POLYMER SCIENCE: GLORIOUS PAST, PRESENT CHALLENGES AND EXCITING FUTURE

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POLYMER SCIENCE: PAST, PRESENT AND FUTURE

- What are polymers?
- Its origins and history
- What are the new frontiers in polymer science?

- How relevant is polymer science today?
- How will this science address some of the most pressing problems of our society?
- The transition from visible to invisible: The future of polymer science
THE AGES OF HUMAN KIND

Human Civilization has been marked by several ages, which are all material based:

- **Stone Age**
- **Bronze Age**
- **Iron Age (Steel, Aluminum)**
  - **Polymer Materials Age (Carbon based materials)**
Polymer (< Gk *poly* “many” + *meros* “parts”)

- A substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few constitutional unit. **Source:** IUPAC (International Union of Pure & Applied Chemistry)

- It is solid in its finished state in most cases and can be shaped by flow into a finished article.

- “Plastic” and “resin” are often used synonomously with “polymer”,
  - “Plastic” & “resin” refers to polymers with various additives (such as pigments and stabilizers) that turn the polymer into a practical product
What are Polymers?

Polymer are made up of many Monomers.

Many Units
One Unit

Small Molecules and Monomers:

- H₂O Water
- CO₂ Carbon Dioxide
- O₂ Oxygen
- NaCl Sodium Chloride (table salt)
- C₆H₁₂O₆ Sugar
- C₆H₈ Styrene
- C₂H₄ Ethylene

Macromolecules (Polymers):

- Polyethylene

H₂C=CH₂ → \underbrace{H₂C-CH₂-H₂C-CH₂-H₂C-CH₂-H₂C-CH₂-H₂C-CH₂-H₂C-CH₂}_{n}
What is polymerization?

**Mono**mer

\[
\text{Repeat Unit} \\
M_{RU} = 16 + 76 + 42 + 76 + 16 + 12 + 16 = 254
\]

\[
M = \bar{M}_{SU} \times DP = M_{RU} \times n
\]

\[
DP = \text{no. SU}
\]
The most important feature of a polymer is its “length” or molecular weight.

Repeat Unit Molecular Weight = $M$  
Number of repeat units = $n$

$(M = \text{number of atoms} \times \text{weight of each atom})$

Molecular weight $M_w = nM$

Each polymer has a minimum molecular weight $M_e$ necessary for entanglements.

$M > M_e \Rightarrow$ polymer bends and forms knots with itself and other polymers.  

How Big is Big?
Example: Polyethylene

Monomer: Ethylene

- Molecular Weight = 28 g/mol
- Colorless, Flammable Gas at room Temperature

Polymer: Polyethylene

- Composed of hundreds to thousands of ethylene units
- Molecular Weight = 1,500 - 100,000 g/mole
- Milky white plastic solid that “melts” at 85°C to 100°C

Polymers consist of large number of repeat units
Length + Flexibility Make it Happen...

<table>
<thead>
<tr>
<th>Short Molecules</th>
<th>Long Molecules</th>
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</thead>
<tbody>
<tr>
<td>Can separate easily</td>
<td>Completely entangled</td>
</tr>
<tr>
<td>Too short to entangle</td>
<td>Molecules do not easily move independently</td>
</tr>
<tr>
<td>Behave independently</td>
<td>Bowl of Spaghetti</td>
</tr>
</tbody>
</table>

Bowl of Rice
Thermoplastic Polymers

THERMOPLASTIC ("THERMO" = HEAT + "PLASTIC" = FORMABLE)

- Are large, linear, unconnected molecules
- Undergo no chemical reaction during molding
- Properties:
  - soften with heat to a high viscosity melt
  - hard at room temperature
  - can be re-melted and re-processed (recyclable)
  - molecules are entangled but not bonded to one another
  - resist breaking but can be attacked by solvents

Examples: Polyethylene, Polystyrene, Polycarbonate
Polymers : Family Tree

- Synthetic
  - Thermoplastic "Plastics"
    - Crystalline
    - Amorphous
  - Thermosets
  - Polysaccharides
  - Proteins
- Natural
  - Starch
  - Lignin
  - Cellulose
- Natural Rubber
**Thermoplastic Polymers**

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Examples: Polyethylene, Polystyrene, Polycarbonate
Thermoplastics: Amorphous vs. Crystalline

**AMORPHOUS:**

- Have a glass transition temperature (Tg) - the temperature at which the polymer transforms from glassy state (hard) to rubbery state (soft).

**CRystALLINE**

- Have both crystalline (ordered) and amorphous regions
- Have an amorphous phase Tg; Crystalline phases characterized by melting temperature Tm > Tg.

**Characteristics:**

- Random Entanglement of Chains
- Chemical Susceptibility
- Moderate Heat Resistance
- Impact Resistance
- Low Shrinkage
- Wide Softening Range
- Typically transparent in thicker sections.

**Characteristics:**

- Chemical Resistance
- High Heat Resistance
- Notch Sensitivity
- High Shrinkage
- Fatigue Endurance
- Wear Resistance
- Typically opaque in thicker sections
Thermoset Polymers

THERMOSET ("THERMO" = HEAT + "SET" = HARDEN)

- Begin as small molecules (low viscosity liquid)
- React ("cures") by heat, catalysis, or other chemical means to form an infinite molecular network
- Properties of Glassy Thermosets
  - rigid at room temperature
  - network is permanent, so it is not re-processable
  - tend to break more easily than thermoplastics ("brittle")
  - solvent resistant

Example: Epoxy, Phenolics
Elastomers

• Thermosets that are soft at room temperature (above the glass transition temperature)

• Stretchy and recover when applied stress is released.

• “Stretchiness” is due to the fact that polymers extend upon deformation but are prevented from permanent flow by cross-links.

Examples: “Rubbers”, Silicones
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

THE POLYMER PYRAMID

Acronyms for high-performance plastics from Solvay Advanced Polymers are shown in black
Synthetic Polymers

- Poly (ethylene terephthalate) {PET}
  - Soda bottles, laundry detergent containers
- High Density Polyethylene {HDPE}
  - Milk jugs, shampoo bottles, landfill liners
- Poly (Vinyl Chloride) {PVC}
  - Shower curtains, siding, piping
- Low Density Polyethylene {LDPE}
  - Garbage bags, tape, disposable diapers
- Polypropylene {PP}
  - Chip and cookie bags, tupperware
- Polystyrene {PS}
  - Packing foam, disposable cups
CHEMISTRY OF MATERIALS
- Natural materials
- Synthetic materials
- Hybrid Materials
- Nanomaterials

CHEMISTRY OF LIFE
- Origin of life
- Understanding biological processes
- Understanding diseases/search for cure
- Deeper insight into consciousness and human aging

CHEMISTRY OF ENERGY
- Newer forms of energy
- Light and water as energy
- Interconversion of energy
- Efficient use of energy

CHEMISTRY OF ENVIRONMENT
- Global climatic changes
- Stratosphere ozone depletion
- Conservation of biosphere
- Quality of air/water
- Adverse consequence of excessive consumption on environment
Polymer Materials: 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!
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
THE TALE OF TWO HERMAN(N)’S: THE POLYMER PIONEERS

X Ray Crystallography of macromolecules to show that a molecule could be larger than its unit cell (1926-28)

Herman Mark
(1895-1992)

Concept of macromolecules as large molecules linked together by covalent bonds (1920)

Hermann Staudinger
(1881-1965)
STAUDINGER AND THE ORIGIN OF MACROMOLECULAR CHEMISTRY

• He propounded the revolutionary concept, that macromolecules can be formed by linking of a large number of small molecules by means of covalent bonds
• Created the “molecular blueprint” that led to the explosive growth of man made organic materials
• Through sheer audacity of intuition and imagination, he proposed that polymers were composed of large number of base units linked together by covalent bonds (Ber. Dtsch. Chem. Ges., 53, 1073 (1920). At that time he had no experimental evidence for his hypothesis.
• Wieland told him “Dear colleague, abandon your idea of large molecules; organic molecules with molecular weights exceeding 5000 do not exist. Purify your products and they will turn out to be low molecular weight materials”
• His ideas met with much resistance and criticism from eminent chemists of the period, notable amongst them, Emil Fischer. People called the chemistry being pursued by Staudinger as “Grease Chemistry”. After one of the lectures given by Staudinger in Zurich in 1925, one of the speakers termed Staudinger`s championship of long chain molecules as akin to some traveler in Africa reporting that he had seen a zebra 400 meters long!
• Staudinger persevered in spite of being ostracized by the scientific community. From 1926, he abandoned research in organic chemistry and shifted exclusively to macromolecules.
STAUDINGER AND THE ORIGIN OF MACROMOLECULAR CHEMISTRY

• First experimental evidence for existence of long chains came in 1922. Hydrogenation of natural rubber was not accompanied by the formation of volatile cyclic hydrocarbons \textit{(Staudinger and Fritschi, Helv. Chim. Acta, 5, 785 (1922)}

• First time the term “macromolecules” was used in chemistry

• The first definition of macromolecules: “For such colloid particles, in which the molecule is identical with the primary particle, and in which the individual atoms of this colloid molecule are linked together by covalent bonds, we propose for better differentiation the name macromolecule \textit{(Staudinger, Ber. Dtsch. Chem. Ges., 57, 1203 (1924)}

• Much of the rigorous proof for the existence of macromolecules will come from physical measurements (viscosity measurements, molecular weight measurements by ultracentrifuge, osmometry and light scattering as well as X Ray diffraction)

• But being quintessentially an organic chemist, Staudinger was skeptical of physical measurements. Staudinger believed polymers to possess “rigid rod like structure”, a belief he will not abandon for several years. When evidence began building up that polymers have flexible chains, Staudinger ignored them.
Mark, along with Staudinger and Carothers can be credited as a cofounder of Polymer Science

Mark was trained as an organic chemist. His PhD thesis was on the chemistry of free radicals under the supervision of Schlenk

With Polanyi, Mark began to explore the technique of Crystallography (X Ray and electron diffraction) for the study of organic molecules at Kaiser Wilhelm Institute

One of the materials chosen was cellulose fiber. They found that cellulose fiber upon stretching leads to increase in modulus

Mark presents his results in a meeting of the Society of German Natural Scientists at Dusseldorf in 1926; He says that important information can be obtained from unit cells and space groups, even if detailed molecular structures are not known; He proposes that in polymers “lattice forces are comparable to intramolecular forces and the entire crystallite behaves like a large molecule”
In 1926, Mark becomes the Director of research at IG Farbenindustrie in Ludwigshafen, a large producer of rayon and cellulose acetate. Here he develops the first commercial process for producing styrene.

Mark and Meyer solve the crystal structure of Cellulose in 1928, the first crystal structure of a polymer which reconciles the X-Ray pattern with the chemical composition.

Using X-Ray, Mark establishes that natural rubber is a polymer of isoprene, namely, 1,4-polyisoprene and that isoprenes are in a cis configuration in the polymer chain.

It is interesting that although Mark provided the most unequivocal support to the macromolecular hypothesis of Staudinger, he and Staudinger were not in good terms. Staudinger felt that macromolecular chemistry was his field and he looked upon physicists and physical chemists as interlopers, who stole his ideas.

Mark left IG Farben in 1932 and returned to the University of Vienna. It was in Vienna that he along with Eugene Guth proposed the statistical theory of rubber elasticity and developed the Mark Houwink relationship, relating dilute solution viscosity of a polymer solution to its molecular weight.

One of his famous students in Vienna was Max Perutz who went on to found the Medical Research Council at Cambridge which became a centre of excellence in protein crystallography.
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 he establishes the equivalence of organic and polymer forming reactions, namely esterification and polyesterification
WALLACE CAROTHERS AND THE BIRTH OF RATIONAL POLYMER SYNTHESIS

With Julian Hill, extends the reaction to adipic acid and hexamethylene diamine, a polyamide forming reaction, leading to the first synthesis of Nylon-66 in 1934. Nylon-66 goes into production in 1939.

Develops a theoretical understanding of the polycondensation reaction relating the average degree of polymerization to fractional conversions (Carother`s Equation)

Carothers had been troubled by periods of mental depression since his youth. Despite his success with nylon, he felt that he had not accomplished much and had run out of ideas.

His unhappiness was compounded by the death of his sister, Isobel, and on the evening of April 28, 1937 he checked into a Philadelphia hotel room and committed suicide by drinking a cocktail of lemon juice laced with potassium cyanide.

His daughter, Jane, was born seven months later on November 27, 1937.
STUDIES ON POLYMERIZATION AND RING FORMATION

Twenty eight papers from 1929 to 1935

Carothers addressed one important question:

(a) If two bifunctional molecules, e.g., one dibasic acid and one glycol or diamide, react, two possibilities occur. The reaction can result (1) in a chain polymer of lower or higher molecular weight, which still bears either hydroxyl or carboxyl terminal groups or (2) in a smaller or larger ring, which does not contain the reactive group.

Under what conditions does either of these two possibilities take place and what is the molecular weight of the resulting compound?
IX. Polymerization*

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   3. Linear and non-linear polymers
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   5. Types of polymerization
   6. Condensation polymerizations and bi functional reactions

II. Condensation polymerization
   1. Polyesters
      a. The self-esterification of hydroxy acids  
      b. Polyesters from dibasic acids and glycols

* Wallace H. Carothers; Chemical Reviews 8, 353-426 (1931); Communication No. 55 from the Experimental Station of the E. I. du Pont de Nemours and Company. Received March 21, 1931. Published June 1931.
THE DAWN OF THE CHEMICAL INDUSTRY: THE MANUFACTURE OF BAKELITE

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, heralding the age of plastics, a discovery considered as revolutionary

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

Baekland named his new material Novolak

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

Leo Baekland (1863-1944)

When asked why he chose to work in the field of synthetic resins, he replied, “to make money”
CRystalline HIGH PolYMERS OF α-OLEFINS

Sir:

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

G. Natta

JACS 77, 1708, 1955
( March 20, 1955 )
Tacticity in Polymers: eg., Polypropylene

- **Isotactic**
- **Syndiotactic**
- **Atactic**
Polymerization with stereo-specificity/ regio-specificity:

Stereoisomerism in polymers arises from different spatial arrangements or configuration of the atoms or substituents which can be inter-converted only by the breakage and reformation of the chemical bond

Regularity in configuration of successive chiral, asymmetric or pseudochiral carbon (C*) determines the tacticity of the polymer chain
POLYPROPYLENE

CH₂=CH-CH₃

"PROCHIRAL"

H       CH₃
CH₃ H    H CH₃
H     CH₃ H
H  CH₃ H

ISOTACTIC

H CH₃ CH₃ H CH₃ CH₃ H CH₃ CH₃ H CH₃

SYNDIOTACTIC

H CH₃ H CH₃ H CH₃ H CH₃ H

ATACTIC

H CH₃ H CH₃ H CH₃ H CH₃ H CH₃ H CH₃

FISCHER PROJECTIONS

Tm°C % X

ISOTACTIC 165-170 55-65
SYNDIOTACTIC 125-131 50-70
ATACTIC - 0
Tacticity in Polymers

- Isotactic and syndiotactic polymers have ordered arrangements of groups. Hence, the chains can pack closely together and develop high crystallinity.

- Atactic polymers cannot and, therefore, are generally amorphous in nature.
• Global chemical industry today is valued at US $3 trillion. Bulk petrochemicals and polymers account for one third of this value, US $1 trillion. Asia including Japan accounts for a one third share, ~US $0.3 trillion

• Today we consume ~ 250 million tons of polymer materials

• Growth is driven predominantly by India and China. India will become the third largest consumer of polymers by 2012
## Polymer Demand Outlook

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<tr>
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Source: CPMA

POTENTIAL TO BE THE 3\textsuperscript{RD}, LARGEST MARKET BY 2010
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…
(Global consumption exceeds 250 million tons)

**Precursor 19th Century → Semi Synthetics**
- 1839: Natural Rubber
- 1843: Vulcanite / Gutta Percha
- 1856: Shellac / Bois Durci
- 1862: Parkesine
- 1863: Celluloid
- 1894: Viscose Rayon
- 1898: Poly Carbonate

**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: Thermo plastic Polyester
- 1978: LLDPE
- 1985: Liquid Crystal Polymers

**Natural Polymers**

**Semi Synthetics**

**Plastics in Packaging**

**High Performance Plastics**
I am inclined to think that the development of polymerization is, perhaps, the biggest thing that chemistry has done, where it has the biggest effect on everyday life

Lord Alexander Todd (1907-1997)
Nobel Laureate, 1957
THE NEW DIMENSIONS OF MATERIAL SCIENCE

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

STRUCTURAL MATERIALS

MACROCOMPOSITES
- Shear
- wetting
- Orientation

FUNCTIONAL MATERIALS

BIOCOMPOSITES
- Molecular self assembly
- Hydrogen bonding
- Hydrophobic interaction

NANOCOMPOSITES
- Intercalation and exfoliation
- In-situ polymerization
- Polymerization in constrained spaces
- Nanofibers and nanotubes
ADCVANCED AND FUNCTIONAL MATERIALS

- Functional polymers
- Polymers with precisely defined shape, size and topology (e.g. Dendrimers and hyper branched polymers)
- Stimuli responsive materials
- Super and supra-molecular materials
- Nano-materials
- Bio-molecular materials

Research driven by emerging developments in electronics, photonics, information technology and medicine. All new discoveries likely to occur at the interface of polymer science with chemistry, biology and physics
COMPLEX POLYMER SYSTEMS

- Organic – inorganic hybrids, stimuli responsive polymers, polymer networks with defined functions and control, block and hetero- copolymers, polymers that self assemble into large supramolecular forms with hierarchical order and polymer materials capable of interacting with other materials, especially biological materials

- Key fundamental scientific challenges:
  - Directing structures via controlled kinetic and thermodynamic pathways
  - Complex structure via chain architecture
  - Entropy driven assembly in multi-component hybrid systems
  - Template assisted synthesis of complex systems
NEW DIRECTIONS IN ADVANCED MATERIALS RESEARCH

• Multiphase polymer blends
• Organic - inorganic hybrid materials
• High temperature resistant materials
• Easy processing polymers
• Stiff main chain materials
• Novel processing techniques
  – Reactive processing
  – Solid and gel state processing
• Functional polymers with specific electrical, optical, barrier properties
• Intelligent materials
• Biocompatible and bio-molecular materials
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
POLYMER MATERIALS : FUTURE

• Speciality or advanced materials
  – Functional polymers
  – Polymers with precisely defined shape, size and topology
  – Stimuli responsive materials
  – Super and supramolecular materials
  – Nanomaterials
  – Biomolecular materials

Research driven by emerging developments in electronics, photonics, information technology and medicine. All new discoveries likely to occur at the interface of polymer science with chemistry, molecular biology and physics.
POLYMER MATERIALS : FUTURE

- Commodity and engineering polymers
  - Improved properties
  - Advanced computational tools and engineering principles
  - Reduced manufacturing cost
  - Easier processability/new processing technique
  - Blends, alloys and composites

New Polymers will emerge, not from new monomers, but by creating new structures from existing inexpensive monomers
INTELLIGENT MATERIALS

- Heterogeniety
- Dynamics
- Cooperativity

*Time dependent response of a surface to an external stimuli / environment is often called “Intelligence”*
INTERDISCIPLINARY ROLES OF DENDRIMERS AND DENDRIGRAFTS

LIFE SCIENCES
Dendrimer (DNA, antibodies, proteins) conjugates
Gene therapy
Biomimetics
Drug delivery
Immunoassays

NANO DEVICES
Molecular antennae
Electroconductive dendrimers
Ball and chain constructs (amphiphiles)

MATERIALS SCIENCES
New dendrimer compositions
Molecular ball bearings (flow regulators, processing aids)
Liquid crystal constructs
INTERDISCIPLINARY ROLES OF DENDRIMERS AND DENDRIGRAFTS

INTERFACIAL SCIENCES
Dendrimer catalysts (homogeneous/heterogeneous)
Electro-catalysis
Monolayers/multilayers
Coatings

SUPRAMOLECULAR SCIENCES
Molecular encapsulation
Host-guest interactions
Dendrimer box
Lock and key complexes
Self assembling dendrimers
Micelle mimics and inverted micelle mimics
POLYMER MATERIALS: SUSTAINABILITY CHALLENGE

- Excessive dependence on fossil fuel; a finite natural resource

- Persist in the environment
Over 30 billion liters of bottled water is consumed annually. Every second we throw away about 1500 bottles. What is the solution? Poly(ethylene terephthalate) (PETE)
Can a part of the chemicals / materials manufacturing progressively shift to renewable carbohydrate resources

Is such a virtuous cycle just a dream?
FROM PETROLEUM TO BIOREFINERIES

Biorefinery

Biomass
Wastes
CO₂
Recycling
Fuels
Heat and Electricity
Chemical and Materials
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

Feed-stocks for polymers will slowly, but certainly, shift to renewable and sustainable resources during the next two decades
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
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-tocks is about *selectively removing* functionality (examples, dehydration, decarboxylation, decarbonylation, deoxygenation)
PET MANUFACTURE: PETRO- AND BIO-BASED

BIOMASS DERIVED DICARBOXYLIC ACIDS FOR PET

Biomass

Cellulose
Bioethanol
5-(Hydroxymethyl)furfural
Hydrogenation
2,5-Dimethylfuran
Diels-Alder reaction

Glycerides
Transesterification
Fatty acid methylester (Biodiesel)

C6-Based Carbohydrates (Glucose or fructose)
Acid-catalyzed dehydration
5-Hydroxymethyl furfural
Oxidation with air over different catalysts
Furan-2,5-dicarboxylic acid (FDCA)

HOOC
\[\text{CHO}\]

HOOC
\[
\text{COOH}
\]

Terephthalic acid
Sustainability in the chemical industry: Grand Challenges,
The National Academy of Sciences, USA, 2005
NEW DESIGN PARADIGMS IN POLYMER SYNTHESIS

Controlled Polymer synthesis

- Polymerization through rational catalyst / initiator design
- Mono-disperse step growth polymers through iterative synthetic methods
- Molecular self assembly methods applied to synthesis of polymers with novel topologies
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 sequences
**CHAIN ISOMERISM**

**Determines ……**
- Thermal behavior
- Morphology
- Crystallinity

**Polymer stereochemistry**
- Geometrical isomerism
- Regioisomerism
- Stereoisomerism

**Challenge…..**
- Control polymer stereochemistry through rational design of catalysts
Chain Topology

Determines ……

- Crystalline properties, solubility and rheological behavior

Diversity of polymer architectures

- Linear, Branched, Hyper-branched
- Stars, Dendrimers
- Catenanes, Rotaxanes
- Ribbons, Wires

Challenge…..

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

**Monomer**

\[
\text{CH}_2=\text{C}^+ \quad \text{R}^1 \quad \text{X} \quad \text{MX}_n
\]

**Initiator**

\[
\text{R} \quad \text{MX}_n \quad \text{MX}^+ \quad \text{XMX}_n
\]

**Living Polymer**

\[
\text{CH}_2=\text{C} \quad \text{R}^1 \quad \text{X} \quad \text{MX}_n
\]

**Reversible Activation**

- Dormant (Covalent)
- Reversible Heterolytic
- Active (Cationic)

**Lewis Acid**

\[
\text{MX}_n
\]

**Monomer**

\[
\text{CH}_2=\text{C} \quad \text{R}^1 \quad \text{X}
\]

**Transition Metal Complex**

\[
\text{M}^n
\]

**Initiator**

\[
\text{R}^* \quad \text{X} \quad \text{MX}^+ \quad \text{XMX}_n
\]

**Reversible Activation**

- Dormant (Covalent)
- Reversible Homolytic
- Active (Radical)

**Living Polymer**

\[
\text{CH}_2=\text{C} \quad \text{R}^1 \quad \text{X} \quad \text{MX}_n
\]

**Metal Complex**

\[
\text{M}^n
\]

**Monomer**

\[
\text{CH}_2=\text{C} \quad \text{R}^1 \quad \text{X}
\]
What Can Controlled/ Living Polymerizations Do?

\[ \text{DP}_n = \Delta [M] /[I]_o; \quad 200 < M_n < 10^6 \text{ (or more?)}; \quad 1.01 < M_w/M_n < 1.5 \text{ & designed MWD; tacticity} \]

**Topologies:**
- linear
- star
- comb/brush
- network/crosslinked
- dendritic/hyperbranched

**Compositions:**
- homopolymer
- periodic copolymer
- block copolymer
- random copolymer
- tapered/gradient copolymer
- graft copolymer

**Functionalities:**
- side-functional groups
- end-functional polymers
- telechelic polymers
- site-specific functional polymers
- macromonomers
- multifunctional

**Monomers:**
- Vinyl: \((\text{Me})\)
- \(-\text{Ar (Sty), Vi (Bu & IP), Pyr, CN, Cl, Br, Me, H}\)

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

**Transformations:**
- Z-N
- ROMP
- PCond.
- Hybrids: synthetic/natural organic/inorganic surfaces; IPN; etc.
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
GOALS OF POLYMERIC SCIENCE

- Techniques of controlled polymer synthesis
- Concepts and goals of material science
- Molecular scale phenomena
- Macroscopic functions
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

In the future, functions will be more important than molecules. Molecules are no longer enough (they never really were)
THANK YOU