
## SCIENTIFIC FRONTIERS AND TECHNOLOGY FRONTS

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

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 NEW BUZZWORD

MEGATRENDS!

Security
- Hacking is free

Religion
- Expanding impact

Government & Society
- Flattening world
- Pockets of instability

Demographics
- Older consumer

Science & Technology
- Bandwidth is distance
- Context is king

Health
- Longer life
- Healthier life
- Chronic is normal

Work
- Automation of "normal"
- Skills gap and need for reskilling

Transportation
- Security challenged
- Infrastructure impacted
- Tight economics

Environment
- Business measure
- Need to know

Economic
- Better educated
- Distance learning

Education
- Stable currently but linked to environment

Law
- Relative stability

* Not all the world may participate

SOURCES & FURTHER READING

THIERRY MALLERET

Click to LOOK INSIDE!

THE NEW BUZZWORD

MEGATRENDS!

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ACKNOWLEDGEMENTS

THANKS TO CHARLIE DI PLUM CREATIVE

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Chart maker: Richard Watson.
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

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 : BIRTH OF AN INDUSTRY

- 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 MATERIALS

- Global production: 250 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

Polymers are a post war industry, fuelled by the availability of inexpensive hydrocarbon resources; industry grew from zero to present capacities in about fifty years.
NEW TO THE WORLD POLYMERS : THE GOLDEN ERA IN POLYMER SCIENCE

- PVC (1927): Replaces natural rubber as cable insulation/sheathing
- Polystyrene (1930): First commercial production by IG Farben
- Neoprene, Poly(chloroprene (1931): The first man made elastomer
- LDPE (1935): radar, telecommunication cables
- PMMA (1936): Canopies and cockpit covers for airplanes
- Nylon (1938): Replaces silk and rayon, used in parachutes
- Poly(ethylene terephthalate) (1941): The Terylene (ICI) and Dacron (DuPont) fibers
- Synthetic rubber (1940-45): Replaces NR; GR-S (SBR), Butyl, the largest mobilization of chemists and engineers towards war effort, part of the Manhattan project. Synthetic rubber capacity grew from close to zero in 1940 to 700,000 tpa in 1945
- Silicones (1943): Eugene Rochow, GE R&D
- Poly(tetrafluoroethylene) (1946): Teflon by DuPont
- Epoxy Resins(1947): Araldite by CIBA
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

**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

**Source:** British Plastic Federation Website

Plastics in Packaging

Hi Tech Plastics
THE POLYMER PYRAMID

PAI = TORLON® polyamide-imide
PK = KADEL® polyketone
PPSU = RADEL® R polyphenylsulfone
LCP = XYDAR® Liquid Crystal Polymer
PES = RADEL® R polyethersulfone
PSU = UDEL® polysulfone
PPS = PRIMEF® polyphenylene sulfide
PPA = AMODEL® polyphthalamide
PA MXD6 = Ixef® polyarylamide

High-Performance Polymers
- PAI/PI
- PK
- PPS
- PPA
- PA MXD6
- PCT
- PVDF

Mid-Range Polymers
- PC
- PPO
- PBT
- PET
- PA 6/6,6
- PE-UHMW

Commodity Polymers
- PS
- SAN
- PP
- PE-HD
- PE-LD
- PVC

Amorphous

Semi-Crystalline
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Commercialized</th>
<th>Years</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinylchloride</td>
<td>1928</td>
<td>27</td>
</tr>
<tr>
<td>Polymethyl-methacrylate</td>
<td>1933</td>
<td>5</td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>1934</td>
<td>3</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1936</td>
<td>27</td>
</tr>
<tr>
<td>PTFE</td>
<td>1950</td>
<td>12</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>1955</td>
<td>3</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>1957</td>
<td>3</td>
</tr>
<tr>
<td>Polycarbonate</td>
<td>1968</td>
<td>15</td>
</tr>
<tr>
<td>Polyether imide</td>
<td>1982</td>
<td>15</td>
</tr>
<tr>
<td>Polyethylene naphthalate</td>
<td>1999</td>
<td>24</td>
</tr>
<tr>
<td>Polyethylene (metallocenes)</td>
<td>2000</td>
<td>18</td>
</tr>
</tbody>
</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.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Company</th>
<th>Cost in million US Dollars</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene/propylene CO (1985-2001)</td>
<td>Shell (Carilon) BP (Ketonex)</td>
<td>300-600</td>
<td>Abandoned; unable to displace nylon, PBT and polyacetal</td>
</tr>
<tr>
<td>Syndiotactic polystyrene (1989 - )</td>
<td>Dow (Questra)</td>
<td>-</td>
<td>Abandoned; 40,000 tpa plant at Schkopau, Germany; competes with PBT</td>
</tr>
<tr>
<td>Hydrogenated polystyrene (1995 - )</td>
<td>Dow (PCHE)</td>
<td>-</td>
<td>Abandoned; unable to displace PC</td>
</tr>
<tr>
<td>Ethylene-styrene copolymers (1990 - )</td>
<td>Dow (Index)</td>
<td>-</td>
<td>Abandoned; 25000 tpa Sarnia, Ontario; No further expansion contemplated</td>
</tr>
<tr>
<td>Ethylene-norbornene (1990 - )</td>
<td>Ticona (Topas)</td>
<td>32000</td>
<td>32000 tpa Oberhausen, Germany; Only niche markets have emerged; Competes with PVC, PC</td>
</tr>
<tr>
<td>Poly(trimethylene terephthalate)</td>
<td>Shell (Coterra) DuPont (Sorona)</td>
<td>20000</td>
<td>20000 tpa (Shell) W.Va; Plans to build a 100,000 tpa plant in Canada; 12000 tpa (DuPont) at Kingston, NC</td>
</tr>
<tr>
<td>Poly(lactic acid)</td>
<td>Dow-Cargill (Nature Works)</td>
<td>750 + 250</td>
<td>140,000 tpa plant at Blair, Nebraska; Targets: fibers/packaging</td>
</tr>
</tbody>
</table>
TRENDS IN THE GLOBAL POLYMER INDUSTRY

• Customers demand more variety and content
• Environment and safety regulations will be the key driver of change
• Competitive advantage of Feedstocks: A geographic advantage
• Competition is unrelenting
• Market pressures restrict price increases
• Margins are progressively squeezed
BARRIERS TO INNOVATION

• Ability to meet stiff economic challenges
• Access to capital to demonstrate technologies and manufacturing
• Time to market getting longer
• Too little emphasis by industry on “Game-changer technologies” or “breakthrough innovations”; Too much emphasis on customer led incremental developments
• Inefficient use of resources (financial, human) in driving innovation
• Diminishing access to high quality trained personnel
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

Can the materials needs of humankind be based on the concept of sustainability of both resources and environment?
Over 30 billion liters of bottled water is consumed annually.

What is the solution?

Every second we throw away about 1500 bottles.

Poly(ethylene terephthalate)
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 structural features.
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?
FROM HYDROCARBONS TO CARBOHYDRATES

• The polymer industry is increasingly focused on the concept of sustainability
• There is only so much petroleum on earth and with time, oil will become increasingly rare
• Chemicals / feed stocks manufacturing will progressively shift to natural gas in the short term and renewable carbohydrate resources in the long term

Will feed-stocks for polymers shift to renewable and sustainable resources progressively?
POLYMERS FROM RENEWABLE RESOURCES

Biodegradable polymers

- Polyesters
- Starch

Bio-derived monomers and polymers

- PET/PTT / PBS
- Nylon-11
- Ethylene from ethanol and polyethylene

- Environmental sustainability
- CO₂ mitigation – closing the carbon cycle
- Food Vs material

- Reduce cost of feedstock
- Reduce dependence on fossil fuel
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
Scientific Challenges

- Creating monomers from fossil fuel based feedstocks is about **selectively introducing functionality** (oxidation, dehydrogenation, oxychlorination, epoxidation etc).

- Creating monomers from bio based feeds-stocks is about **selectively removing functionality** (examples, dehydration, decarboxylation, decarbonylation, deoxygenation).
THE BIOVALUE PYRAMID

- CO2 Neutral
- Competition for resources (water, land and food)
- Operating cost competitiveness at $100/barrel of fossil fuel
- Capex Equivalence

Bio derived chemicals and materials must be developed because they work and make economic and environmental sense; not merely because they are plant based
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)
ADVANCED MATERIALS: EMERGING OPPORTUNITIES

• ENERGY SYSTEMS
  - Flexible photovoltaics
  - Fuel cell materials

• SEPARATION TECHNOLOGIES
  - Nano-filtration using polymer membranes
  - Porous polymers
  - Polymers with tuned cavities
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.)
FUTURE OF POLYMER SCIENCE

- Systems, not molecules
- Functions, not molecular structure

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

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

<table>
<thead>
<tr>
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</thead>
<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>
</tr>
<tr>
<td>Phase separation, thermodynamics and diffusivity in miscible blends</td>
<td>Morphology of stereoblock PP</td>
<td></td>
</tr>
<tr>
<td>Chiral polymers</td>
<td>Band gap modifications in polymers</td>
<td>Molecular dynamics, DFT and simulations</td>
</tr>
<tr>
<td>Conformation in glasses and gels</td>
<td></td>
<td>Nano-templating and patterning</td>
</tr>
<tr>
<td>Light induced phase transitions</td>
<td></td>
<td>Polymer thin films</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polymer electrolytes</td>
</tr>
</tbody>
</table>
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
- 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
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.
POLYMER SCIENCE AT CROSSROADS

• Polymer science is at the end of one wave of development and struggling to begin another; perceptible shift in the centre of gravity of the discipline
• There are still many important opportunities in both fundamental and applied science
• The disciplines offers fewer puzzles to solve; What confronts are large number of problems
• Longer term curiosity driven research is more important than in the past, but harder to justify
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THANK YOU