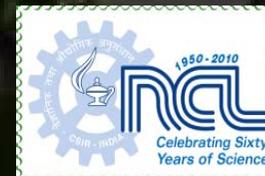


# **SCIENCE OF POLYMERS : PAST, PRESENT AND FUTURE**

**Recent Advances in Polymer and Rubber Science and Technology  
(RAPT 2014)**

**Department of Polymer Science and technology, University of Calcutta**

**January 22, 2014**



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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 Berthollet, 1860  
(1827- 1907)***

***Berthollet gave the first general discussion on polymerism, that is, materials which have the same chemical composition, but differ only in their molecular weights***



## BERTHELOT AND THE BIRTH OF CHEMISTRY

- Was the bridge between Alchemists interpretation of matter and the modern science; Extensively studied the practice of Alchemie and wrote a book “Les Origines de l’Alchemie”, Paris, 1885
- Disproved the theory of Vitalism, the belief that organic compounds are infused with a unique force, not amenable to human interventions
- The beginning of the philosophy of reductionism in science
- The belief became prevalent that all problems can be solved by breaking them into parts



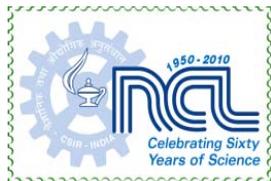
Collection des  
anciens  
alchimistes  
grecs... Avec  
la ...

Marcellin Berthelot,  
Ch.-Em Ruelle



## ***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



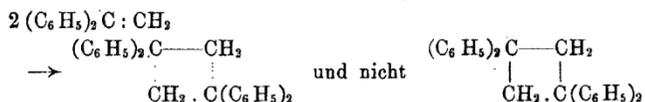
### 125. H. Staudinger: Über Polymerisation.

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

(Eingegangen am 13. März 1920.)

Vor einiger Zeit hat G. Schroeter<sup>1)</sup> 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<sup>2)</sup>; 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<sup>3)</sup>, 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:



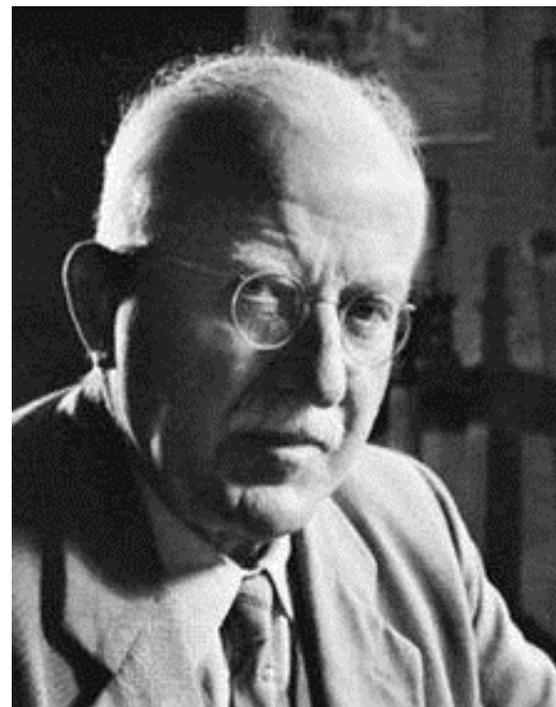
Solche Annahmen sind heute in der organischen Chemie sehr verlockend, nachdem eine große Anzahl gut charakterisierter Verbindungen, z. B. die Chinhydrone, nach den Untersuchungen von Pfeiffer<sup>4)</sup> als Molekülverbindungen, die durch Nebenvalenzen zusammengehalten werden, aufgefaßt werden. Und 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;

<sup>1)</sup> B. 49, 2697 [1916].

<sup>2)</sup> Vergl. H. Staudinger, Die Ketene, Verlag F. Enke, Stuttgart 1912, 46.

<sup>3)</sup> H. Hildebrand, Über die Polymerisation des *asymm.* Diphenyl-äthylens, Dissert., Straßburg 1909.

<sup>4)</sup> 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***

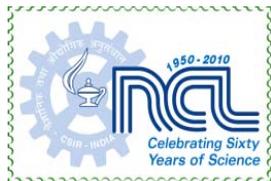
- He propounded the revolutionary concept, that macromolecules can be formed by linking of a large number of small molecules by means of covalent bonds
- Through sheer audacity of intuition and imagination, he proposed that polymers were composed of large number of base units linked together by covalent 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.



# 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)

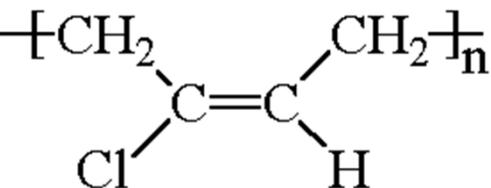


## **WALLACE CAROTHERS AND THE BIRTH OF RATIONAL POLYMER SYNTHESIS**



- 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



***Poly(chloroprene)***

- 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

# 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.

042,699. Specification of Letters Patent. Patented Dec. 7, 1909.  
No Drawing. Application filed July 12, 1907. Serial No. 283,884.

To all whom it may concern:

Be it known that I, LEO H. BAEKELAND, a citizen of the United States, residing at Sang Hook, 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.

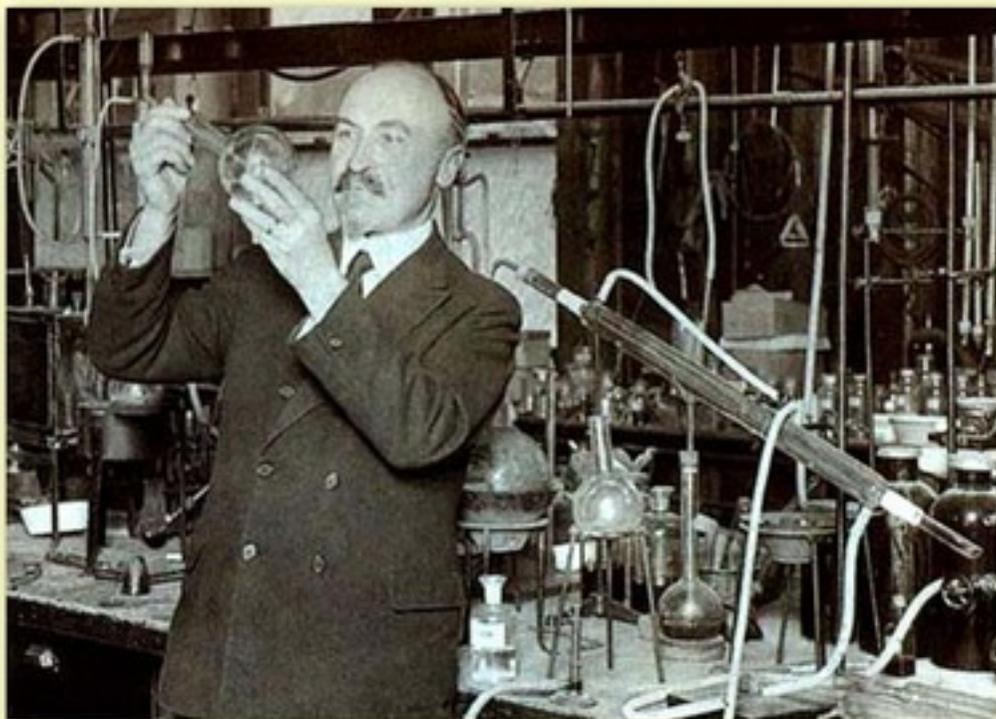
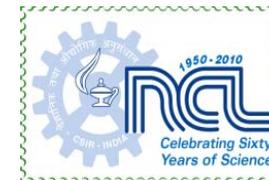
The present invention relates to the production of hard, insoluble and infusible condensation products of phenols and formaldehyde.

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 consistency. 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, alkalis 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 oxide, 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)***

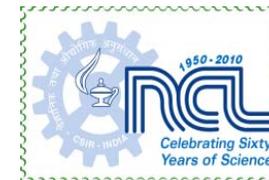
***When asked why he chose to work in the field of synthetic resins, he replied, "to make money"***



SCIENCEPHOTOLIBRARY



# PVC : REPLACEMENT FOR A RENEWABLE RESOURCE



**78 rpm  
Gramophone  
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



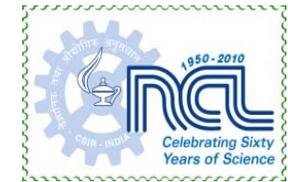


## **SCIENTIFIC FRONTIERS AND TECHNOLOGY FRONTS**

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

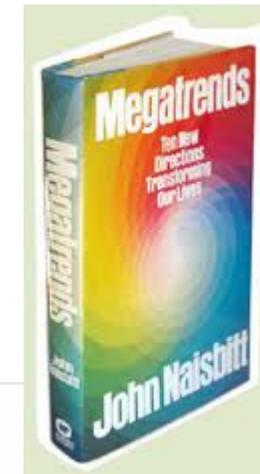
***New science can lead to technology; similarly emergence of technology can stimulate science***

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



# THE NEW BUZZWORD

## MEGATRENDS !



**Security**

- Hacking is free

**Religion**

- Expanding Impact

**Business**

- New competitors
- Coopition everywhere
- Peak everything

**Health**

- Longer life\*
- Healthier life\*
- Chronic is normal

**Work**

- Automation of "normal"
- Skills gap and need for reskilling
- Technology-enhanced employees

**Law**

- Relative stability

**Government & Society**

- Flattening world
- Pockets of instability

**Demographics**

- Older consumer

**Science & Technology**

- Bandwidth is distance
- Context is king

**Energy**

- Oil important, not king

**Economy**

- Water as currency

**Transportation**

- Security challenged
- Infrastructure impacted
- Tight economics

**Environment**

- Business measure
- Need to Know

**Education**

- Better educated\*
- Distance learning

**Food & Agriculture**

- Stable currently but linked to environment

# MEGATRENDS

\* Not all the world may participate

Click to **LOOK INSIDE!**

## SIX GLOBAL MEGA-TRENDS AND HOW TO MAKE THEM WORK FOR YOU

THIERRY MALLERET

kindle edition

1. Virtual experiences  
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](http://www.futuretrendsbook.com) and [www.nowandnext.com](http://www.nowandnext.com)

**PRINTING & PRINTED COPIES**  
High resolution digital files for this table and ready printed copies can be obtained from: [richard@nowandnext.com](mailto:richard@nowandnext.com)

**ACKNOWLEDGEMENTS**  
Thanks to Charlie @ Plum Creative

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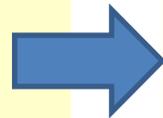
KEY				MEGATRENDS																														
S	T	E	E	Gd	Um	Cs	P	Lr	Ex	Mc	Am	Sv	I	Pm																				
Society	Technology	Energy	Environment	Globalisation & deregulation	Urbanisation & migration	Climate change & sustainability	Population & demographic growth	Localism & re-regulation	Extreme weather events	Expansion of global middle class	Resurgence of US manufacturing	Shared water creation	Focus on the self	Purpose & meaning																				
Economy	Employment	Population	Politics	Identity	Global risk	Global risk	High probability	Uncategorised	Po	B	A	Br	Se	Pt																				
									Population growth	Loss of biodiversity	Rise of Africa	Shift to the BRICs	Sense of entitlement	Move & part time working																				
H	Eg	Sr	Ir	Er	Cf	Na	Sb	Sw	Hg	Au	Ai	Uub	Db	Tc	Ga	Fa	Ac	C	Sc	N	Bh													
Hyper connectivity	Government	Scarcity of resources	Integrating resurgence	Erosion of trust	Clean fuels	Nano materials	Synthetic biology	Semantic web	Holographs & 3D web	Augmented & virtual worlds	Artificially intelligent devices	Ubiquitous sensors & tracking	Desert based solar	Technology convergence	3D printing	Open source discovery & invention	Ocean acidification	Carbon pricing	State capitalism	Normalisation of obesity	Back homeing of outsourcing													
V	Mg	Rb	Md	Ca	As	It	Nfc	Ha	D3	Os	Li	F	Ar	Te	Ce	In	Xe	Ne	No	Pd	Pg	Cd	Ra	Ge	Bq	Dm	Wr	Sn	Age	Sph	Es	Ag	Uuh	Ic
Volatility	Micro-grids & micro-generation	Robotics & smart objects	Personalised medicine	Contact zones computing	Autonomous systems & devices	Wearable things	Automation	Near-field communication	Haptic technology	3D printing	Urban living	Changing family sizes	Aquifer reduction	Tip soil erosion	Cosmetic enhancement	Intensifying competition	Xenophobia	Non-conventional reserves	Secularism	Predictive personalisation	Personal genomics	Personal clouds	Real-time data & analytics	Geosocial recognition	Battery life and energy storage	Dematerialisation	Wireless re-charging	Social networks	Population ageing	Single person households	Ethical shifts	Precision agriculture	Blurring of real & virtual worlds	Industry consolidation
Fr	Rn	Omg	He	Ci	Ti	Mo	S	Tm	Pr	LoL	U	Paw	Me	Atm	Fr	Rn	Omg	He	Ci	Ti	Mo	S	Tm	Pr	LoL	U	Paw	Me	Atm					
Population migrant & demographic policy	Resource reallocation	Resurgence of religion	Hedonism	Culture of immediacy	Total information transparency	Mobility & portability	Sharing	Too much information	Provenance	Search for happiness	Fragmented attention	Individualism	Atomisation	Fr	Rn	Omg	He	Ci	Ti	Mo	S	Tm	Pr	LoL	U	Paw	Me	Atm						
Re	Bt	Eu	Op	Np	Sws	Fp	Fi	Gp	Cw	Ua	Si	Rc	Mq	Re	Bt	Eu	Op	Np	Sws	Fp	Fi	Gp	Cw	Ua	Si	Rc	Mq							
Regulatory change	Biological terrorism	European concentration	Oil price spikes	Nationism & protectionism	Skilled worker shortages	Food price volatility	Fiscal imbalances	Global pandemic	Cyber viruses and data theft	Unwired access to food & water	Severe income inequality	Dogma employee	Mega-trends in megacity	Re	Bt	Eu	Op	Np	Sws	Fp	Fi	Gp	Cw	Ua	Si	Rc	Mq							
Gg	Nt	Ed	Up	Mm	Kr	Csf	Ws	Pk	Pi	Cn	Oa	Cc	Vol	Gg	Nt	Ed	Up	Mm	Kr	Csf	Ws	Pk	Pi	Cn	Oa	Cc	Vol							
Global governance failure	Nuclear terrorism	European disintegration	Overstated population growth	Empty managed migration	Explosion of North Korea	Critical systems failure	Collapse of welfare state	Collapse of Pakistan	Palatium vs. Iraq war	Collapses of China	Failure to treat obesity epidemic	Failure to adapt to climate change	Summertime amplification	Gg	Nt	Ed	Up	Mm	Kr	Csf	Ws	Pk	Pi	Cn	Oa	Cc	Vol							
Gg	Nt	Ed	Up	Mm	Kr	Csf	Ws	Pk	Pi	Cn	Oa	Cc	Vol	Gg	Nt	Ed	Up	Mm	Kr	Csf	Ws	Pk	Pi	Cn	Oa	Cc	Vol							
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High probability  
Low probability  
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

*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

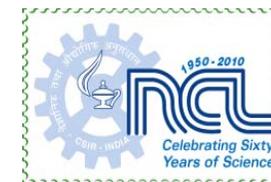
***Polymers are a post war industry, fuelled by the availability of inexpensive hydrocarbon resources; industry grew from zero to present capacities in about fifty years***

## **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 19<sup>th</sup> 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

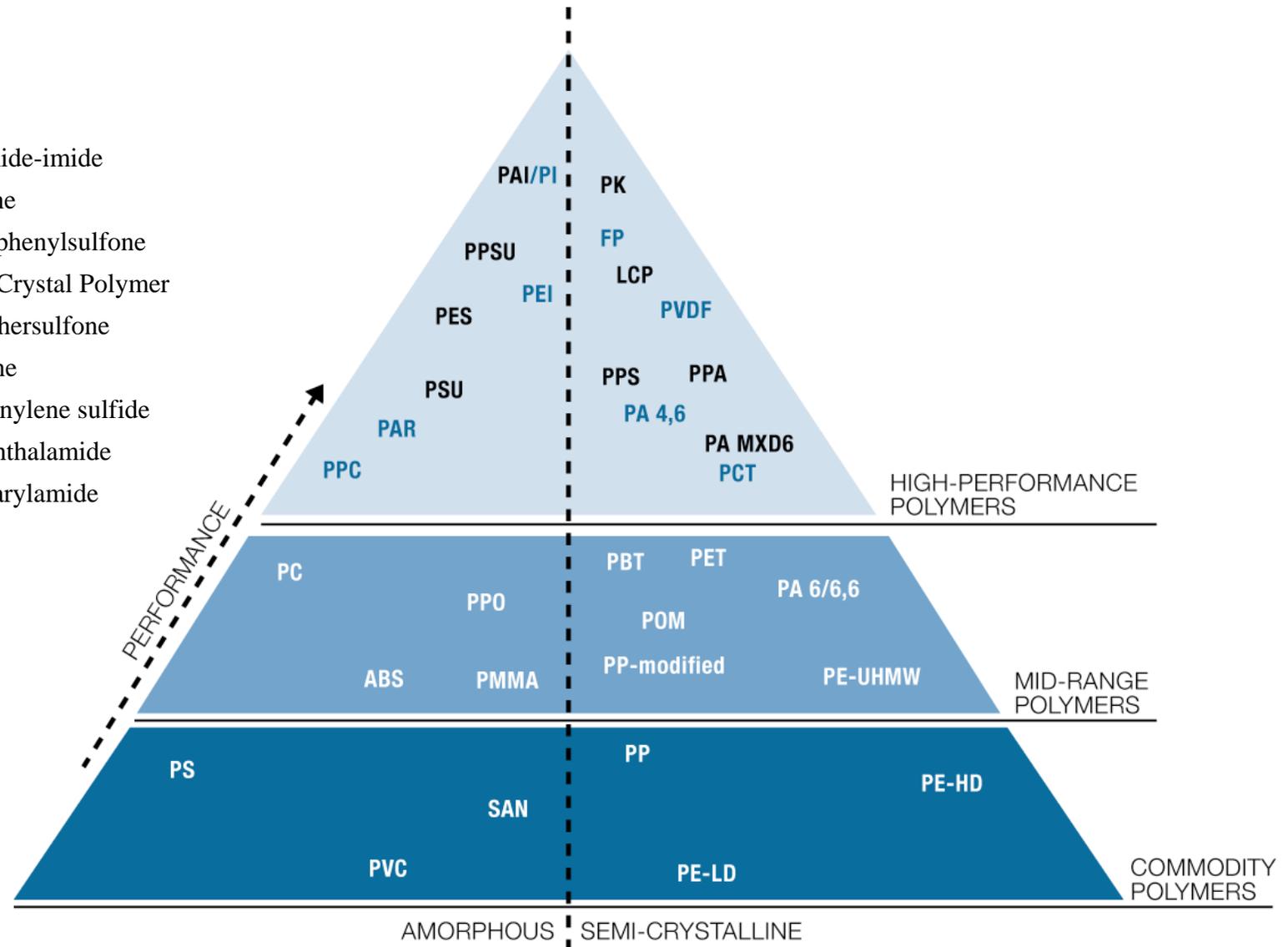


### Hi Tech Plastics



# THE POLYMER PYRAMID

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



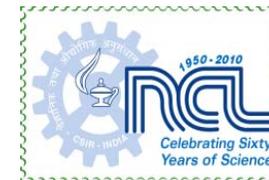


## ***FROM CONCEPT TO MARKET PLACE***

---

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

## ***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**

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



## ***TRENDS IN THE GLOBAL POLYMER INDUSTRY***

- Customers demand more variety and content
- Environment and safety regulations will be the key driver of change
- Products have shorter life cycles
- Competition is unrelenting
- Market pressures restrict price increases
- Margins are progressively squeezed

***To revive margins, innovation is necessary***



## ***TECHNOLOGY EXPLOSION***

- Ninety percent of everything we know in sciences has been generated since 1950 – will double in the next 15 years
- 90% of all scientists and engineers who ever lived are living now
- No single company can have all the resources nor be a master of all skills
- Need to leverage effectively the technology infrastructure as well as the National Innovation Systems



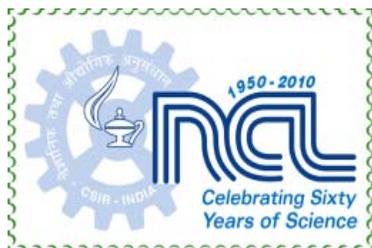
## ***INNOVATE OR EVAPORATE***

- Period of massive change including discontinuities
- Demise of nation-state system
- Capital and information flow @ speed of light
- Basic reality – every industry will restructure from now on – so management of continuous change
- Rapid obsolescence of physical assets
- Ownership of knowledge assets is increasingly critical



## ***BARRIERS TO INNOVATION***

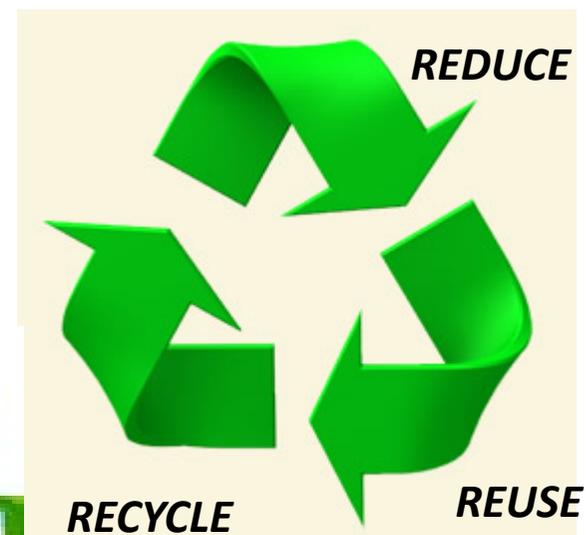
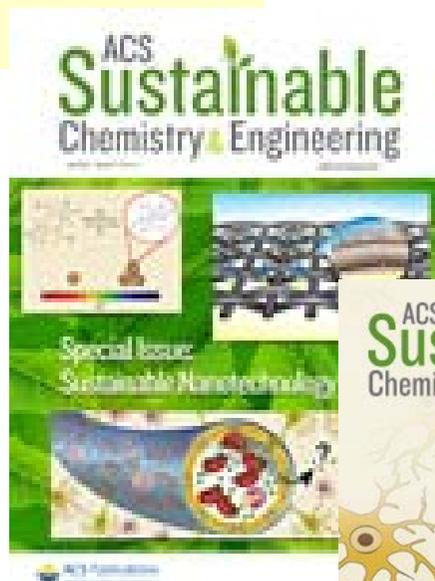
- Ability to meet stiff economic challenges
- Access to capital to demonstrate technologies and manufacturing
- Time to market getting longer
- Too little emphasis by industry on “Game-changer technologies” or “breakthrough innovations”; Too much emphasis on customer led incremental developments
- Inefficient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



## **ORGANIC POLYMERS SUSTAINABILITY ISSUES**

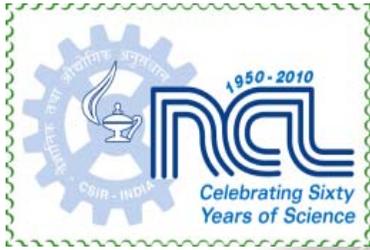
- **Exclusive dependence on fossil fuel based resources**
- **Generation of wastes that need disposal**

***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?***





***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***

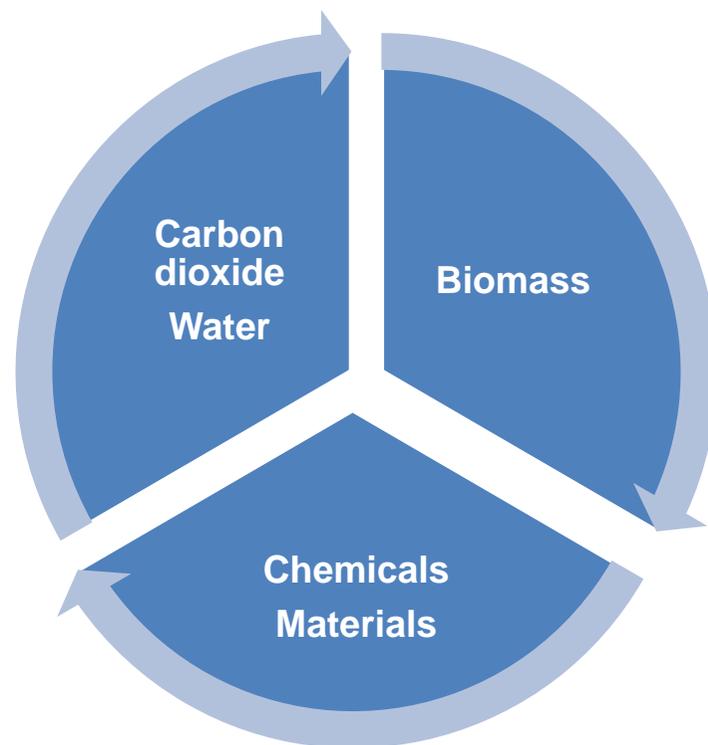
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Nature designs material with great care and attention to details

- Economy in the use of raw materials
- Minimum use of energy
- Easy to recycle under ambient conditions

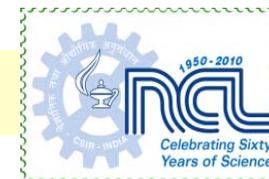
***Nature achieves this sophistication through highly organized fabrication methods and hierarchies of structural features***

## **FROM HYDROCARBONS TO CARBOHYDRATES : FROM NON RENEWABLES TO RENEWABLES**



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

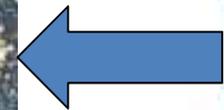
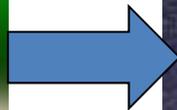
***Is such a virtuous cycle just a dream ?***



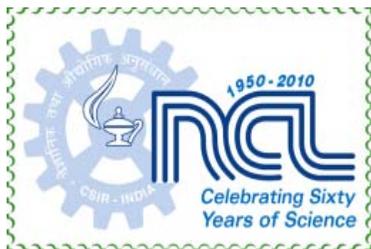
# ***POLY(LACTIC ACID)S : AN ALIPHATIC POLYESTERS FROM A SIMPLE AB MONOMER***



- 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<sub>2</sub> emitted per kg of PLLA produced versus 3.4 kg of CO<sub>2</sub> per kg of PET



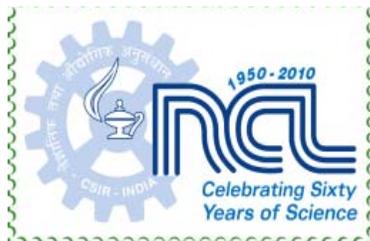
***IF PLLA IS SO ATTRACTIVE FROM A SUSTAINABILITY POINT OF VIEW, WHY IS IT STILL NOT A PART OF OUR EVERY DAY LIFE ?***



## **“DROP- IN” BIOPOLYMERS : DOES IT MAKE SENSE ?**

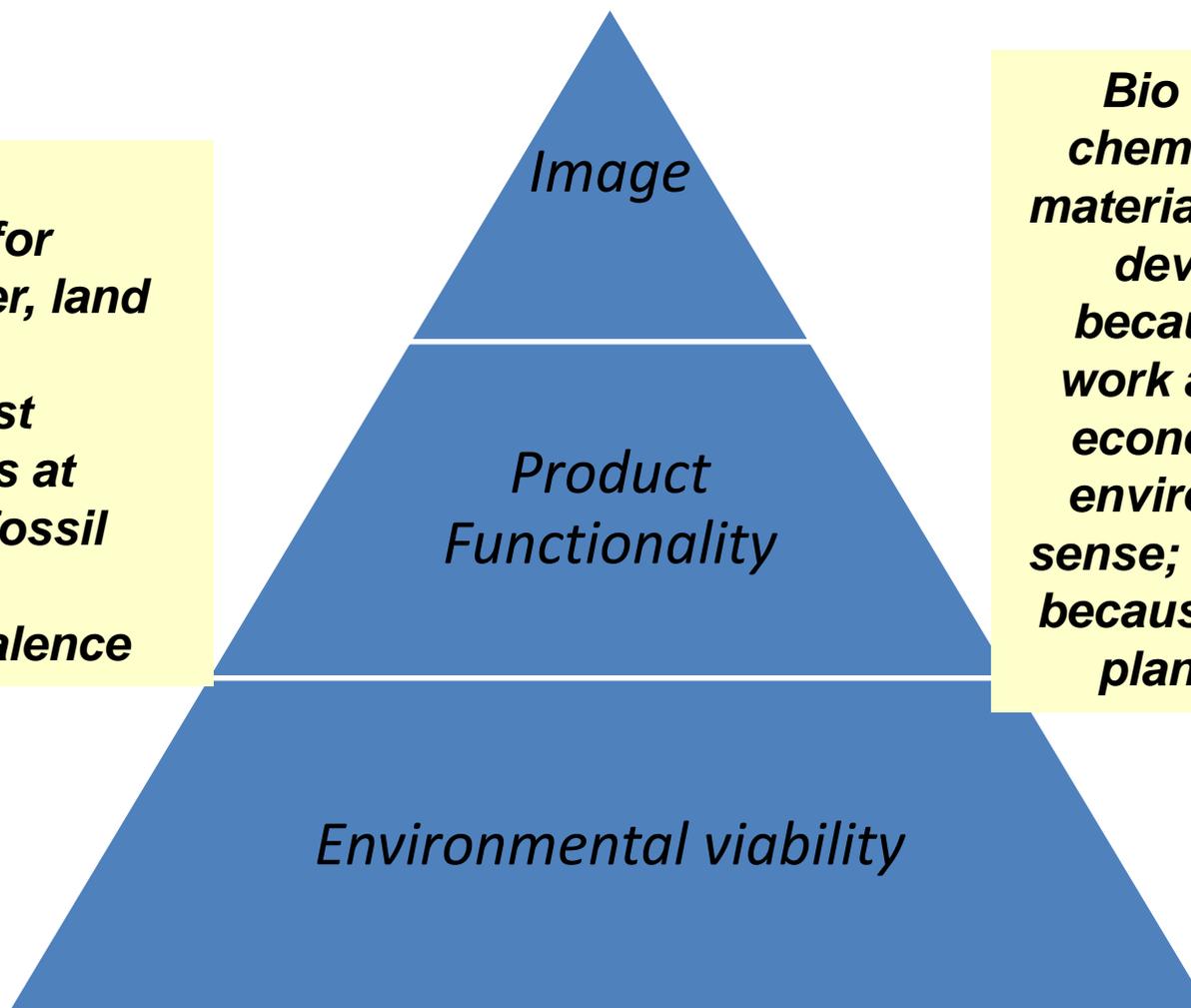
- Bio PE, Bio PP, Bio PET, Bio PVC , Bio Butyl, Bio butadiene !
- All monomers derived from sugar ethanol
- Apart from competition from food large scale fermentation processes are not carbon neutral; every Kg of ethanol by fermentation results in 1 Kg of carbon dioxide
- Poor atom efficiency; starch 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***



## **THE BIOVALUE PYRAMID**

- **CO<sub>2</sub> 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.)

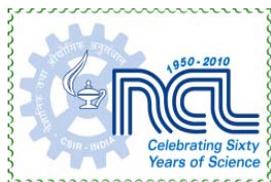


## ***FUTURE OF POLYMER SCIENCE***

- Systems, not molecules
- Functions, not molecular structure

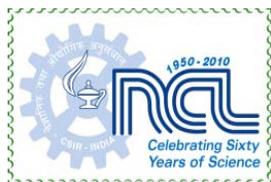
***No longer “What is it?” but “What does it do?”***

*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***

<b>January 1990</b>	<b>January 2000</b>	<b>November 12, 2013</b>
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

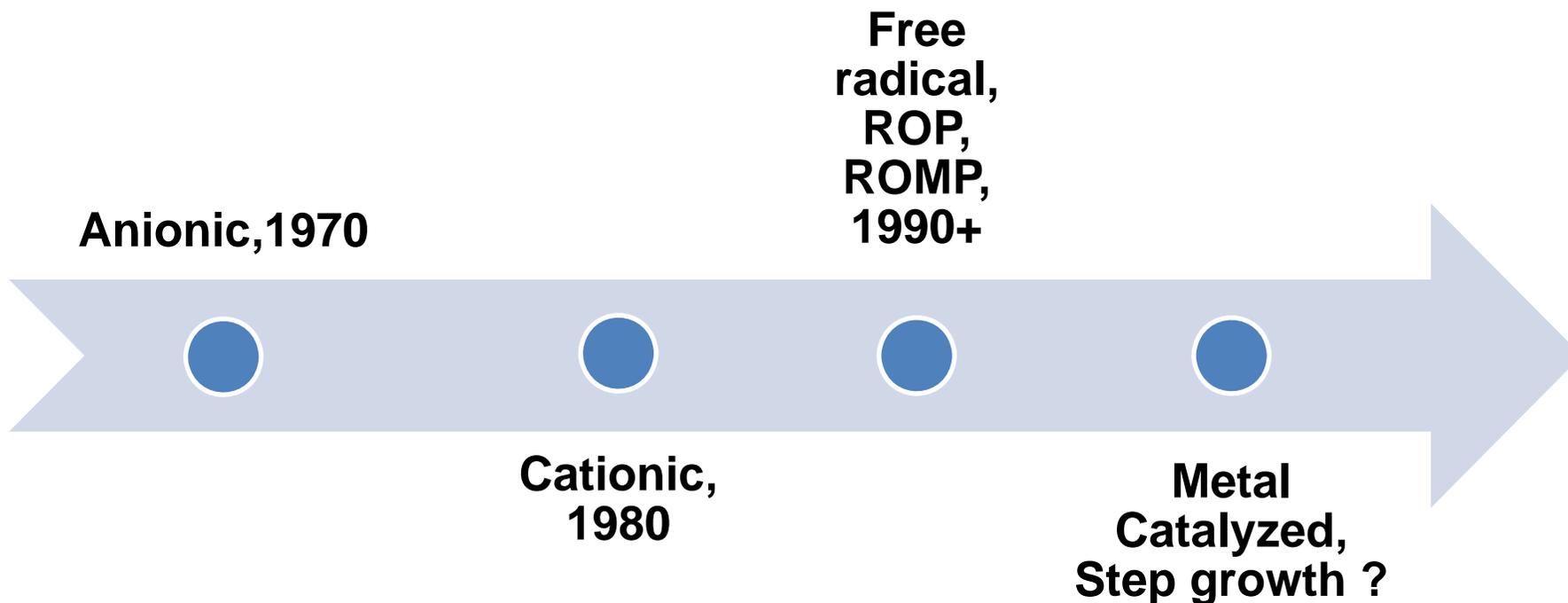


## ***EVOLUTION OF RESEARCH TOPIC IN POLYMER SCIENCE, 1990-2013***

January 1990	January 2000	November 12, 2013
<p>Mean square radius of gyration and hydrodynamic radii Theta temperature Phase separation, thermodynamics and diffusivity in miscible blends</p>	<p>Second virial coefficient in miktoarm star polymers Order disorder transitions in diblock copolymers Morphology of stereoblock PP</p>	<p>Thermal, mechanical, solvent, photo-responsive soft matter Transport, thermal, phase and solution properties of brush, ring, networks and entangled polymers</p>
<p>Chiral polymers Conformation in glasses and gels Light induced phase transitions</p>	<p>Band gap modifications in polymers</p>	<p>Molecular dynamics, DFT and simulations Nano-templating and patterning Polymer thin films Polymer electrolytes</p>



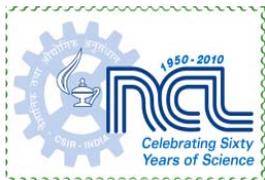
## **ARE THERE STILL OPPORTUNITIES IN POLYMER SYNTHESIS ?**



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

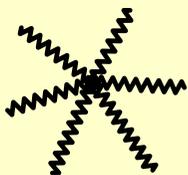


# STRUCTURES ACCESSIBLE VIA TECHNIQUES OF CONTROLLED POLYMER SYNTHESIS

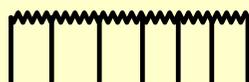
## Topology



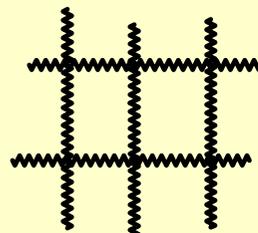
Linear



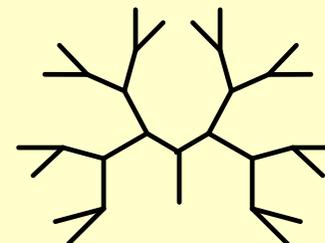
Star /  
Multi-Armed



Comb Polymers



Networks



(Hyper) Branched

## Composition



HomoPolymers



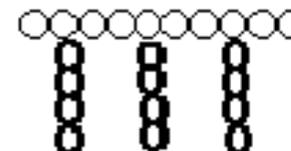
Block  
Copolymers



Statistical  
Copolymers



Tapered / Gradient  
Copolymers



Graft

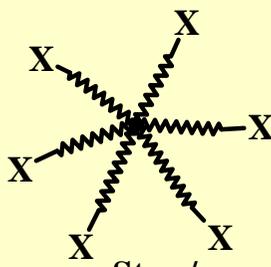
## Functionality



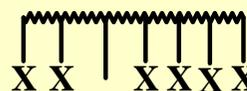
Homo / Hetero  
Telechelic



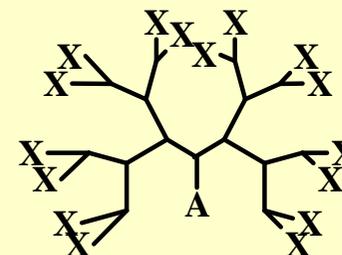
Macromonomers



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 absolutely uniform length for a wide range of polymers**



## **CHAIN SEQUENCE**

*Determines .....*

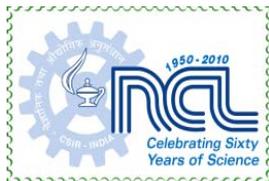
- Thermal behavior
- Crystalline properties

*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***



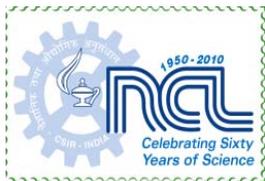
# COMPLEX POLYMER SYSTEMS

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  $T_g$  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**

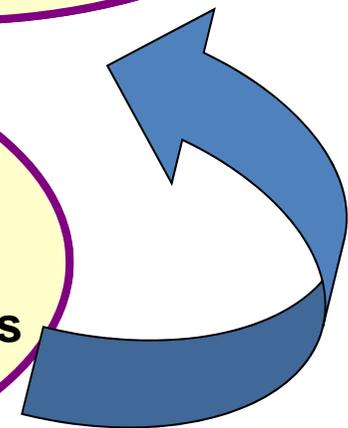
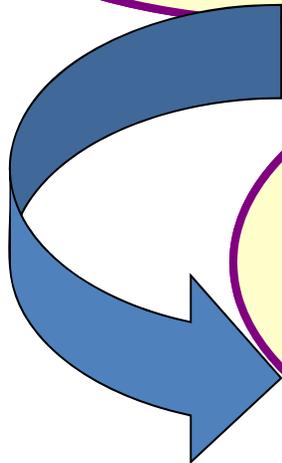
- Shear
- wetting
- Orientation

## **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

**PAUL FLORY AND BASIC RESEARCH**  
**( C&EN, February 28, 1977)**

*“ Significant inventions are not mere accidents. This is an erroneous view . Happenstance usually plays a part, but there is much more to invention than the popular notion of a bolt out of the blue. Knowledge in depth and breadth are virtual prerequisites. Unless the mind is thoroughly charged before hand, the proverbial spark of genius, if it should manifest itself, probably will find nothing to ignite..... Creative invention without a firm grasp of underlying principles becomes increasingly rare..... This asertion contradicts the prevalent view that measure of practical value of basic research lies in its success in uncovering nuggets of truth that can be commercialized..... I am convinced that basic research has a more pervasive mission in advancing knowledge, in providing incicisve concepts an in sharpening insights. These are the ingredients that nurture enduring innovations of the broadest scope..... Basic research must not be treated as an dispensible adjunct whose cultivation can be postponed at the pleasure of the profit margin ”*

Goethe once said about science: "To one man it is the highest thing, a goddess; to another it is a productive cow who supplies them with butter. We must honor the goddess and feed the cow."

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***THANK YOU***

