SCIENCE OF POLYMERS : PAST, PRESENT AND FUTURE

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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

Ber. Dtsch. Chem. Ges., 53, 1073 (1920)

125. H. Staudinger: Über Polymerisation.

[Mitteilung aus dem Chem. Institut der Eidgen. Techn. Hochschule, Zürich.]

(Eingegangen am 13. März 1920.)

Vor einiger Zeit hat G. Schroeter[1]) interessante Ansichten über die Zusammensetzung von Polymerisationsprodukten, speziell über die Konstitution der polymeren Ketene veröffentlicht. Danach sollen diese Verbindungen Molekülverbindungen darstellen und sollen keine Cyclobutan-Derivate sein, wie früher angenommen wurde[2]); denn diese polymeren Ketene unterscheiden sich nach den Schroeterschen Untersuchungen in wesentlichen Punkten von Cyclobutan-Derivaten, die durch Synthese aus Aceton-dicarbonester-Derivaten zugänglich sind.

Die gleichen Ansichten über die Zusammensetzung von Polymerisationsprodukten hat schon im Jahre 1909 H. Hildebrand in einer im Thieleschen Laboratorium ausgeführten Dissertation ausgesprochen[3]), anschließend an eine Untersuchung über die Polymerisation des *asymm.* Diphenyl-äthylens. Das dimolekulare Polymerisationsprodukt soll nicht das Tetraphenyl-cyclobutan darstellen, sondern es soll eine Molekülverbindung sein, bei der Partialvalenzen den Zusammenhalt der ungesättigten Moleküle herbeiführen:

$$2\,(C_6H_5)_2C:CH_2 \rightarrow \begin{array}{l}(C_6H_5)_2C\text{——}CH_2\\ \quad\vdots\qquad\vdots\\ CH_2\,.\,C(C_6H_5)_2\end{array} \quad \text{und nicht} \quad \begin{array}{l}(C_6H_5)_2C\text{——}CH_2\\ \quad|\qquad|\\ CH_2\,.\,C(C_6H_5)_2\end{array}$$

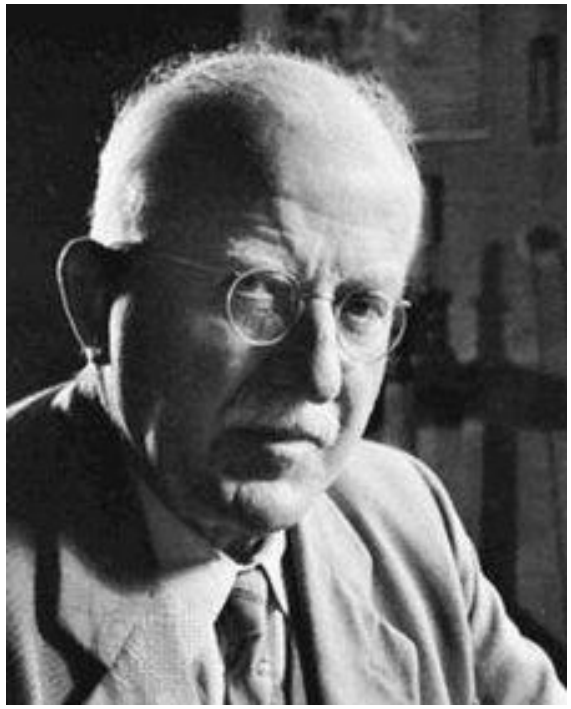
Solche Annahmen sind heute in der organischen Chemie sehr verlockend, nachdem eine große Anzahl gut charakterisierter Verbindungen, z. B. die Chinhydrone, nach den Untersuchungen von Pfeiffer[4]) als Molekülverbindungen, die durch Nebenvalenzen zusammengehalten werden, aufgefaßt werden. Und doch glaube ich, daß nach dem vorliegenden Beobachtungsmaterial solche Annahmen zur Erklärung des Entstehens der Polymerisationsprodukte nicht gemacht zu werden brauchen; vielmehr können die verschiedenartigsten Polymerisationsprodukte, wie ich im Folgenden zeigen möchte, durch normale Valenzformeln eine genügende Erklärung finden;

[1]) B. **49**, 2697 [1916].

[2]) Vergl. H. Staudinger, Die Ketene, Verlag F. Enke, Stuttgart 1912, 46.

[3]) H. Hildebrand, Über die Polymerisation des *asymm.* Diphenyl-äthylens, Dissert., Straßburg 1909.

[4]) A. **412**, 253 [1917]; **404**, 1 [1914].



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

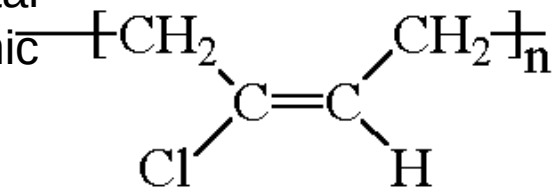
- His ideas met with much resistance and criticism from eminent chemists of the period, notable amongst them, Emil Fischer.

AT IS THE ORIGIN OF THE TERM POLYMER ?

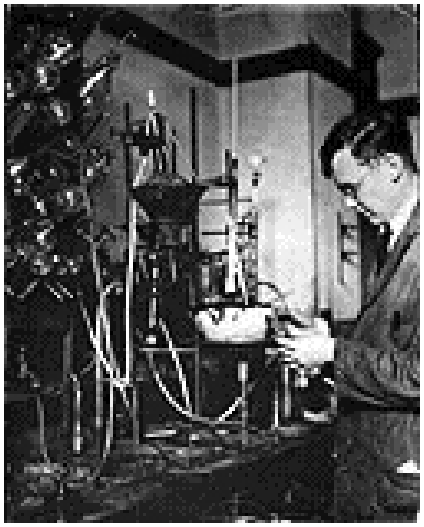
- Faraday in 1826 was puzzled by the fact that ethylene and butene differed in their gas density , but had the same elemental composition
- Berzelius was astounded by Faraday`s observation and suggested that butene be referred to as a “polymer” of ethylene (1827, 1832). All through the nineteenth century, 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

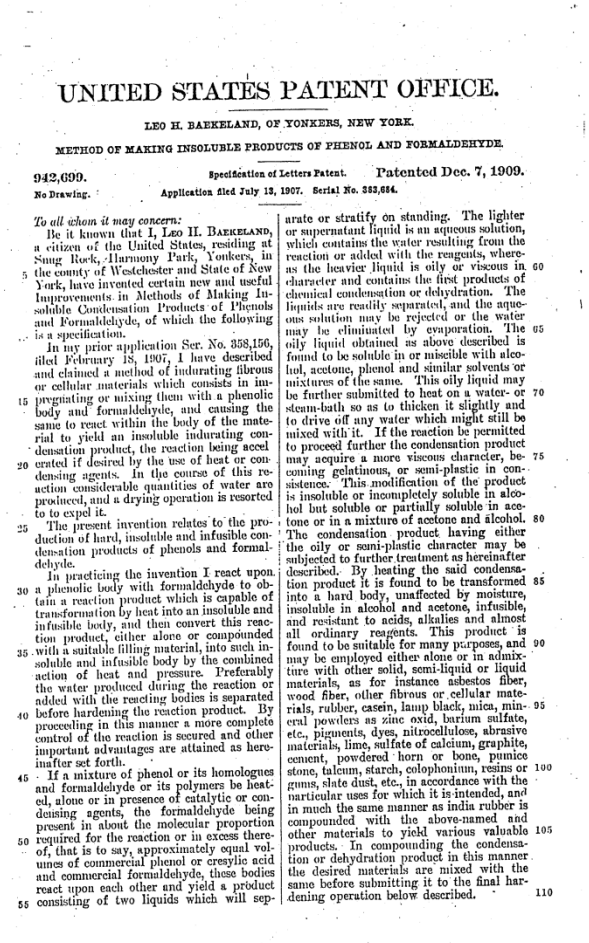
- Trained as an organic chemist with Roger Adams, PhD, 1924; hired as a faculty at Harvard
- DuPont lured him to Wilmington Delaware to lead a fundamental research programme in organic chemistry and polymers
- By 1931, he had synthesized chloroprene and polymerized to a new synthetic rubber, called by 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



Poly(chloroprene)



THE DAWN OF THE CHEMICAL INDUSTRY: THE MANUFACTURE OF BAKELITE



UNITED STATES PATENT OFFICE.

LEO H. BAEKELAND, OF YONKERS, NEW YORK.

METHOD OF MAKING INSOLUBLE PRODUCTS OF PHENOL AND FORMALDEHYDE.

942,699. Specification of Letters Patent. Patented Dec. 7, 1909.

No Drawing. Application filed July 13, 1907. Serial No. 383,884.

To all whom it may concern:

Be it known that I, LEO H. BAEKELAND, a citizen of the United States, residing at Snug Rock, Harmony Park, Yonkers, in the county of Westchester and State of New York, have invented certain new and useful Improvements in Methods of Making Insoluble Condensation Products of Phenols and Formaldehyde, of which the following is a specification.

In my prior application Ser. No. 358,156, filed February 18, 1907, I have described and claimed a method of indurating fibrous or cellular materials which consists in impregnating or mixing them with a phenolic body and formaldehyde, and causing the same to react within the body of the material to yield an insoluble indurating condensation product, the reaction being accelerated if desired by the use of heat or condensing agents. In the course of this reaction considerable quantities of water are produced, and a drying operation is resorted to to expel it.

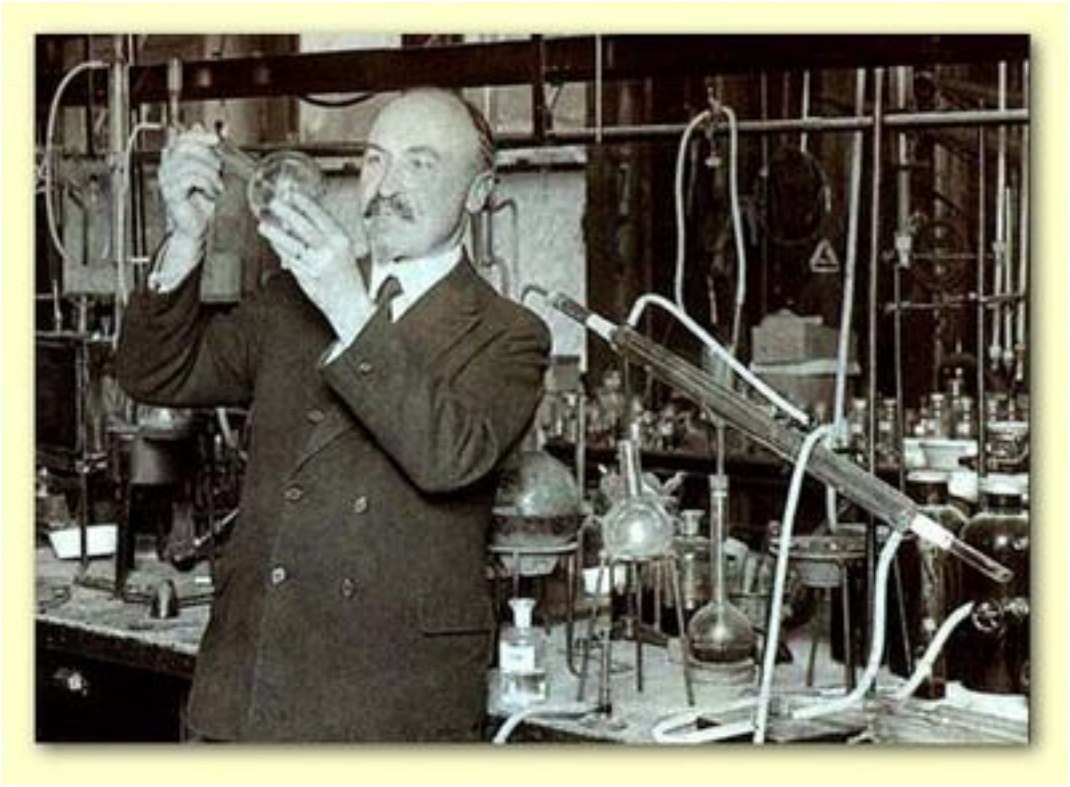
The present invention relates to the production of hard, insoluble and infusible condensation products of phenols and formaldehyde.

In practicing the invention I react upon a phenolic body with formaldehyde to obtain a reaction product which is capable of transformation by heat into an insoluble and infusible body, and then convert this reaction product, either alone or compounded with a suitable filling material, into such insoluble and infusible body by the combined action of heat and pressure. Preferably the water produced during the reaction or added with the reacting bodies is separated before hardening the reaction product. By proceeding in this manner a more complete control of the reaction is secured and other important advantages are attained as hereinafter set forth.

If a mixture of phenol or its homologues and formaldehyde or its polymers be heated, alone or in presence of catalytic or condensing agents, the formaldehyde being present in about the molecular proportion required for the reaction or in excess thereof, that is to say, approximately equal volumes of commercial phenol or cresylic acid and commercial formaldehyde, these bodies react upon each other and yield a product consisting of two liquids which will separate or stratify on standing. The lighter or supernatant liquid is an aqueous solution, which contains the water resulting from the reaction or added with the reagents, whereas the heavier liquid is oily or viscous in character and contains the first products of chemical condensation or dehydration. The liquids are readily separated, and the aqueous solution may be rejected or the water may be eliminated by evaporation. The oily liquid obtained as above described is found to be soluble in or miscible with alcohol, acetone, phenol and similar solvents or mixtures of the same. This oily liquid may be further submitted to heat on a water- or steam-bath so as to thicken it slightly and to drive off any water which might still be mixed with it. If the reaction be permitted to proceed further the condensation product may acquire a more viscous character, becoming gelatinous, or semi-plastic in consistence. This modification of the product is insoluble or incompletely soluble in alcohol but soluble or partially soluble in acetone or in a mixture of acetone and alcohol. The condensation product having either the oily or semi-plastic character may be subjected to further treatment as hereinafter described. By heating the said condensation product it is found to be transformed into a hard body, unaffected by moisture, insoluble in alcohol and acetone, infusible, and resistant to acids, alkalies and almost all ordinary reagents. This product is found to be suitable for many purposes, and may be employed either alone or in admixture with other solid, semi-liquid or liquid materials, as for instance asbestos fiber, wood fiber, other fibrous or cellular materials, rubber, casein, lamp black, mica, mineral powders as zinc oxid, barium sulfate, etc., pigments, dyes, nitrocellulose, abrasive materials, lime, sulfate of calcium, graphite, cement, powdered horn or bone, pumice stone, talcum, starch, colophonium, resins or gums, slate dust, etc., in accordance with the particular uses for which it is intended, and in much the same manner as india rubber is compounded with the above-named and other materials to yield various valuable products. In compounding the condensation or dehydration product in this manner the desired materials are mixed with the same before submitting it to the final hardening operation below described.

- 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



Leo Baekland (1863-1944)

When asked why he chose to work in the field of synthetic resins, he replied, "to make money"

PVC : REPLACEMENT FOR A RENEWABLE RESOURCE

78 rpm Gramaphone records

33 rpm long playing records (vinyls)

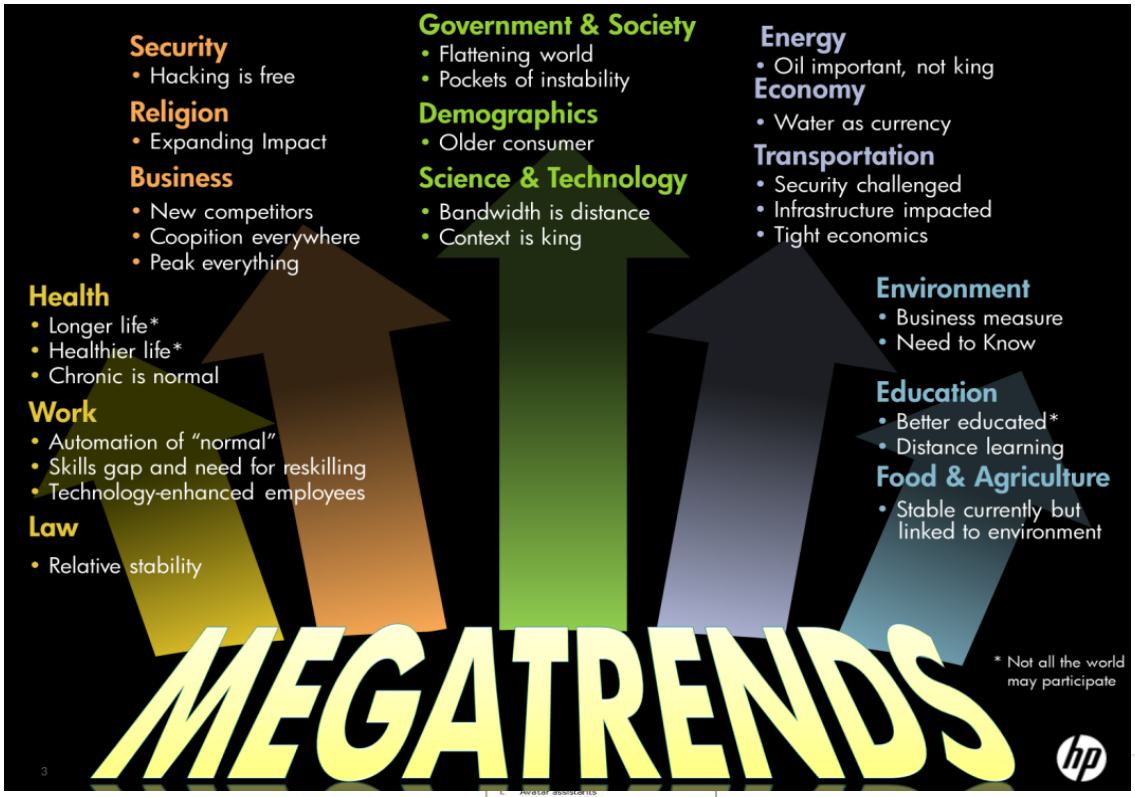
Shellac, a natural resin secreted by the female lac bug on trees; Main constituent : Aleuritic acid; In the early part of twentieth century , India was the largest supplier of Shellac to the world

SCIENTIFIC FRONTIERS AND TECHNOLOGY FRONTS

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

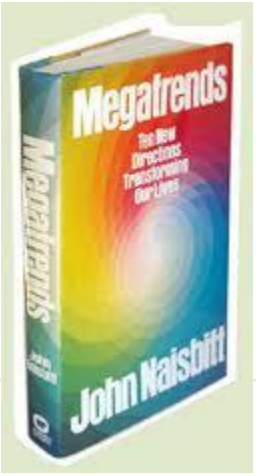
New science can lead to technology; similarly emergence of technology can stimulate science

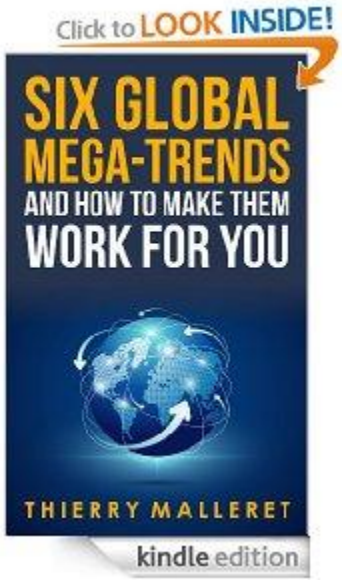
It is a two way street; science leads technology and technology leads science



THE NEW BUZZWORD

MEGATRENDS !





1. Avatar assistants
2. Biomimicry
3. Clean coal
4. Comfort eating
5. Contextual deficit
6. Diminishing use of email
7. Decline of voice communication
8. Electrification of transport
9. Facial recognition on mobile phones
10. Gene hacking
11. Holographic telepresence
12. Increasing complexity
13. Local living
14. Mobile money
15. Peak water
16. Peer-to-peer lending/giving
17. Quantum computing
18. Reverse migration
19. Self-tracking
20. Smart infrastructure
21. Slow education
22. Shift from products to experiences
23. Ultra-efficient solar
24. Value redefinition
25. Voluntary simplicity

SOURCES & FURTHER READING

The Future: 50 Ideas You Really Need to Know by Richard Watson

See www.futuretrendsbook.com and www.nowandnext.com

PRINTING & PRINTED COPIES

High resolution digital files for this table and ready printed copies can be obtained from: richard@nowandnext.com

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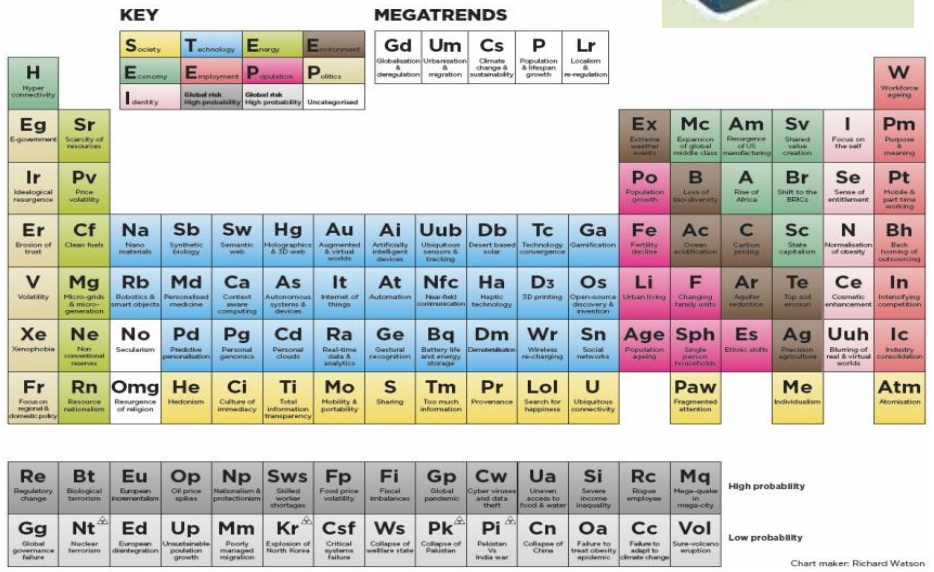
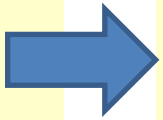
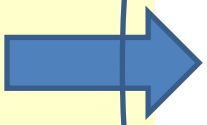


MEGATRENDS USEFUL FOR PREDICTING THE FUTURE OF TECHNOLOGY

- 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)

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

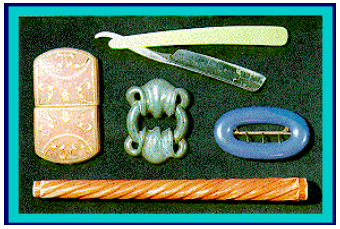
POLYMERS FULFILLING MATERIAL NEEDS OF SOCIETY…

Precursor 19th Century → Semi Synthetics

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

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

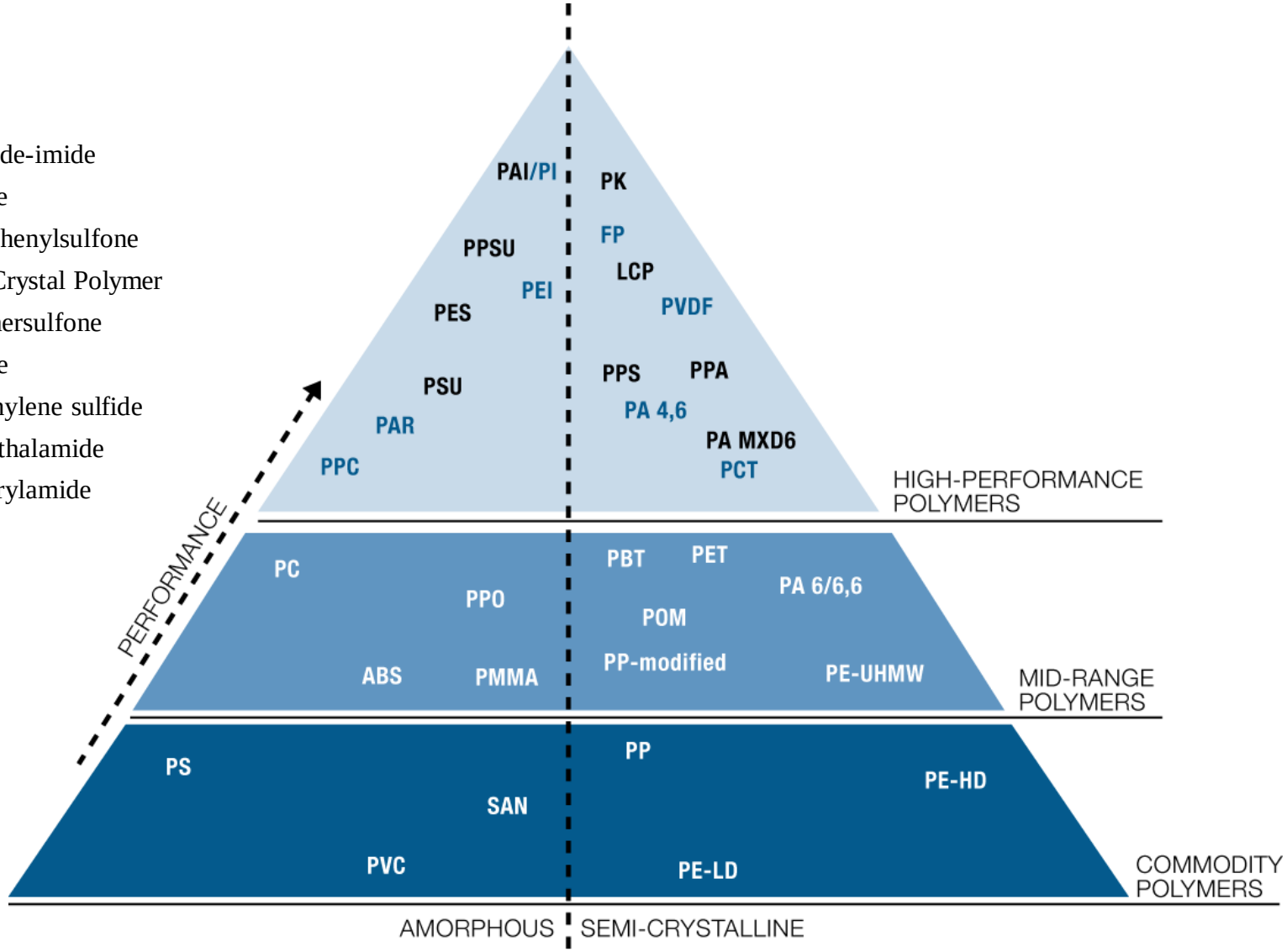
Plastics in Packaging

Hi Tech Plastics

Source : British Plastic Federation Website

THE POLYMER PYRAMID

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



FROM CONCEPT TO MARKET PLACE

Polymer	Commercialized	Years
Polyvinylchloride	1928	27
Polymethyl-methacrylate	1933	5
Nylon 6,6	1934	3
Polystyrene	1936	27
PTFE	1950	12
Polyethylene	1955	3
Polypropylene	1957	3
Polycarbonate	1968	15
Polyether imide	1982	15
Polyethylene naphthalate	1999	24
Polyethylene (metallocenes)	2000	18

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.

NEW POLYMER INTRODUCTION : ENTRY BARRIERS

Polymer	Company	Cost in million US Dollars	Status
Ethylene/ propylene-CO (1985-2001)	Shell (Carilon) BP (Ketonex)	300-600	Abandoned ; unable to displace nylon, PBT and polyacetal
Syndiotactic polystyrene (1989 -)	Dow (Questra)	-	Abandoned ;40,000 tpa plant at Schkopau, Germany; competes with PBT
Hydrogenated polystyrene (1995 -)	Dow (PCHE)	-	Abandoned; unable to displace PC
Ethylene-styrene copolymers (1990 -)	Dow (Index)	-	Abandoned ;25000 tpa Sarnia, Ontario ; No further expansion contemplated
Ethylene-norbornene (1990 -)	Ticona (Topas)		32000 tpa Oberhausen, Germany; Only niche markets have emerged;Competes with PVC, PC
Poly(trimethylene terephthalate)	Shell (Coterra) DuPont (Sorona)		20000 tpa (Shell) W.Va; Plans to build a 100,000 tpa plant in Canada; 12000 tpa (DuPont) at Kingston, NC
Poly(lactic acid)	Dow-Cargill (Nature Works)	750 + 250	140,000 tpa plant at Blair, Nebraska; Targets : fibers/ packaging

TRENDS IN THE GLOBAL POLYMER INDUSTRY

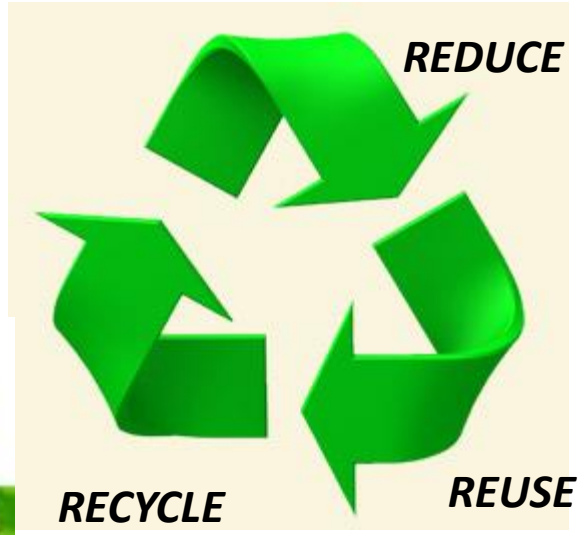
- Customers demand more variety and content
- Environment and safety regulations will be the key driver of change
- Competitive advantage of Feedstocks : A geographic advantage
- Competition is unrelenting
- Market pressures restrict price increases
- Margins are progressively squeezed

BARRIERS TO INNOVATION

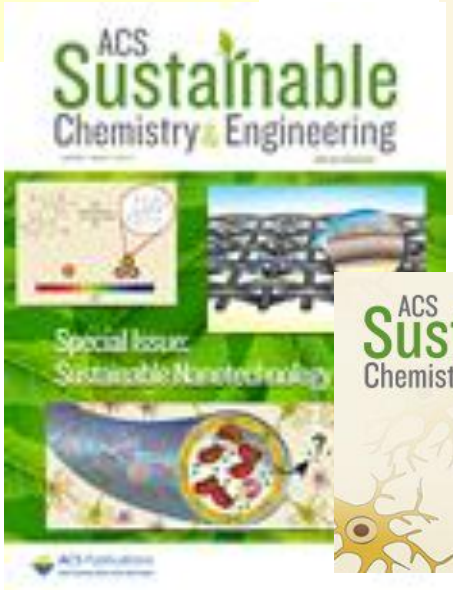
- Ability to meet stiff economic challenges
- Access to capital to demonstrate technologies and manufacturing
- Time to market getting longer
- Too little emphasis by industry on “Game-changer technologies” or “breakthrough innovations”;Too much emphasis on customer led incremental developments
- Inefficient 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?

1
PETE

Poly(ethylene terephthalate)

Every second we throw away about 1500 bottles

Over 30 billion liters of bottled water is consumed annually

What is the solution ?

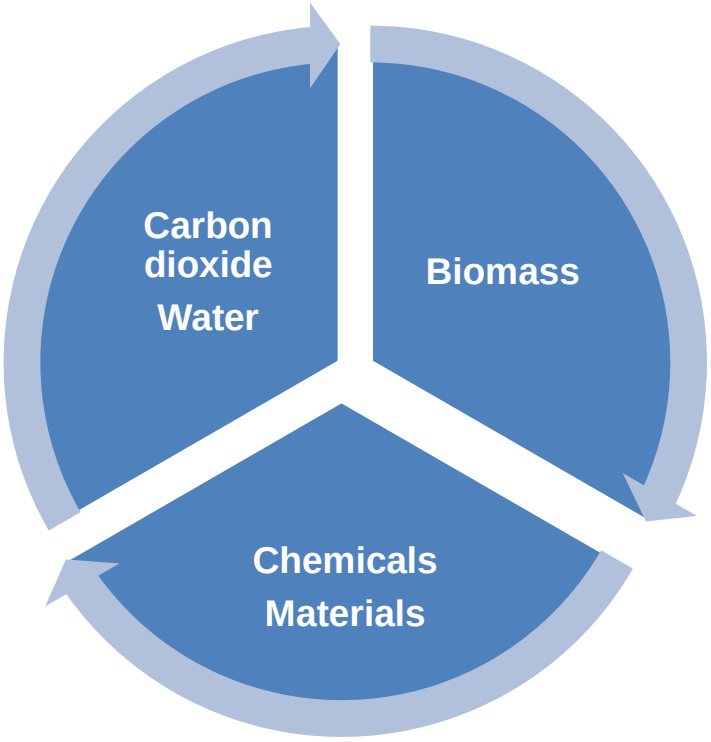
NATURE'S APPROACH TO SUSTAINABLE MATERIALS

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



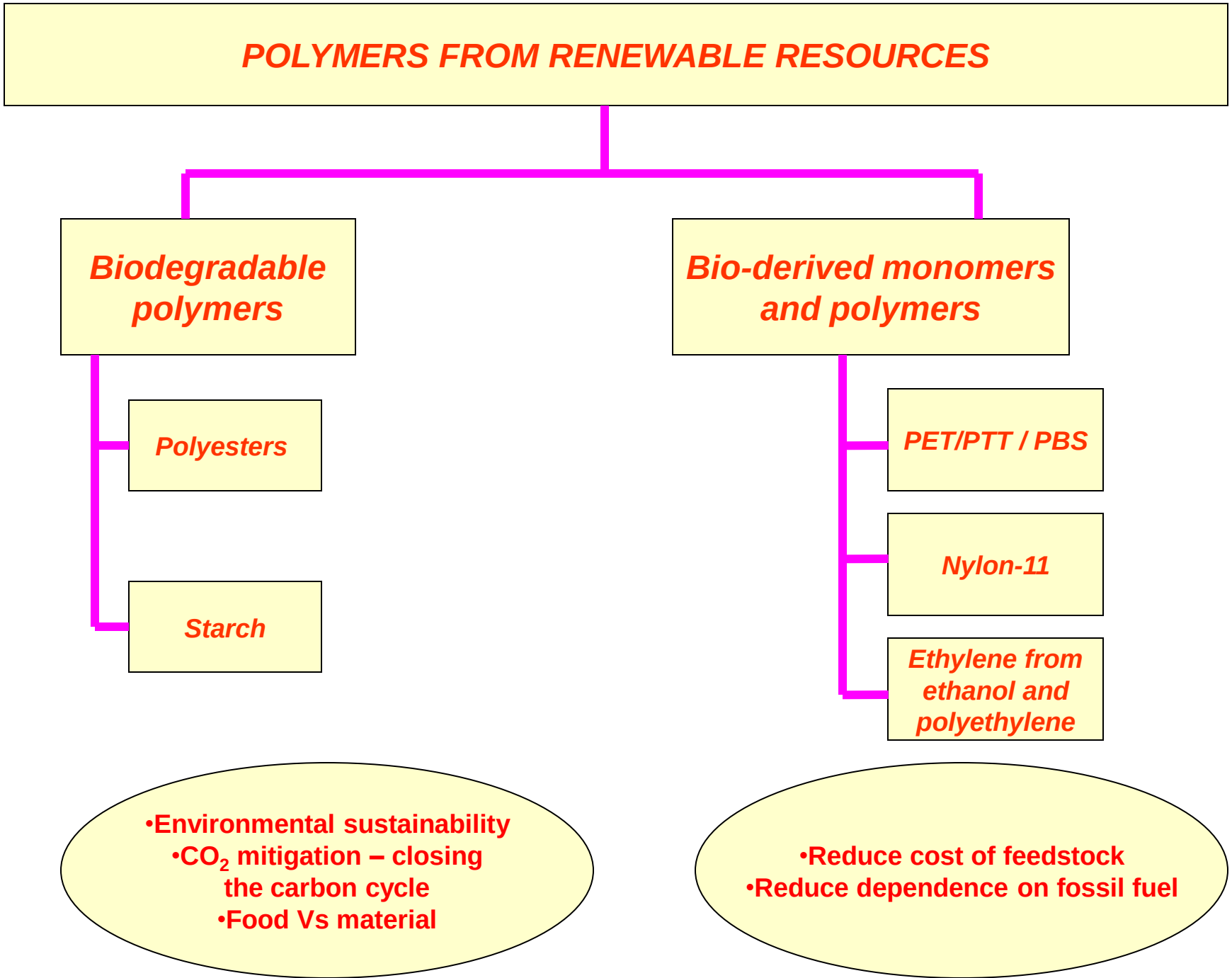
Can a part of the chemicals / materials manufacturing progressively shift to renewable carbohydrate resources (biomass) ?

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
Bio-derived monomers and polymers
Polyesters
Starch
PET/PTT / PBS
Nylon-11
Ethylene from ethanol and polyethylene
•Environmental sustainability
•CO_2 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 CO_2 emitted per kg of PLLA produced versus 3.4 kg of CO_2 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

BIO BASED MONOMERS FOR POLYMERS

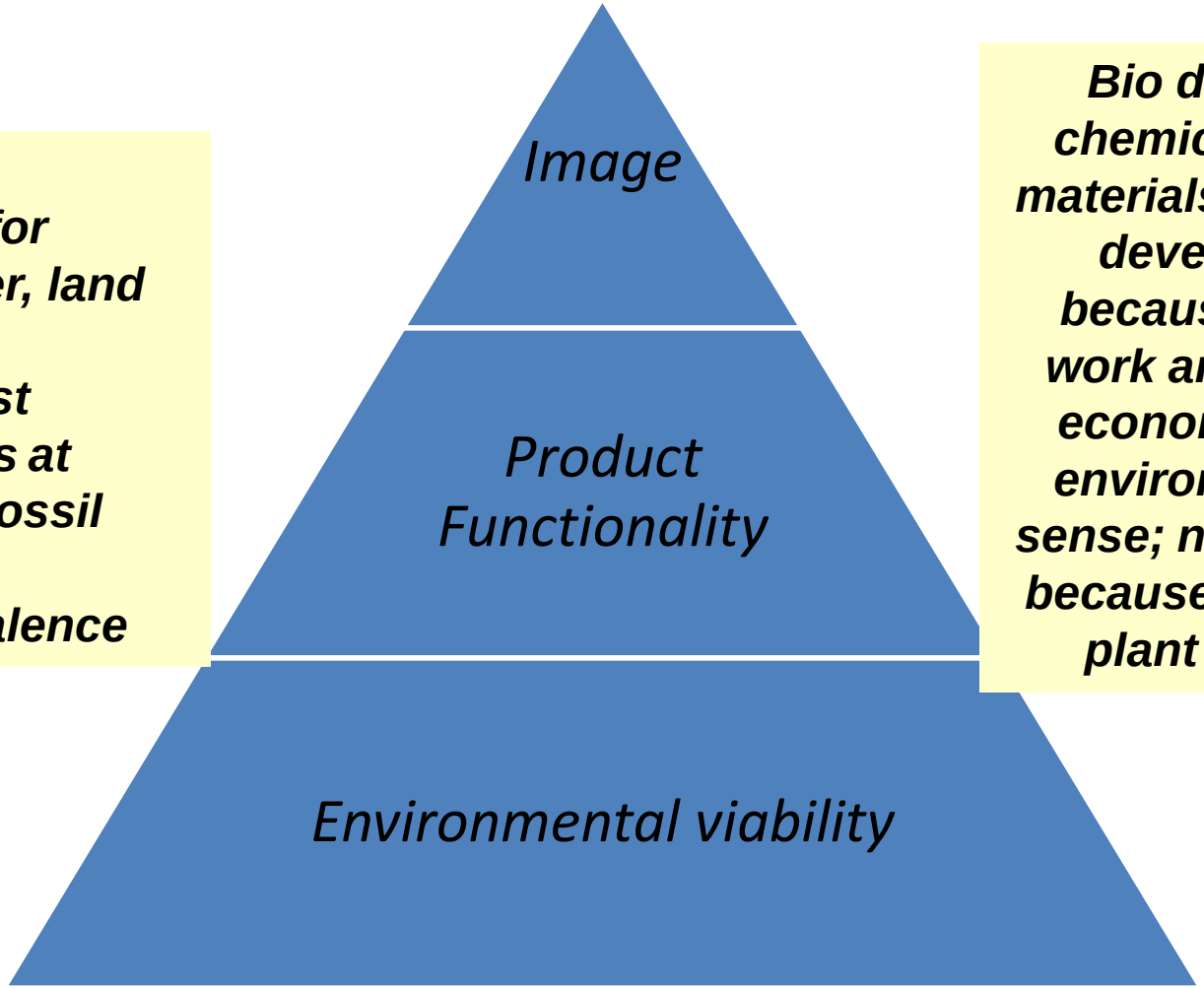
Scientific Challenges

- ***Creating monomers from fossil fuel based feed-stocks 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)***

THE BIOVALUE PYRAMID

- ***CO_2 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

www.rolandberger.com/chemicals 2030

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?"

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

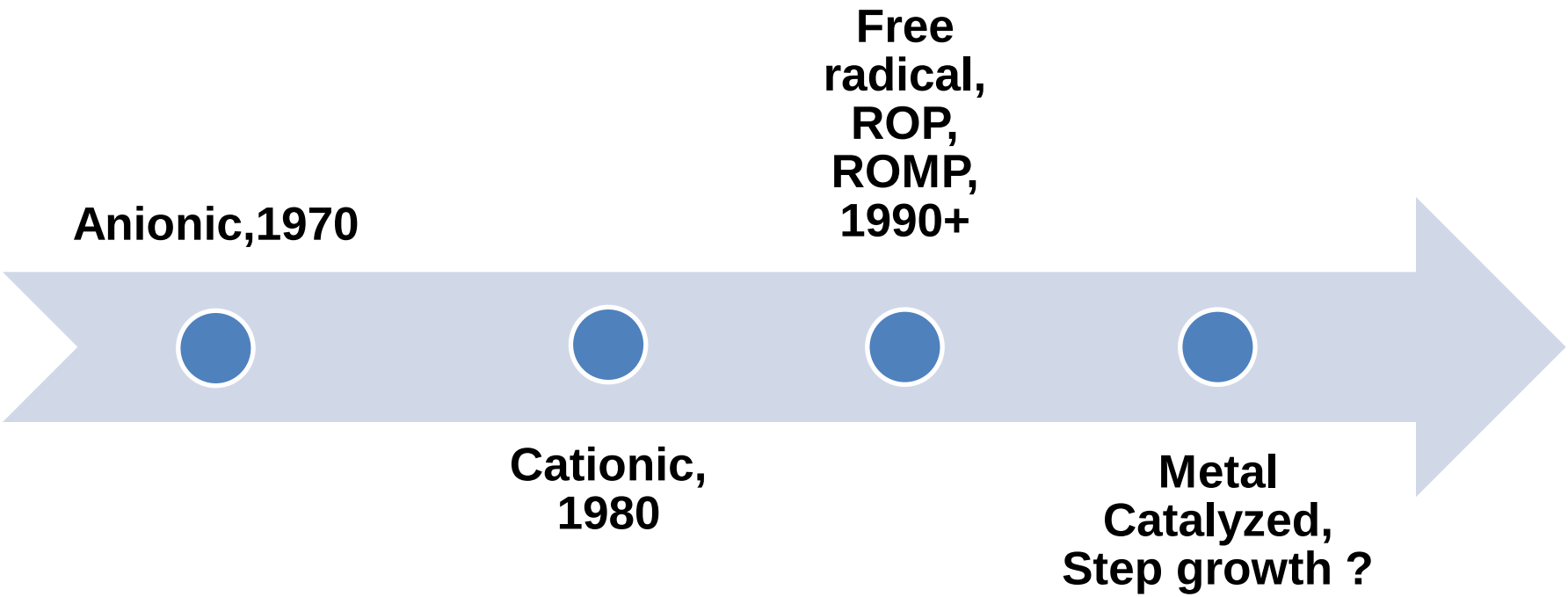
EVOLUTION OF RESEARCH TOPIC IN POLYMER SCIENCE, 1990-2013

January 1990	January 2000	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

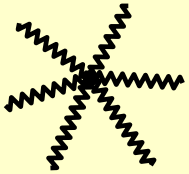
Catalytic controlled polymerization is still not a general technique in metal catalyzed polymerization

Step growth polymerization under equilibrium conditions has problems of control

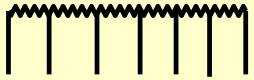
STRUCTURES ACCESSIBLE VIA TECHNIQUES OF CONTROLLED POLYMER SYNTHESIS

Topology

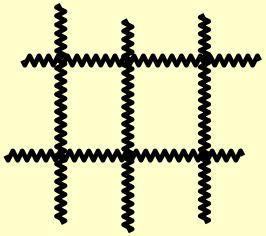
Linear



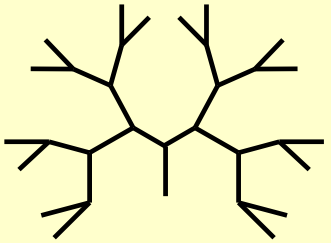
Star / Multi-Armed



Comb Polymers



Networks



(Hyper) Branched

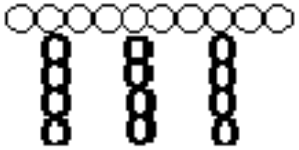
Composition

HomoPolymers

Block Copolymers

Statistical Copolymers

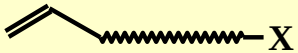
Tapered / Gradient Copolymers



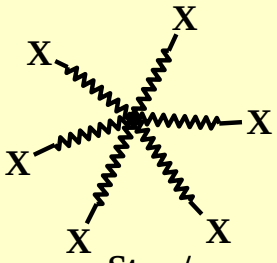
Graft

Functionality

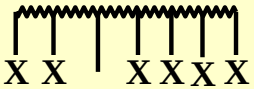
Homo / Hetero Telechelic



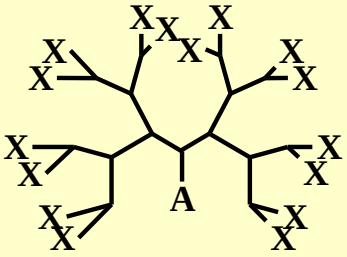
Macromonomers



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 <u>absolutely</u> 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

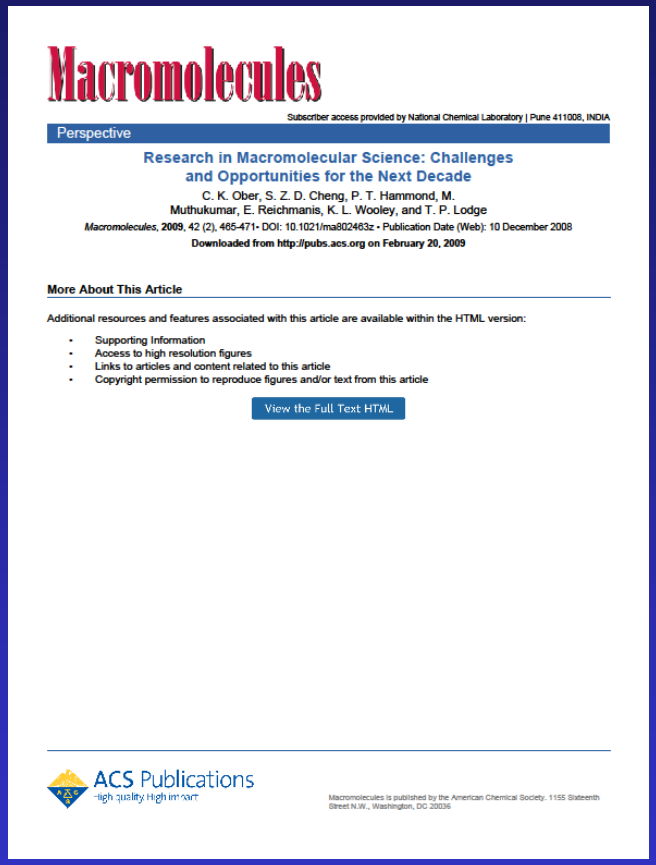
POLYMER MATERIAL SCIENCE : THE NEXT WAVE

- 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

POLYMER SCIENCE : QUO VADIS



Macromolecules

Perspective

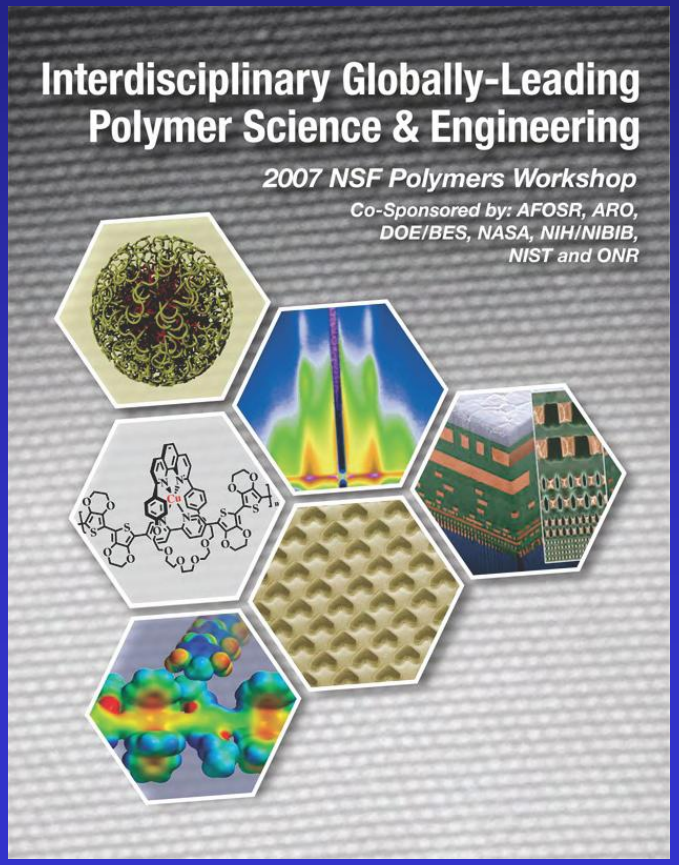
Research in Macromolecular Science: Challenges and Opportunities for the Next Decade

C. K. Ober, S. Z. D. Cheng, P. T. Hammond, M. Muthukumar, E. Reichmanis, K. L. Wooley, and T. P. Lodge

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

Macromolecules 42, January 27, 2009

Research in Macromolecular Science: Challenges and Opportunities for the Next Decade



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