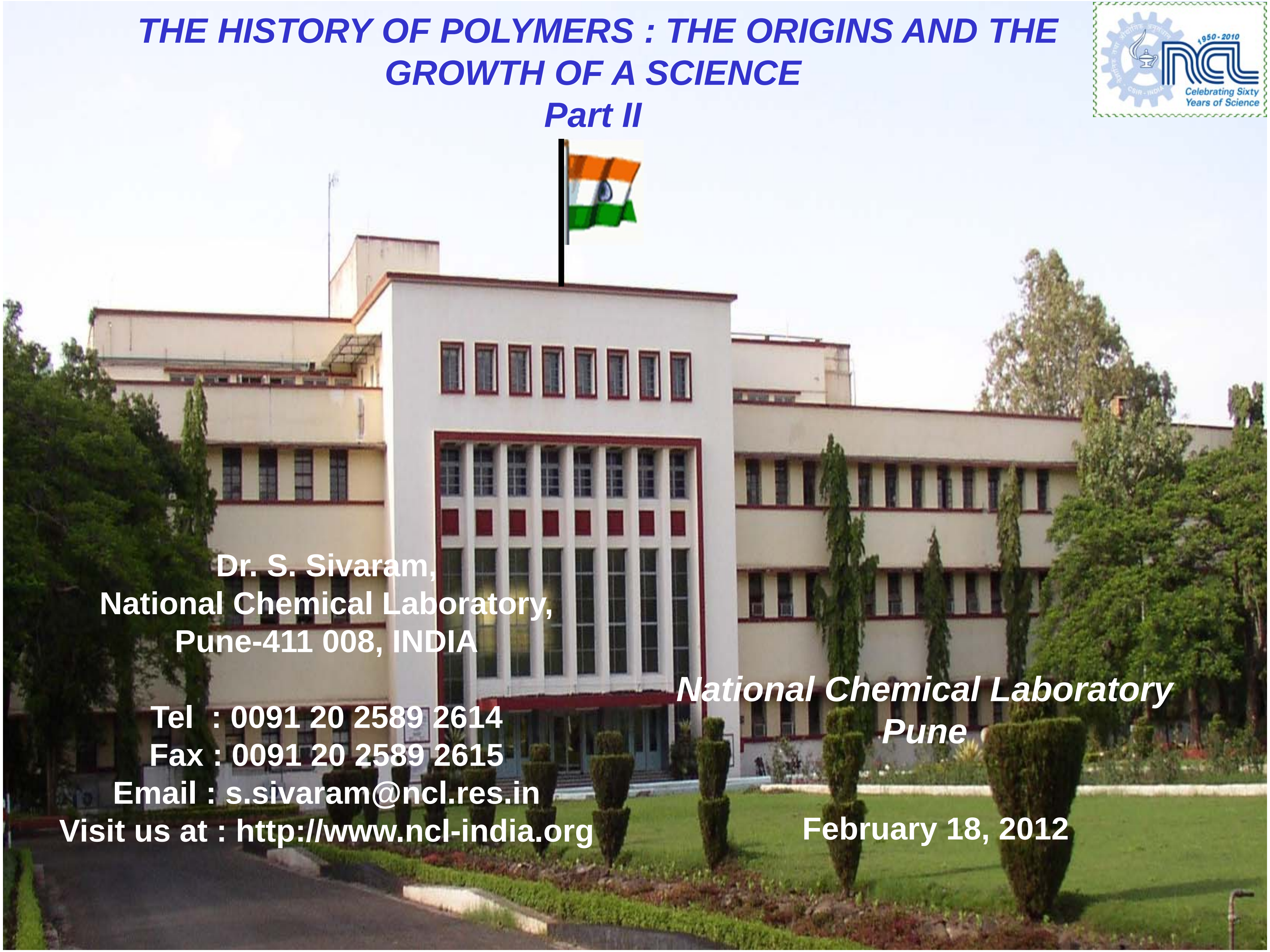
THE HISTORY OF POLYMERS : THE ORIGINS AND THE GROWTH OF A SCIENCE

Part II



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February 18, 2012

WALLACE CAROTHERS AND THE BIRTH OF RATIONAL POLYMER SYNTHESIS

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

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

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

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

His daughter, Jane, was born seven months later on November 27, 1937.

?

A young man joins Carothers at DuPont in 1934 who will go on to make history

SUMMARY OF LECTURE : PART I

- **The tale of two Hermanns : Staudinger and Mark**
- **The link between Mark and Pauling: the “Nature of the Chemical Bond” and the origins of the structural chemistry**
- **Wallace Carothers and the birth of rational polymer synthesis: realization that large macromolecules can be derived using the same laws of chemistry that define small molecules**
- **Paul Flory and the dawn of the physical chemistry of polymers**

Polymers were considered largely an empirical, instinctive and intuitive discipline till the mid twenties. Carothers and Flory changed this perception

NEW TO THE WORLD POLYMERS : THE GOLDEN ERA IN POLYMER SCIENCE

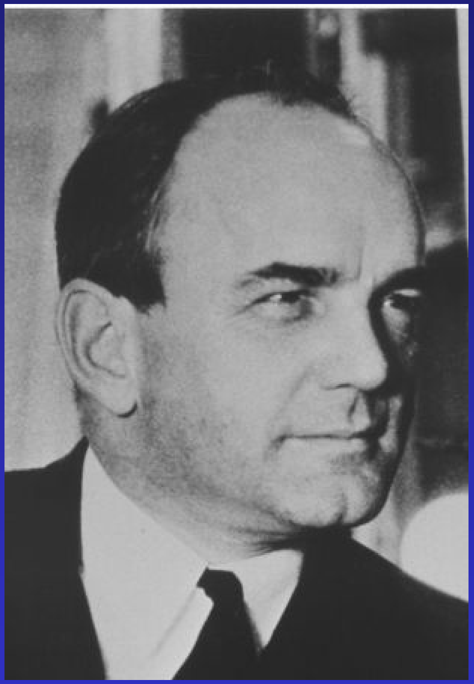
- **PVC (1927) : Replaces natural rubber as cable insulation/ sheathing**
- **Polystyrene (1930) : First commercial production by IG Farben**
- **Neoprene, Poly(chloroprene (1931) : The first man made elastomer**
- **LDPE (1935) : radar, telecommunication cables**
- **PMMA (1936) : Canopies and cockpit 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**

POLYMER SCIENCE : THREE PHASES OF EVOLUTION

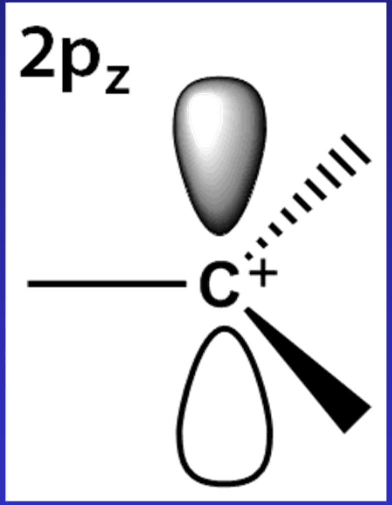
- Post Industrial Revolution (1760-1900)
- World War I and II (1900-1950)
- The Era of Inexpensive Petroleum (1950- 2000)

- 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)

CHEMICAL TRANSFORMATION OF HYDROCARBONS: THE CENTRAL ROLE OF CARBOCATIONS



Frank Whitmore (1887-1947)



- **First to propose the intermediacy of carbocations in hydrocarbon (olefin and paraffin) reactions under acidic conditions**

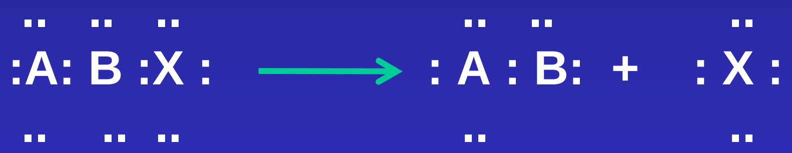
- **Seminal paper on intramolecular rearrangements involving the intermediacy of carbocations published in *J.Amer. Chem. Soc.,54, 3274-3283 (1932)***

- **Author of the first advanced book titled *Organic Chemistry, D. Van Nostrand & Co, 1937, 1090 pages***

Frank Whitmore in J.Amer.Chem.Soc., August 5, 1932

Mechanism of Intra-molecular Rearrangements

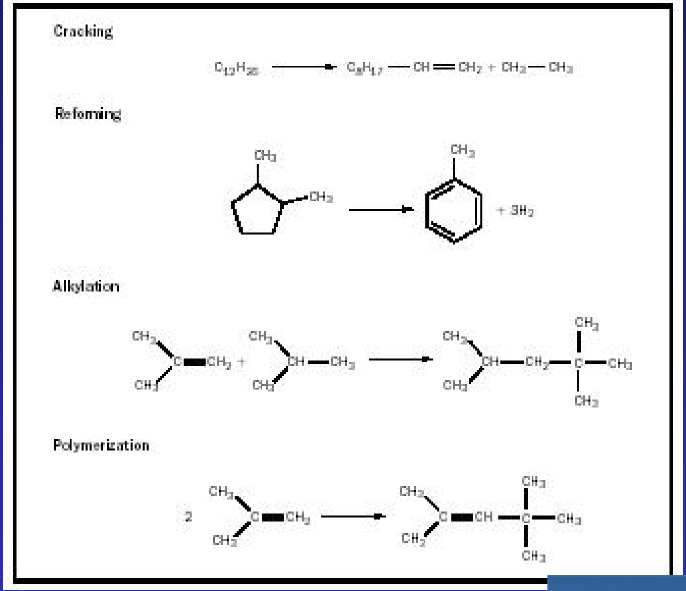
“When a molecule containing system A is brought into a reaction which results in the removal of X from its attachment to B, then, regardless of the mechanism of the process, X keeps a complete octet of electrons and leaves with only a sextet of electron”.



$$:\overset{..}{\underset{..}{A}}:\overset{..}{\underset{..}{B}}:\overset{..}{\underset{..}{X}}: \longrightarrow :\overset{..}{\underset{..}{A}}:\overset{..}{B}: + :\overset{..}{\underset{..}{X}}:$$

Later he was to write; "In the case of such a carbonium ion the plus sign indicates the shortage of a pair of electrons below that needed for a complete octet. It must be emphasized that because of this unstable structure the carbonium ion has no existence like that of other onium ions”

CHEMICAL TRANSFORMATION OF HYDROCARBONS: CATALYTIC REFORMING AND THE DAWN OF THE PETROLEUM REFINING



Cracking of hydrocarbons to olefins and dienes and reforming of cycloaliphatics to aromatics could be accomplished over Lewis and Bronsted Acids as catalysts

Vladimir Ipatieff (1867-1952)

Post WW II petroleum became the provider of building blocks for the chemical industry

BUILDING BLOCKS FOR CHEMICAL INDUSTRY

- **Olefins : Ethylene, Propylene**
- **Higher α-olefins : Butene-1, Hexene-1, Octene-1, …. Octadecene-1**
- **Other olefins : 4-Methyl pentene-1**
- **Cyclic olefins : Cyclopentene, Norbornene, Ethylidene norbornene**
- **Ninety five per cent of the organic chemical industry is derived from ten feed-stocks, namely, methane, ethylene, propylene, C-4 olefins, C-5 olefins, butadiene, benzene, toluene and xylene**
- **Feed-stocks (~10)** → **Basic building blocks (~50)** → **Intermediates (~500)** → **Chemical** products (~70,000)

ARTHUR LAPWORTH (1872-1941)
THE GENESIS OF REACTION MECHANISM IN ORGANIC CHEMISTRY

- **Interpretation of reaction mechanism on the basis of ions**
- **"It is to electrolytic dissociation that the majority of changes in organic compounds may be most probably assigned" (J.Chem.Soc., <u>79</u> 1266 (1901)**
- **Remember JJ Thomson's proposal that chemical bonds are formed by a transfer of a single electron from one atom to another was two years away and theories of G.N. Lewis and Langmuir were fifteen years away.**
- **Elucidated the mechanism of reaction of acetone with HCN and established the intermediacy of the cyanohydrin in 1903, the first approach to understand the mechanism of organic reactions.**
- **Classification of reagents according to charge – anionoid and cationoid, later named as nucleophilic and electrophilic (Nature, <u>115</u> 625 (1925)**
- **Theory of alternating polarities (1920)**

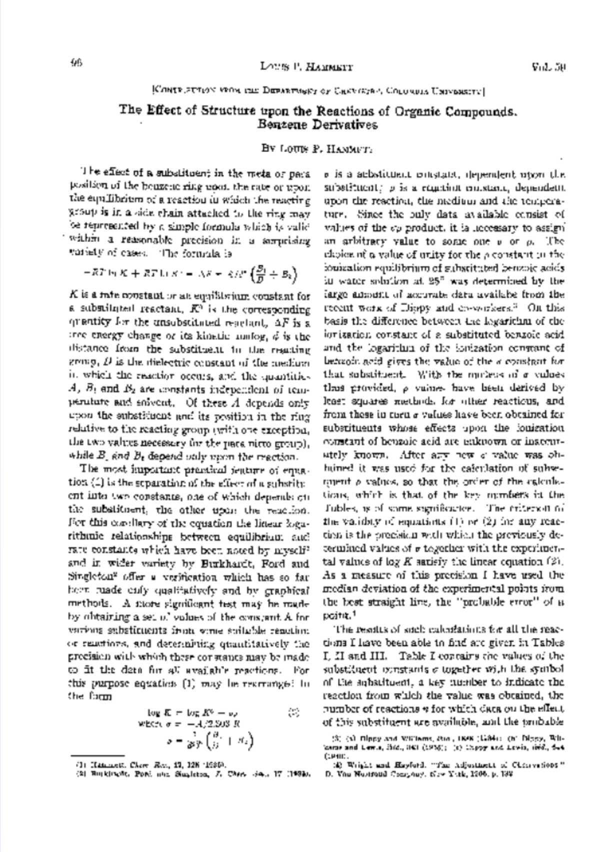
THE WEDDING OF PHYSICAL AND ORGANIC CHEMISTRY : LIFE AND TIMES OF JB CONANT

J.B.Conant (1893-1978) President, Harvard University, 1933- 1953

- **Conant presented a dual thesis to H(1916) with Professor Theodore Richards in electrochemistry and with Professor E.P. Kohler in cyclopropane chemistry**
- **Conant began his research by applying principles of electrochemistry to organic compounds**
- **He predicted the intermediacy of free radicals in organic chemical reaction; e.g., electrochemical coupling of benzophenone to pinacols**
- **He hypothesized that "ability of C-C bond (to form carbon radicals) is to a large extent a function of the branching of the carbon chain"**
- **Conant reported the first example of a radical induced polymerization process (*JACS 52, 1659 (1930); 54, 628 (1932*)**

One of the most influential chemists of his times, Conant's academic career came to an end when he became the President of Harvard in 1933

- **Physical organic chemistry – A term coined by L.P. Hammett and the originator of the chemical sub discipline**
- **Explored relationship between structure and reactivity in organic molecules using tools of physical chemistry (kinetics, thermodynamics and equilibria)**
- **Wrote the definitive book, "Physical Organic Chemistry", 1940, considered as one of the greatest text books of all times, ranked with "Thermodynamics" by Lewis and Randall (1923) and "General Biochemistry" Fruton and Simmonds (1953)**
- **Generation of chemists grew up learning from Hammett's book**
- **The Hammett Equation and The Hammett acidity function (Ho)**
- **Clear formulation of "Transition state model" based on theories of Eyring – Polanyi on rate process**



96 Louis P. Hammett Vol. 59

[Contribution from the Department of Chemistry, Columbia University]

The Effect of Structure upon the Reactions of Organic Compounds. Benzene Derivatives

By Louis P. Hammett

The effect of a substituent in the meta or para position of the benzene ring upon the rate or upon the equilibrium of a reaction in which the reacting group is in a side chain attached to the ring may be represented by a simple formula which is valid within a reasonable precision in a surprising variety of cases. The formula is

$$-RT \ln K + RT \ln K^0 = \Delta F = A/d^2 \left(\frac{B_1}{D} + B_2\right)$$

K is a rate constant or an equilibrium constant for a substituted reactant, K^0 is the corresponding quantity for the unsubstituted reactant, ΔF is a free energy change or its kinetic analog, d is the distance from the substituent to the reacting group, D is the dielectric constant of the medium in which the reaction occurs, and the quantities A, B_1 and B_2 are constants independent of temperature and solvent. Of these A depends only upon the substituent and its position in the ring relative to the reacting group (with one exception, the two values necessary for the para nitro group), while B_1 and B_2 depend only upon the reaction.

The most important practical feature of equation (1) is the separation of the effect of a substituent into two constants, one of which depends on the substituent, the other upon the reaction. For this corollary of the equation the linear logarithmic relationships between equilibrium and rate constants which have been noted by myself[1] and in wider variety by Burkhardt, Ford and Singleton[2] offer a verification which has so far been made only qualitatively and by graphical methods. A more significant test may be made by obtaining a set of values of the constant A for various substituents from some suitable reaction or reactions, and determining quantitatively the precision with which these constants may be made to fit the data for all available reactions. For this purpose equation (1) may be rearranged to the form

$$\log K = \log K^0 + \sigma\rho \quad (2)$$
$$\text{where } \sigma = -A/2.303\,R$$
$$\rho = \frac{1}{d^2 T}\left(\frac{B_1}{D} + B_2\right)$$

σ is a substituent constant, dependent upon the substituent; ρ is a reaction constant, dependent upon the reaction, the medium and the temperature. Since the only data available consist of values of the $\sigma\rho$ product, it is necessary to assign an arbitrary value to some one σ or ρ. The choice of a value of unity for the ρ constant in the ionization equilibrium of substituted benzoic acids in water solution at 25° was determined by the large amount of accurate data available from the recent work of Dippy and co-workers.[3] On this basis the difference between the logarithm of the ionization constant of a substituted benzoic acid and the logarithm of the ionization constant of benzoic acid gives the value of the σ constant for that substituent. With the nucleus of σ values thus provided, ρ values have been derived by least squares methods for other reactions, and from these in turn σ values have been obtained for substituents whose effects upon the ionization constant of benzoic acid are unknown or inaccurately known. After any new σ value was obtained it was used for the calculation of subsequent ρ values, so that the order of the calculations, which is that of the key numbers in the Tables, is of some significance. The criterion of the validity of equations (1) or (2) for any reaction is the precision with which the previously determined values of σ together with the experimental values of log K satisfy the linear equation (2). As a measure of this precision I have used the median deviation of the experimental points from the best straight line, the "probable error" of a point.[4]

The results of such calculations for all the reactions I have been able to find are given in Tables I, II and III. Table I contains the values of the substituent constants σ together with the symbol of the substituent, a key number to indicate the reaction from which the value was obtained, the number of reactions n for which data on the effect of this substituent are available, and the probable

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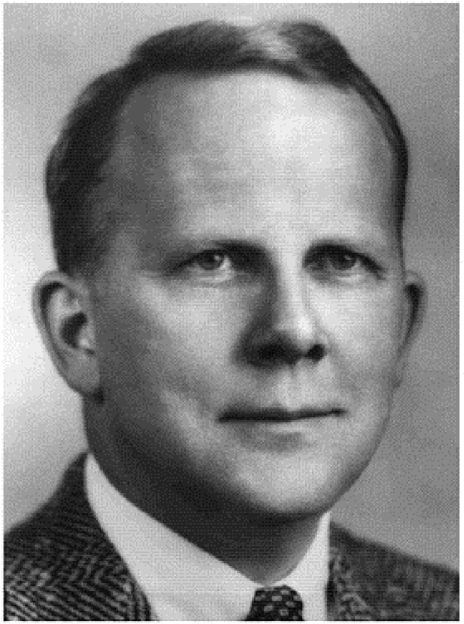
(1) Hammett, Chem. Rev., 17, 125 (1935).

(2) Burkhardt, Ford and Singleton, J. Chem. Soc., 17 (1936).

(3) (a) Dippy and Williams, ibid., 1888 (1934); (b) Dippy, Williams and Lewis, ibid., 343 (1935); (c) Dippy and Lewis, ibid., 644 (1936).

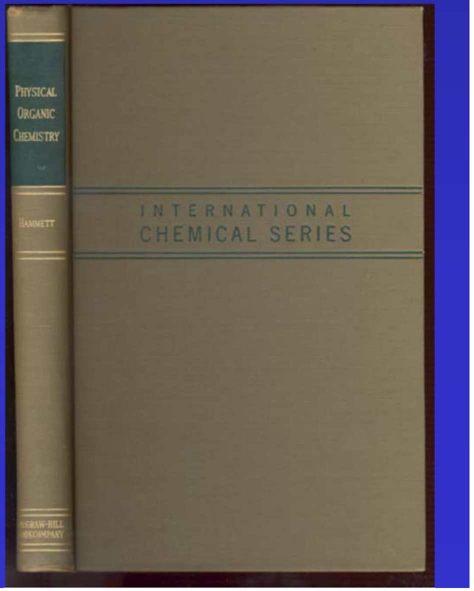
(4) Wright and Hayford, "The Adjustment of Observations," D. Van Nostrand Company, New York, 1906, p. 134.

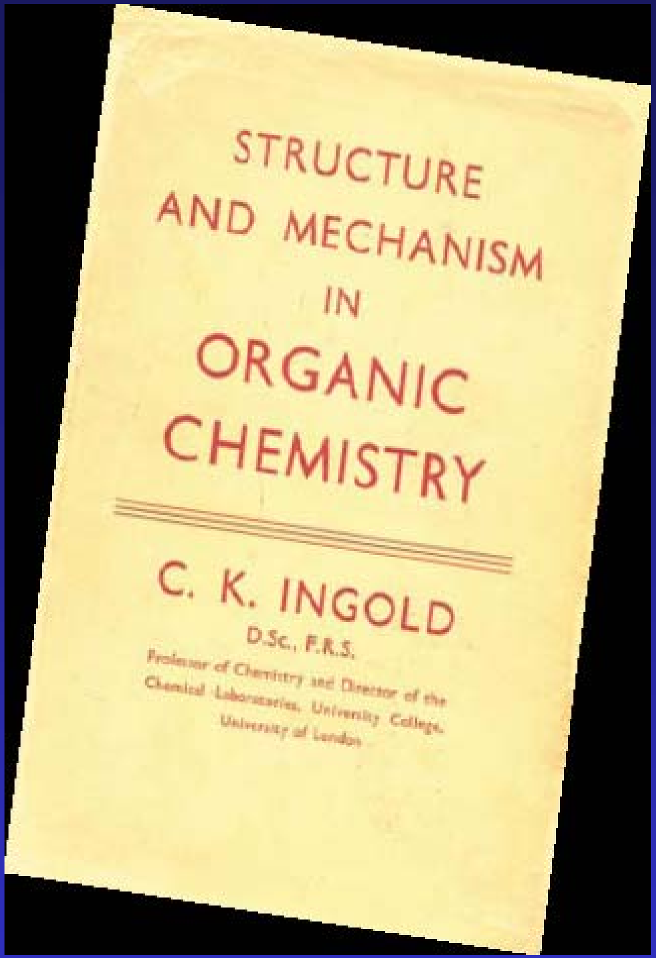
The Effect of Structure upon the Reactions of Organic Compounds. Benzene Derivatives
by Louis P. Hammett
J. Amer.Chem.Soc., 59, 96 (1935)



Louis P Hammett

1894-1987





STRUCTURE
AND MECHANISM
IN
ORGANIC
CHEMISTRY

C. K. INGOLD
D.Sc., F.R.S.
Professor of Chemistry and Director of the
Chemical Laboratories, University College,
University of London

Seminal contributions to the mechanism of aromatic substitution, nucleophilic / electrophilic substitution and elimination reactions and application of electronic theory to organic reactions

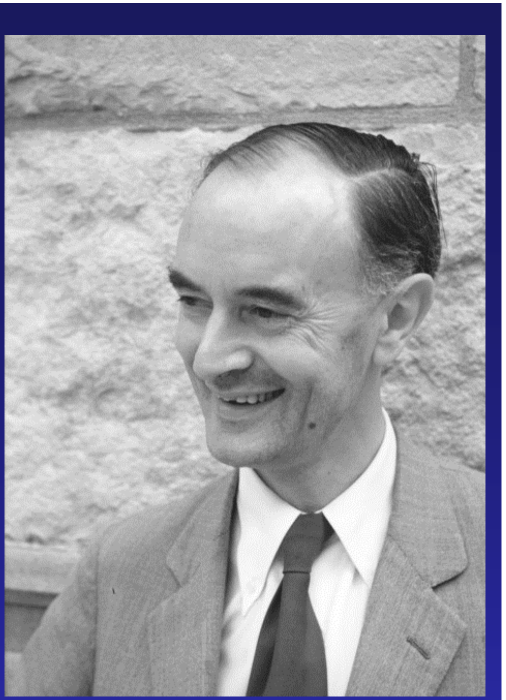
SN1, SN2, E1, E2 mechanisms; connecting kinetic order to the reaction mechanism

A uniquely gifted chemist with unusual power of insight and deduction

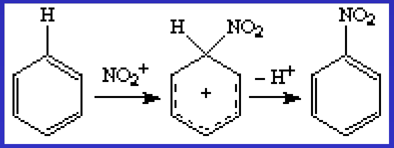
Role of steric and electronic factors in determining the reactivity of organic compounds

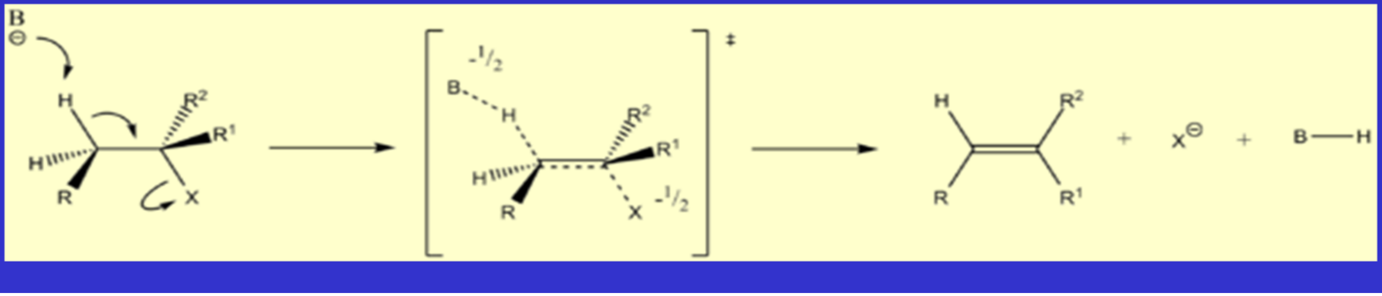
Directive effects in aromatic substitution

Kinetics of organic reactions and isotope effects to probe mechanisms



Sir Christopher Ingold (1893-1970)





NUCLEOPHILIC SUBSTITUTION :UNIMOLECULAR AND BIMOLECULAR

A PERSONAL CONNECTION

This mechanistic distinction has an important bearing on the stereochemistry of the substitution. In two series of papers, Ingold and Hughes established that the SN2 reaction, where a nucleophile attacks and a leaving group departs simultaneously always inverts the three dimensional arrangement of atoms neighbouring the reaction centre – rather like an umbrella turning inside out.

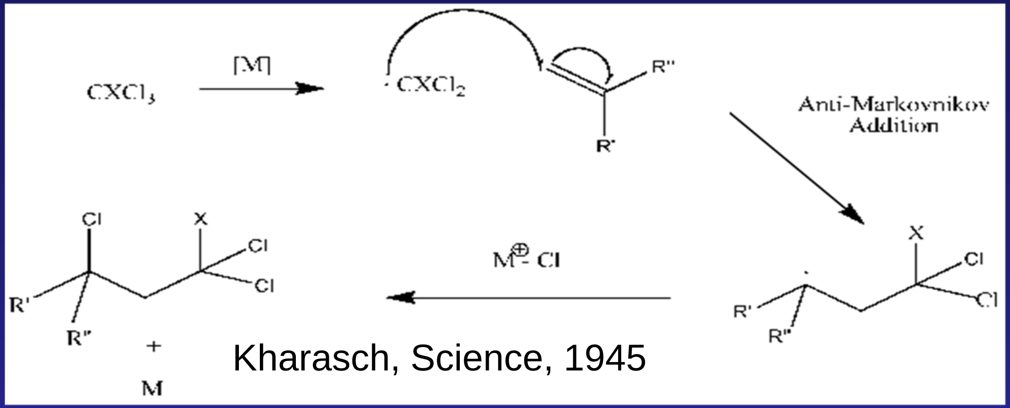
The SN1 reaction, however, can either invert or retain the starting arrangement, since the planar carbocation can be attacked by the nucleophile on either side. The attack on the two sides may not occur to an equal extent because of partial screening by the leaving group. This relationship of the stereochemistry to the detailed mechanism provided an explanation of a long-standing problem in organic chemistry called the Walden inversion – where if a particular substitution reaction was attempted using different conditions, it could be made to either retain or invert stereochemistry

FREE RADICAL CHEMISTRY : ORIGNS AND DEVELOPMENT

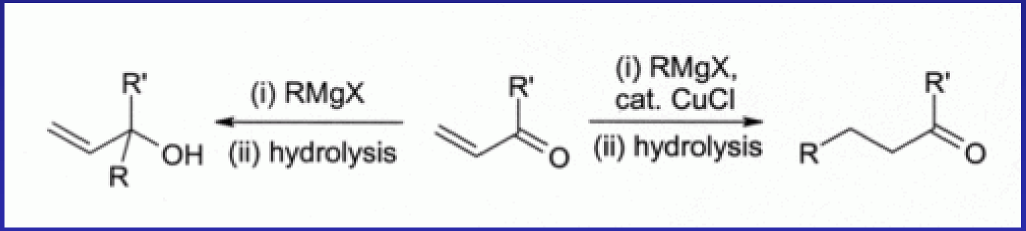
- “The Aliphatic Free Radicals”, F.O Rice and K.K. Rice, 1935, the first treatise to recognize reactions such as combination, disproportionation, hydrogen abstraction, addition and ß-scission.
- In 1937, two land mark events appeared
  - Flory’s analysis of the kinetics of vinyl polymerization treated as a radical chain reaction (JACS, 59, 241 (1937)
  - Kharasch’s proposal that abnormal addition of HBr to olefins in presence of peroxide was a radical chain reaction (Kharasch and Mayo, J.Org. Chem, 2 288 (1937)
- Free radical chemistry was overtaken by two world events that had nothing to do with chemistry.
  - Hitler’s annexation of Poland in 1939
  - Japanese attack on Pearl Harbor in 1941

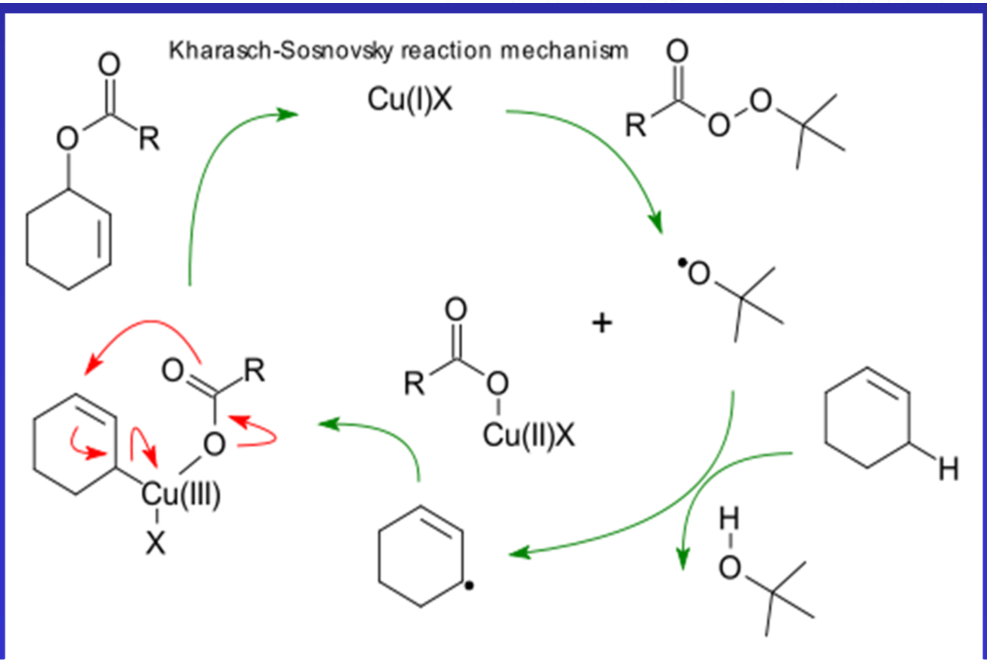
KHARASCH AND FREE RADICAL CHEMISTRY

- **Kharasch transformed free radicals from esoteric species observed in gas phase reactions to the realm of practical organic chemistry; Free radical reactions could be performed in solutions under normal laboratory conditions; He made free radicals a useful tool for the organic chemists.**
- **He showed that free radical reactions could be used for sulfonation, chlorination and carboxylation.**
- **Two of his students, Mayo and Walling went on to make major contributions to free radical polymerizations**



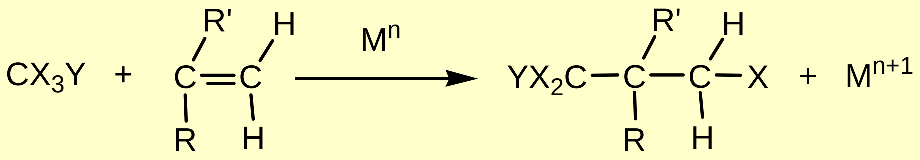
Kharasch, Science, 1945





Atom-transfer Radical Polymerization (ATRP)

- **Atom transfer radical addition**

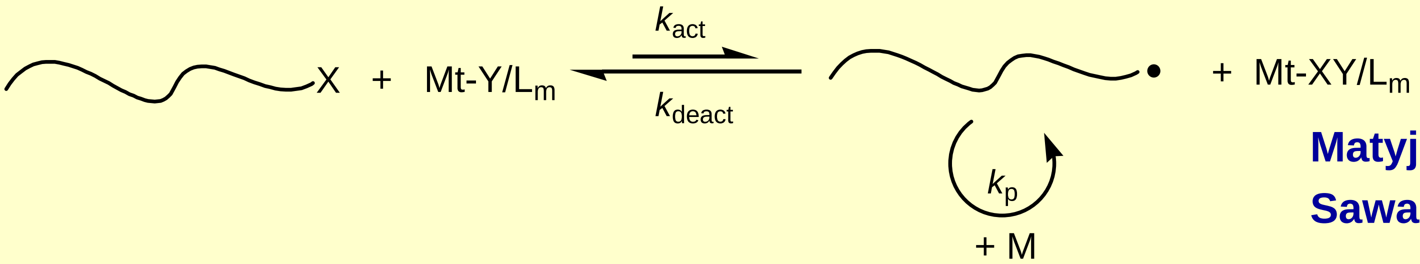


X = halogen; Y = H (or) electronegative group; M = Cu or Ni

Morris Kharash

(1938)

- **Atom transfer radical polymerization**



Matyjaszewski (1995)

Sawamoto (1995)

X and Y- halogen; Mt -Cu^I, Ru^{II}, Fe^{II}, Ni^{II}, etc; M- vinyl monomer, L-Ligand

MAYO AND THE MECHANISM OF VINYL POLYMERIZATION

- **War time crash development programme by the US Government**
- **Mayo and Walling – study the mechanism of vinyl polymerization**

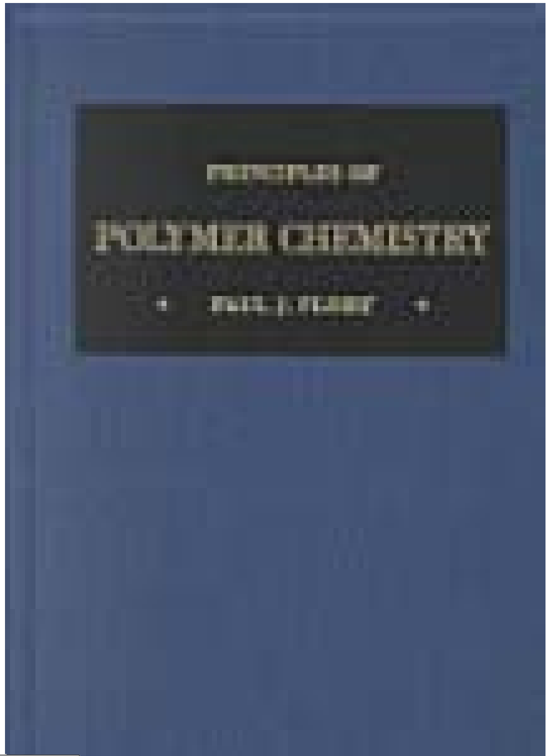
  - Mechanism of chain transfer (F.R. Mayo, JACS 65 2324 (1935)

  - Concept of monomer reactivity ratios (F.R. Mayo, F.M. Lewis, JACS, 66 1594 (1944)

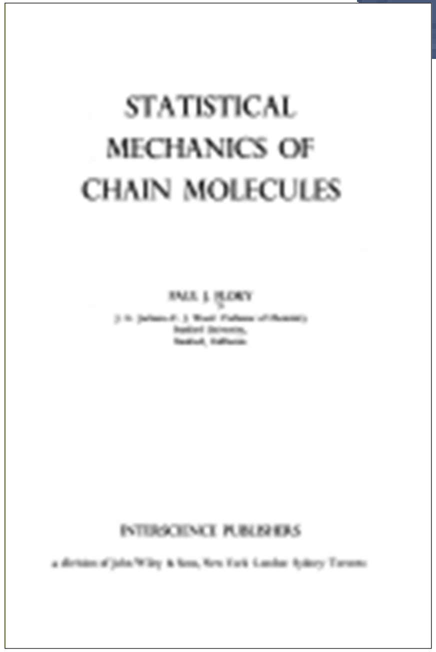
- **Detailed understanding of the structure – activity relationship**
- **Role of initiators (peroxides, azo, redox), inhibitors (degradative chain transfer or allylic termination) and relationship of chain interactions on physical properties of polymers**
- **Emergence of emulsion polymerization – parodoxical observation of high reaction rates with high molecular weight and the elucidation of the mechanism by Harkin (W.D. Harkin, JACS 69, 1428 (1947) and Smith and Ewart (J.Chem. Phys., 16 592 (1948)**

Paul J Flory

Paul John Flory
June 19, 1910–September 8, 1985



PRINCIPLES OF
POLYMER CHEMISTRY
• PAUL J. FLORY •



STATISTICAL
MECHANICS OF
CHAIN MOLECULES

PAUL J. FLORY

INTERSCIENCE PUBLISHERS

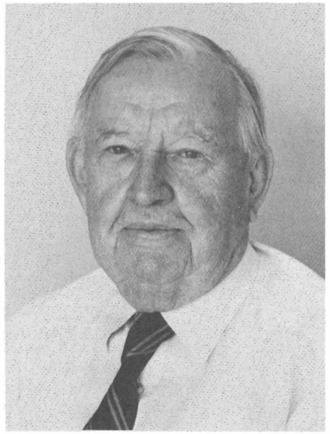
a division of John Wiley & Sons, New York London Sydney Toronto

FLORY'S LASTING LEGACY

- *FLORY HUGGINS INTERACTION PARAMETER*
  - **Defines interaction of polymers with solvent**
- *FLORY REHNER EQUATION*
  - **Extent of swelling of crosslinked polymer**
- *FLORY THETA TEMPERATURE*
  - **a temperature at which polymer – solvent interaction vanishes**
- *SCHULZ – FLORY DISTRIBUTION*
  - **Most probable distribution of molecular weights determined by the rate of chain transfer**

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 "



Carl S. Marvel

Carl Shipp ("Speed") Marvel
1894-1988

THE FATHER OF SYNTHETIC POLYMER CHEMISTRY

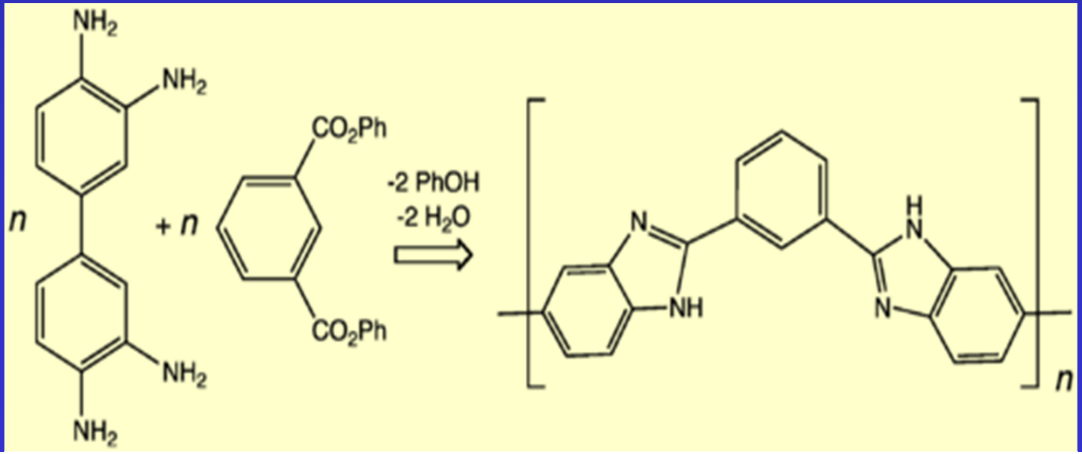
- **A seventy two year career devoted to teaching and research**

- **Mentored 176 PhD's and 145 Post doctoral fellows**

- **War time efforts for the development of SBR; Use of mercaptan as chain transfer agent and redox initiator system for low temperature emulsion polymerization**

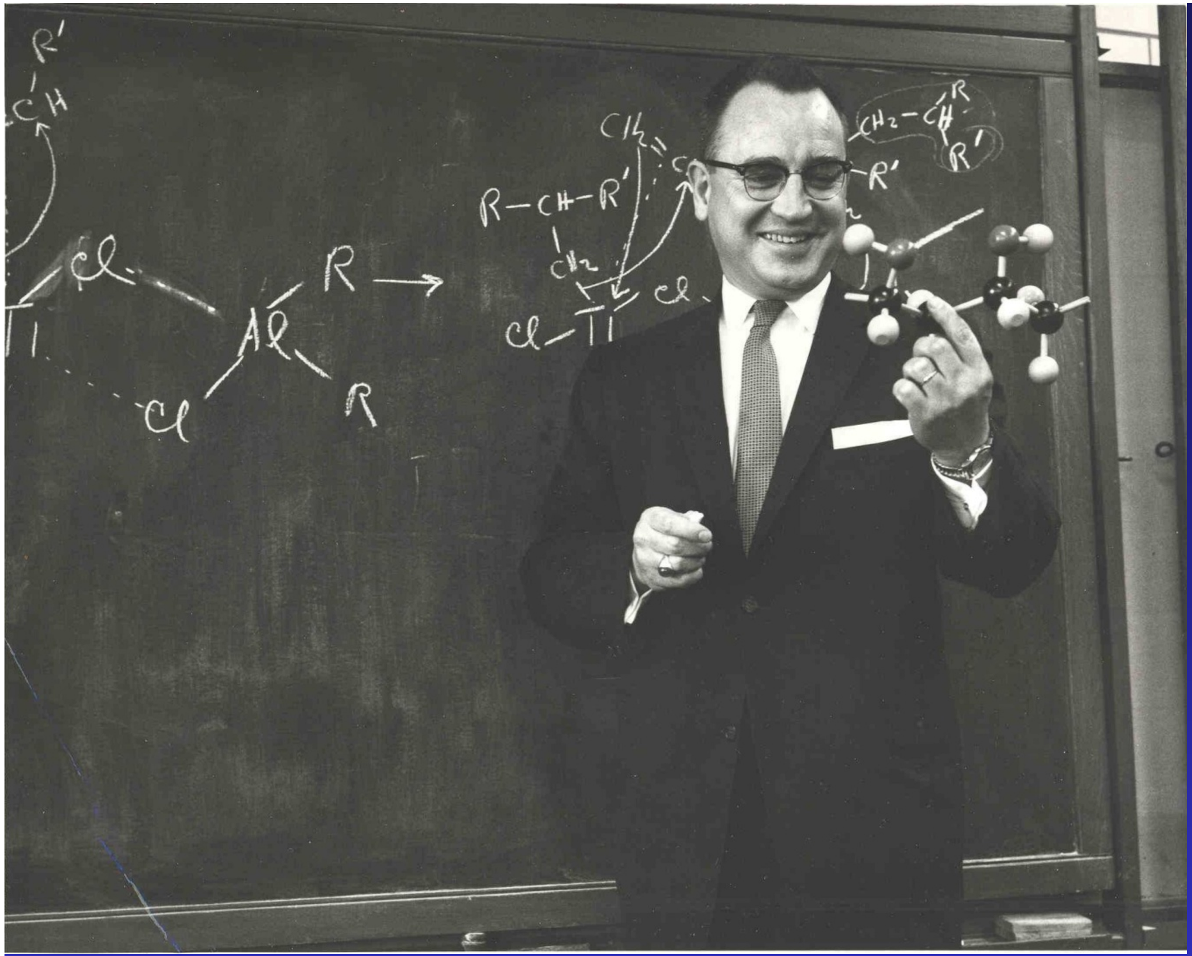
- **Optically active stereoregular polymers *(JACS, 67, 3499 (1945)***

- **High temperature Polymers and adhesives; Syntheis of polyimides and poly(benzimidazoles *(J.Polymer Science,50, 511 (1961)***



WHEN NECESSITY BECAME THE MOTHER OF INVENTION: The US Synthetic Rubber Programme(1939-45)

- **When the US was threatened by a cut off of natural rubber supply immediately after the beginnig of the WW II, it saw a crisis looming**
- **US Government created a mission mode programme with a mandate to produce commercially synthetic rubber (Government Rubber – Styrene)(GRS). It enlisted in the mission industries and academic researchers as well as manufacturing plantsm in a well coordinated manner – a mission that became part of the overall Manhattan Project**
- **Germany had a far advanced synthetic rubber programme that time. Researchers in IG Farben had already produced styrene–butadiene and poly(butadiene) rubber by free radicals and anionic route. These were known as Buna- S and Buna**
- **In a unique arrangement. Four companies, Firestone, Goodrich, Goodyear and US Rubber co agreed to share their knowledge and patents for the benefit of the country**
- **Several leading academics of the day became part of the effort. Whitby (Akron), Debye(Cornell), Morton (MIT), Kolthoff (Minnesota), Kharasch(Chicago), Marvel and Adams(Illinois)**
- **The first bale of synthetic rubber was produced by Firestone in Akron, Ohio on April 16, 1942, followed by Goodyear and Goodrich all in Akron**



Charles Overberger
1920-1997

- **Polymer Synthesis**
- **Synthetic analog of nucleic acids**
- **Enzyme mimetic polymers; polymers containing pendant imidazole groups which show cooperative effects**

Overberger played a seminal role in linking organic chemistry and the emerging science of molecular biology with synthetic macromolecules as useful constructs to understand structure, conformation and functions

A New Approach to the Theory of Rubberlike Elasticity*

MAURICE L. HUGGINS, *Kodak Research Laboratories, Rochester, N. Y.*

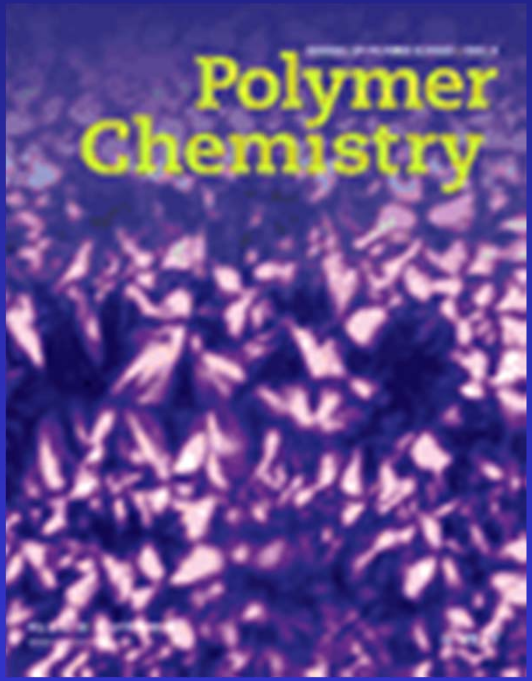
Received November 12, 1945

Synopsis - Equations are derived for stress-strain curves for a hypothetical model substance containing a large number of like systems, each assumed to be in equilibrium between two states having different arrangement of the atoms. With this model one

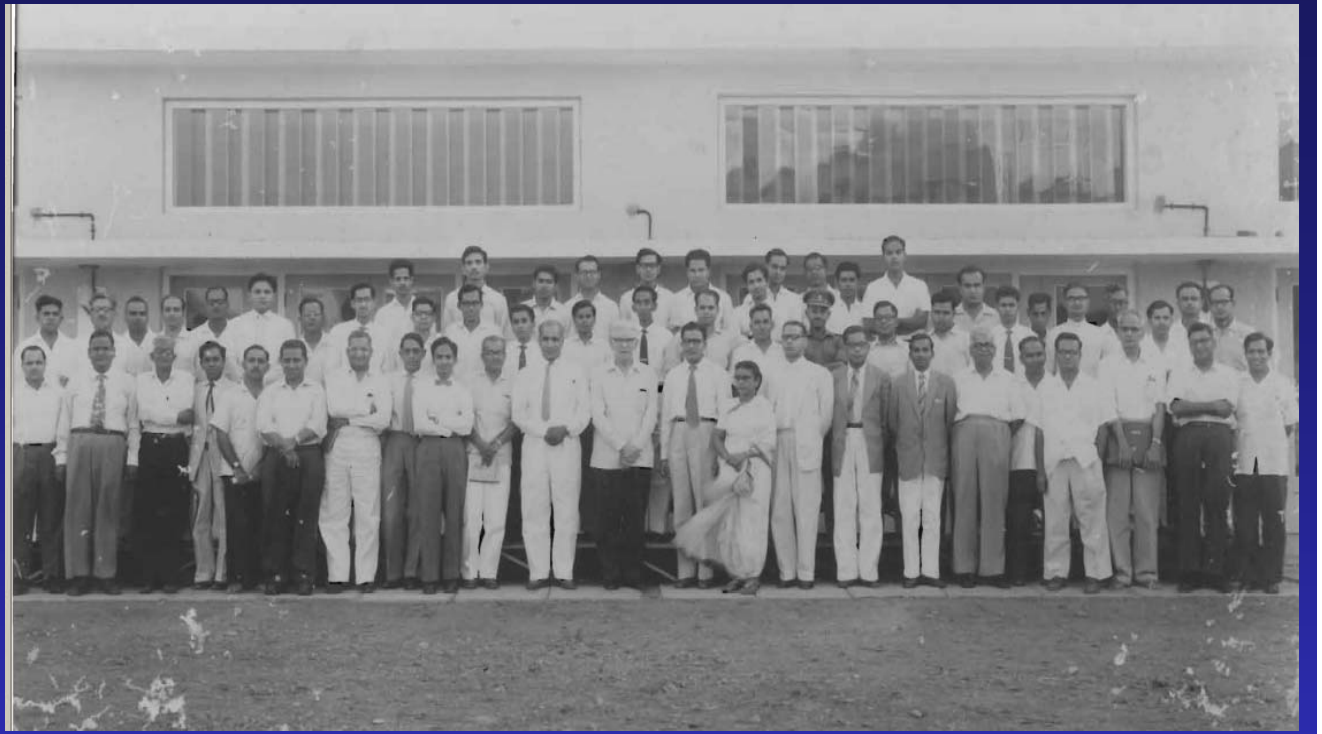
can study the dependence of the initial elastic modulus, the limiting strain (for infinite stress), and the over-all shape of the stress-strain curve on characteristics of the rearranging system their number, the initial energy difference between the two states, the shift of atomic positions, etc. Introduction of an assumed proportionality between the shift per rearrangement and the square of the relative length of the sample (in the direction of the shift) leads to stress-strain curves similar to those determined experimentally for natural rubber and other rubberlike materials.

Two Ph D students of Polymer Research Institute return to India and establish two schools , namely, the Polymer Chemistry Division at NCL (Dr S.L.Kapur) and the Rubber Technology Center at IIT Kharagpur (Dr. M.S.Muthana)

- ***In 1945 Hermann Mark creates the Polymer research institute at Brooklyn Polytechnic***
- ***Establishes a great school of teaching and research in Polymer Science (Overberger, Doty, Tobolsky, Bruno Zimm, Turner Alfrey***
- ***A new medium for publication of polymer science research born***



Journal of Polymer Science
Volume 1, issue 1, January 1946



Herman Mark Visits NCL

S.L.Kapur

The Founder of the Plastics and Resins Department at NCL which later became the Divison of Polymer Chemistry

J.Chem Phys., 55, 2656 (1971)

The theory of reptation by de Gennes explains the dynamical properties of polymer melts of high molecular weight.

The dynamics of such systems is highly influenced by entanglement effects between the long polymer chains.

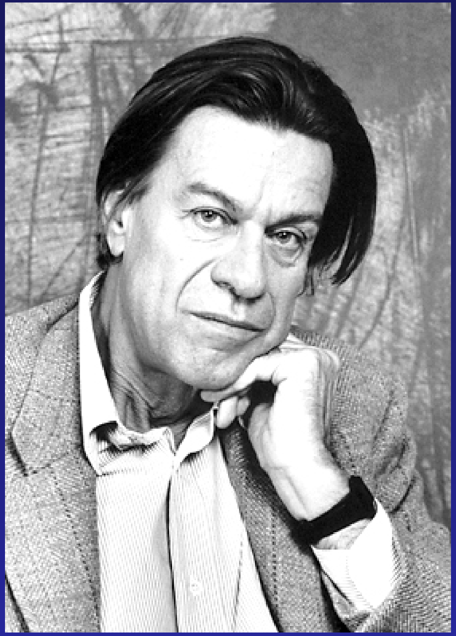
The basic idea of reptation is that each polymer is constrained to move within a topological tube due to the presence of the confining surrounding polymers. Within this tube the polymer performs a snake-like motion (from this the name reptation) and advances in the melt through the diffusion of stored length along its own contour.

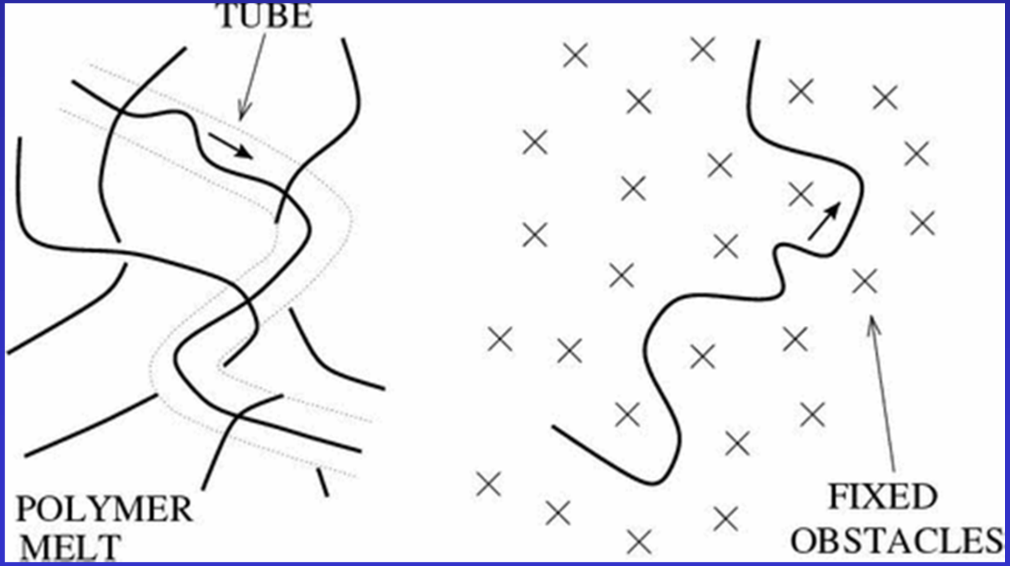
Instead of treating the complicated problem of the motion of all chains, one focuses on the much simpler dynamics of a single test chain in a network of fixed obstacles, assuming that this approximation for sufficiently long chains does not affect the main physical properties of the system.

For a single reptating chain deGennes' theory predicts that the viscosity and longest relaxation time scale as N^3 as function of the polymer length N, while the diffusion constant scales as $D \sim N^{-2}$.

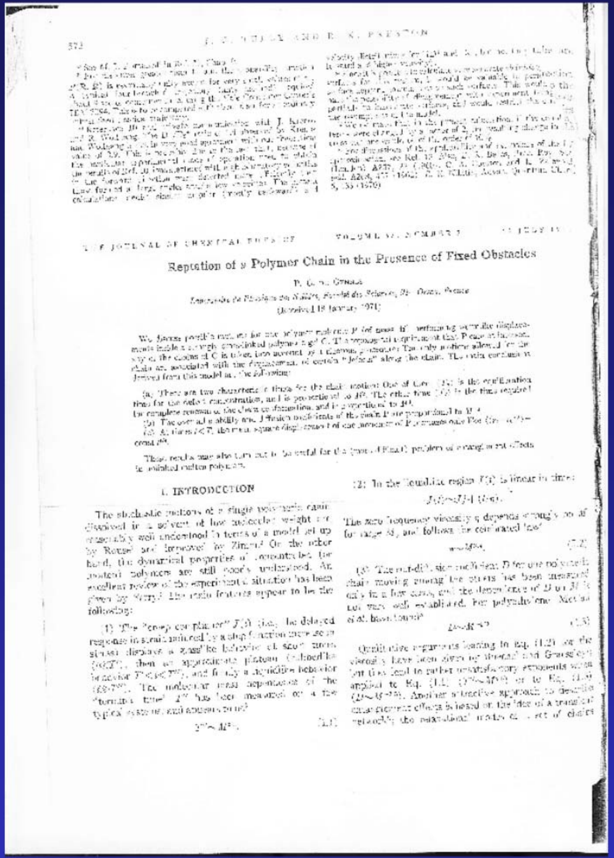
P-G. de Gennes

1932-2007





The Physics of Liquid Crystals (1974)
Scaling Concepts of Polymer Physics (1979,)
Simple Views on Condensed Matter (1992,)
Fragile Objects (1994)
Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves (2003,; with Françoise Brochard-Wyart)



Reptation of a Polymer Chain in the Presence of Fixed Obstacles

I. INTRODUCTION

Reptation of a polymer chain in the presence of fixed obstacles, J. Chem Phys., 55, 572 (1971)

Stephanie Kwolek
(1923-)

US Pat.,3,819,587, 1974

Relying on experience and instinct, Stephanie Kwolek invented one of the modern world's most readily recognized and widely used materials: Kevlar®. Kwolek, a DuPont chemist, specialized in low-temperature processes for the preparation of condensation polymers. In the 1960's, she discovered an entirely new branch of synthetics known as liquid crystalline polymers. She discovered an aramid polymer that most researchers would have rejected, since it was fluid and cloudy, rather than viscous and clear. Kwolek, acting on instinct, insisted on spinning out the solution, and the result was astonishing: synthetic fibers much stiffer and stronger than any created before. The polymer fiber, named Kevlar®, was first marketed in 1971. The fiber was five times stronger than steel (on a strength per weight basis) but about half the density of glass fiber. Kevlar® is best known to the public as the material from which bulletproof vests are made; and in this use alone has saved thousands of lives. In fact, Kevlar® has dozens of important applications, including radial tire cord, brake pads, racing boat sails, aircraft components and suspension bridge cables

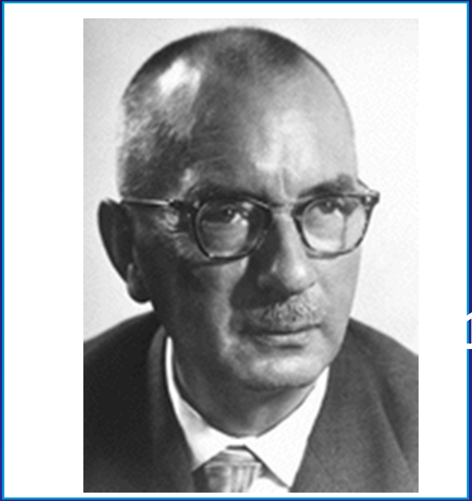
Henry Gilman

1893-1986

His eyesight may have been damned, but his vision was not

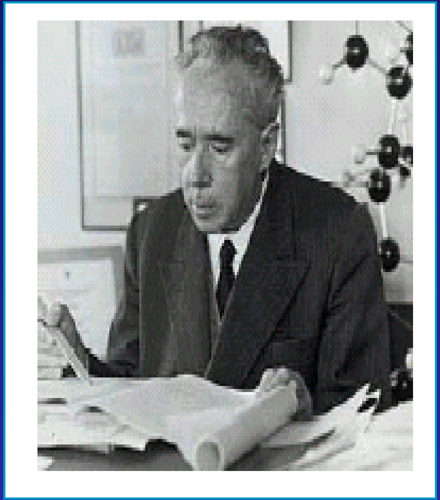
- **PhD with Kohler in Harvard; postdoctoral with Staudinger; a full professor at Iowa State at the age of 30**
- **considered as the father of organometallic chemistry; he covered the periodic table rather generally from lithium to uranium, back in the days when there were few, if any, glove boxes and almost no good way to characterize highly reactive substances,**
- **Explored mechanism of Grignard reactions; organo-silicon chemistry; radical anion chemistry; less well-known is his early work on cadmium and copper compounds; the latter, in the form of cuprates, have been adapted in many laboratories for use in synthetic procedures for many otherwise difficultly accessible substances**
- **organic chemists have used the Gilman color test for formation of Grignard reagents and employed his procedures for the preparation and reactions of organolithium compounds.**
- **In 1947 a combination of glaucoma and detachment of retina, left him blind in one eye and only with 10 % vision in the other eye.**
- **In spite of the disability, Gilman published 510 papers (of a total of 1020 publications) after he lost his eyesight. He continued to mentor PhD students till he was seventy and active in research till he was *82.***

METAL CATALYZED OLEFIN POLYMERIZATION



1898-1973

1903-1979



BUNDESREPUBLIK DEUTSCHLAND

AUSGEGEBEN AM
14. APRIL 1960

DEUTSCHES PATENTAMT

PATENTSCHRIFT

№ 973 626

KLASSE 39c GRUPPE 25o1

INTERNAT. KLASSE C 08f

Z 3799 IVb/39c

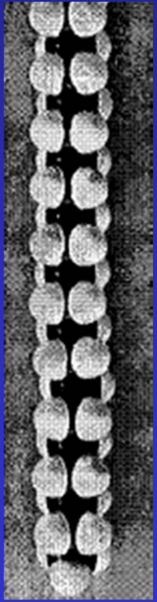
Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr,
Dr. Heinz Breil, Oberhausen (Rhld.), Dr. Erhard Holzkamp, Düsseldorf,
und Dr. Heinz Martin, Mülheim/Ruhr
sind als Erfinder genannt worden

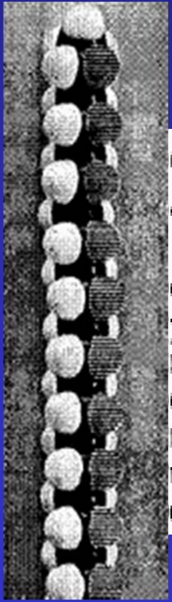
Dr. Dr. e. h. Karl Ziegler, Mülheim/Ruhr

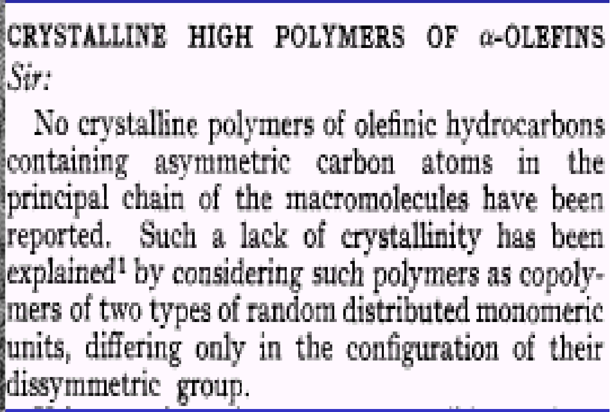
Verfahren zur Herstellung von hochmolekularen Polyäthylenen

Patentiert im Gebiet der Bundesrepublik Deutschland vom 18. November 1953 an
Patentanmeldung bekanntgemacht am 4. Oktober 1956
Patenterteilung bekanntgemacht am 24. März 1960

DE 973626
Nov 18, 1953







CRYSTALLINE HIGH POLYMERS OF α-OLEFINS

Sir:

No crystalline polymers of olefinic hydrocarbons containing asymmetric carbon atoms in the principal chain of the macromolecules have been reported. Such a lack of crystallinity has been explained[1] by considering such polymers as copolymers of two types of random distributed monomeric units, differing only in the configuration of their dissymmetric group.

G.Natta
JACS 77, 1708, 1955
(March 20, 1955)

ZIEGLER-NATTA CATALYSTS AND POLYMERIZATION: THE BIRTH OF A SCIENCE

Process for preparing high molecular weight polyethylene,

Ger Pat 973, 626, 1960 dated November 18, 1953 to K. Ziegler, H. Breil, E. Holzkamp and H. Martin

- ***Exemplary claim***

  A method for preparing high molecular weight polyethylene using aluminum alkyls as catalysts, characterized by bringing together ethylene at pressures >10 atm and temperatures above 50^{o}C with mixtures of aluminum trialkyls and compound of the metals of Group IVa to VIa of the periodic table with the atomic numbers 22 to 74
- **Land mark experiment carried out on October 26, 1953, in the Max Planck Institute fur Kohlenforschung in Mulheim an der Ruhr**
- **A patent was issued to Natta et al (US Pat 3, 112, 200 on June 8, 1954) for the preparation of isotactic polypropylene**

DISCOVERY OF ISOTACTIC POLY(PROPYLENE)S

- **An Italian company Montecatini Edison signed a license from Karl Ziegler to make polyethylene**
- **The Italian company sponsored three of its staff to Mulheim to gain experience in this new chemistry in early 1953**
- **Professor Natta, at Milan Polytechnic, an X-ray crystallographer, was a consultant to Montecatini. He had, therefore, access to all the information from K. Ziegler's laboratory – much of it then unpublished**
- **On March 11, 1954, Natta and coworkers succeeded in polymerizing propylene using Ziegler's catalyst system to a tacky solid (G. Natta, P. Pino and G. Mazzanti, US Pat 3,112,200, June 8, 1954)**

DISCOVERY OF ISOTACTIC POLY(PROPYLENE)S

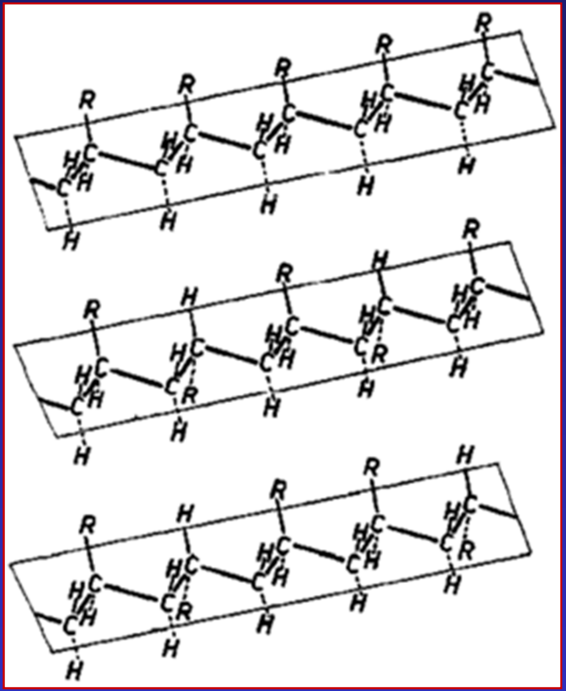
- **Natta recognized that the material is composed of different diastereoisomers. Fractionation from diethylethers and heptane, resulted in an “amorphous” soluble fraction and insoluble “crystalline” fraction (with a Tm ~ 160^{o}C)**
- **Natta applied X-ray crystallography to deduce the structure of crystalline polymer and termed them as isotactic, syndiotactic and atactic**
- **The concept of polymer strereoregularity in conjunction with transition metal catalyzed stereospecific polymerization by means of enantiomorphic catalytically active site had far reaching impact on the progress of polymer science and technology**

DISCOVERY OF ISOTACTIC POLY(ROPYLENE)S

- **Montecatini started manufacture of polypropylene in 1957 at Ferrara, Italy**
- **Natta shares Nobel Prize with Ziegler for chemistry in 1963**

> **"Nature synthesises many stereoregular polymers (cellulose, rubber, biomacromolecules). This ability has so far been thought to be a monopoly of nature operating with biocatalysts known as enzymes. But Professor Natta has broken this monopoly"**

A. Fredga, Nobel Presentations, 1963



Poly(propylene) stereoisomers as proposed by Giulio Natta: isotactic, syndiotactic and atactic

G.NATTA : HIS LIFE AND PHILOSOPHY

- **Natta studied mathematics and industrial chemistry at Milan polytechnic. He studied under Guiseppe Bruni, a student of Jacobus van' t Hoff**
- **Natta was able to see the connection between science and its applications from the very early part of his training..**
- **He said" that the only difference between industrial problem and theoretical is that the former is more difficult to solve because you have to consider many factors that can be ignored in the latter"**
- **He subscribed to the maxim: the essence of knowledge is, once you have got it, apply it."**
- **Natta began his academic career in Milan with the study of Mustard gas, synthesis of methanol using catalysts and studies aimed at catalytic conversion of CO to useful chemicals**
- **An encounter with Staudinger triggered Natta' s interest in polymers**
- **Natta built a very strong relationship with the Italian Chemical industry. He trained a large number of students for industry and thrived on his industrial connections**

“The results described in your manuscript are of extraordinary interest. Perhaps one should call them revolutionary in significance”

P.J. Flory who refereed the manuscript of G. Natta submitted to J. Am. Chem. Soc., published 25, 1024 (1955) in his letter addressed to G. Natta dated June 7, 1955

“I set out to follow a broad course of study in which my only guide was , initially, just the desire to do something which gave me pleasure. The course threw up many interesting conclusions , many of them of highly practical value, and one of them led ultimately to a method of making polyethylene “

Karl Ziegler

Nobel Address

ANIONIC POLYMERIZATION

- **Anionic polymerization has been known since scientists at IG farben trid to polymerize butadiene using Sodium metal (BuNa)**

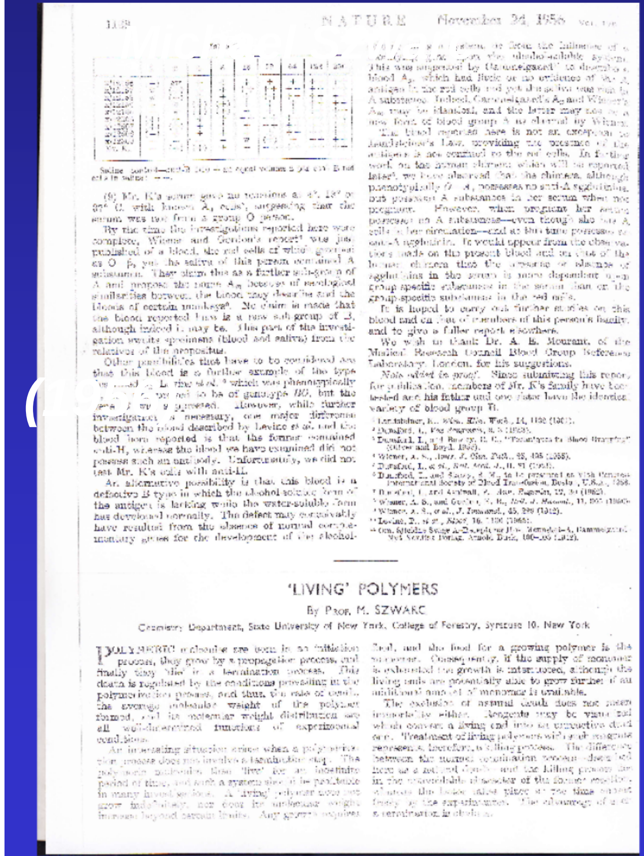
- **However, unlike free radicals and carbocations, they received very little attention from chemists**

- **Ziegler (Germany) and Gilman (US) were pioneers in metal organic chemistry involving lithium and magnesium. Carbon –metal bonds were believed to be anionic character**

- **Techniques of physical organic chemistry were not employed since carbanions were difficult to handle, exist as ion pairs and aggregates and kinetic studies, invariably, led to messy results**

“Polymertic molecules are born in an initiation process, they grow by a propagation process, and finally they “die” in a termination process. The rate of death, the average molecular weight of the polymer formed and its molecualar weight distribution are all well determined functions of experimental conditions

An interesting situation arises when a polymerization process does not involve a termination step. The polymeric molecules then “live” for an indefinite period of time……. Any growth requires food and the food for a growing polymer is the monomer “

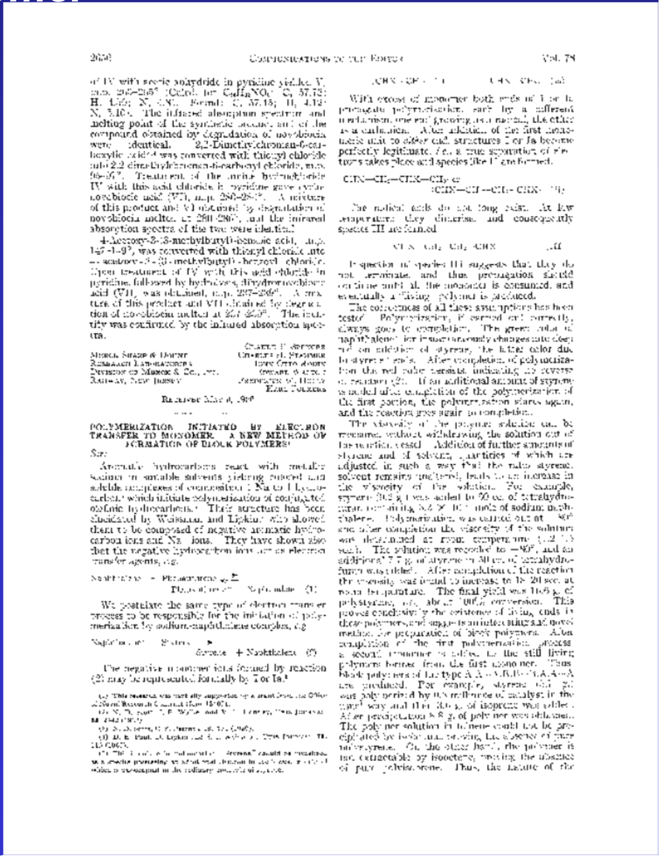


'LIVING' POLYMERS

By Prof. M. SZWARC

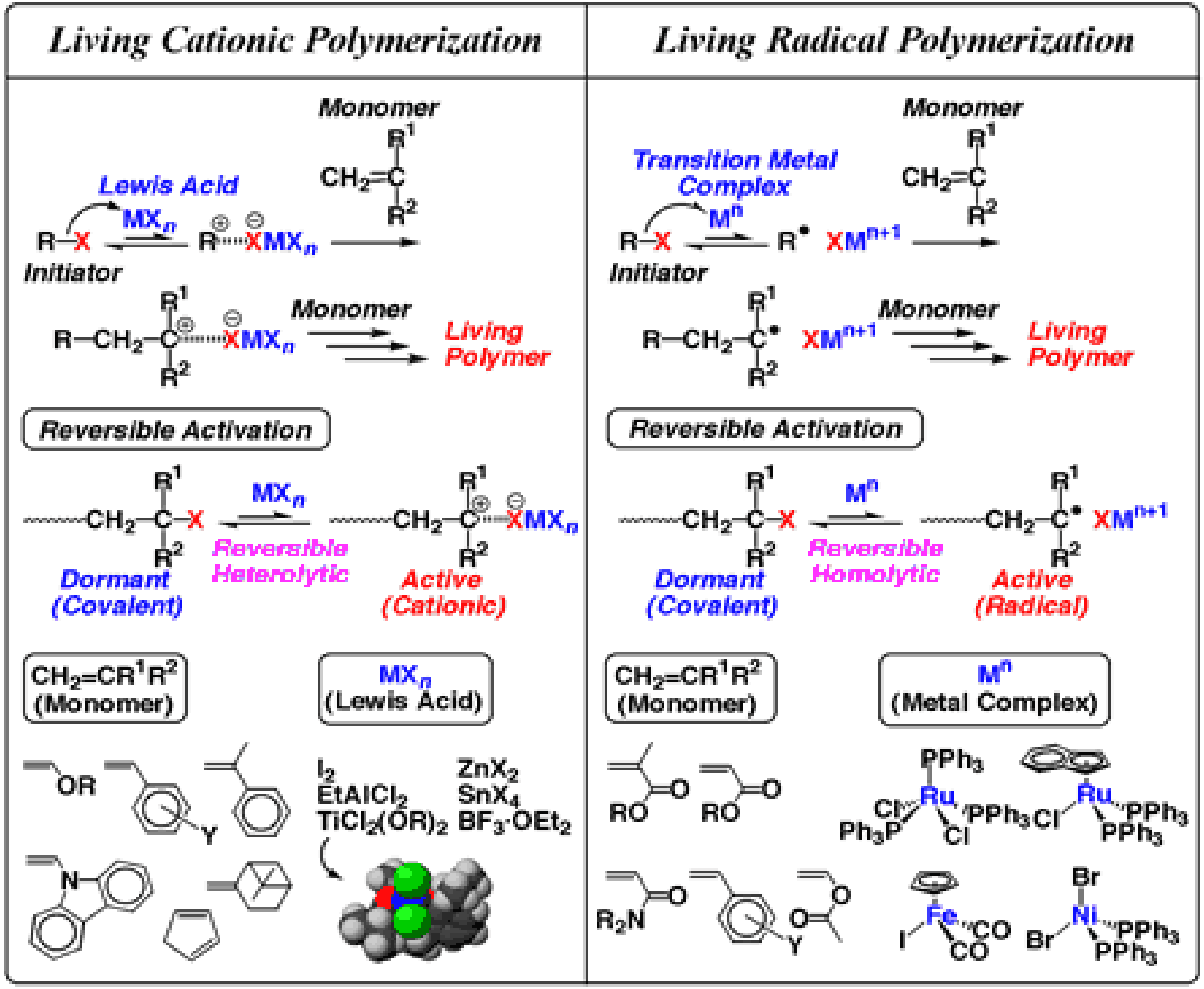
Chemistry Department, State University of New York, College of Forestry, Syracuse 10, New York

Nature, 178, 1168



POLYMERIZATION INITIATED BY ELECTRON TRANSFER TO MONOMER. A NEW METHOD OF FORMATION OF BLOCK POLYMERS

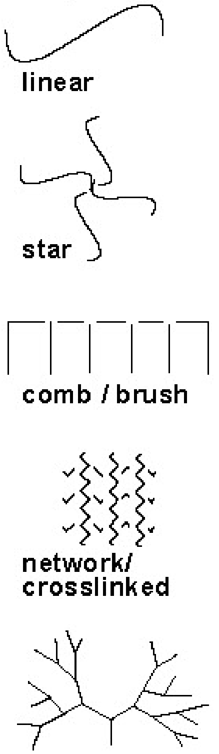
J.Amer.Chem.Soc., 78, 2656 (1956)


Living Cationic Polymerization
Living Radical Polymerization
Monomer
Lewis Acid
MXn
R–X
Initiator
R⊕····X⊖MXn
CH2=CR1R2
R–CH2–C⊕R1R2····⊖XMXn
Living Polymer
Transition Metal Complex
Mn
R• XMn+1
R–CH2–C•R1R2 XMn+1
Reversible Activation
Reversible Heterolytic
Dormant (Covalent)
Active (Cationic)
Reversible Homolytic
Active (Radical)
CH2=CR1R2 (Monomer)
MXn (Lewis Acid)
Mn (Metal Complex)
OR
Y
N
I2
EtAlCl2
TiCl2(OR)2
ZnX2
SnX4
BF3·OEt2
RO
O
R2N
PPh3
Ph3P
Cl
Ru
Fe
CO
I
Br
Ni

What Can Controlled/ Living Polymerizations Do ?

$DP_n = \Delta[M]/[I]_o$; $200<M_n<10^6$ (or more?); $1.01<M_w/M_n < 1.5$ & designed MWD; tacticity

Topologies:



linear

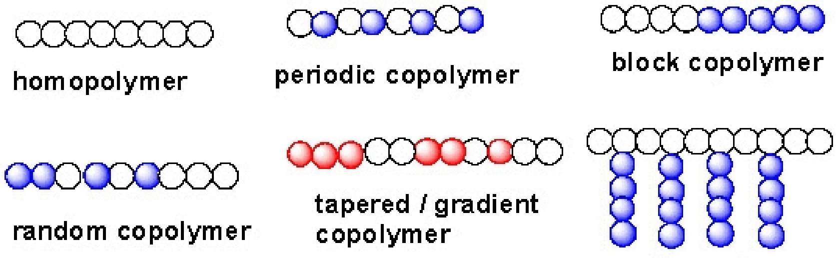
star

comb / brush

network/ crosslinked

dendritic / hyperbranched

Compositions:



homopolymer

periodic copolymer

block copolymer

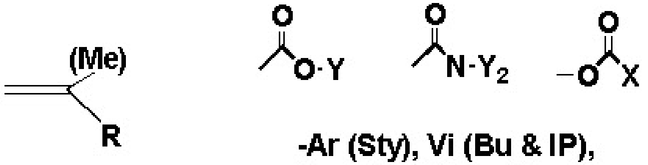
random copolymer

tapered / gradient copolymer

graft copolymer

Monomers:

Vinyl:



-Ar (Sty), Vi (Bu & IP), Pyr, CN, Cl, Br, Me, H

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

Transformations:

⊕ → ⊙

⊖ → ⊙

⊙ → ⊕

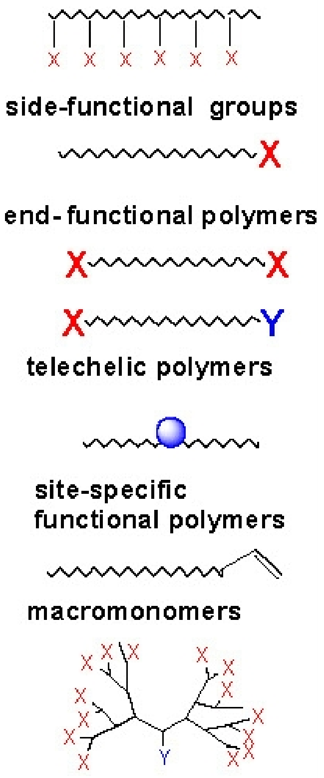
Z-N → ⊙

ROMP → ⊙

PCond. → ⊙

Hybrids:
synthetic/natural
organic/inorganic
surfaces; IPN; etc.

Functionalities:



side-functional groups

end-functional polymers

telechelic polymers

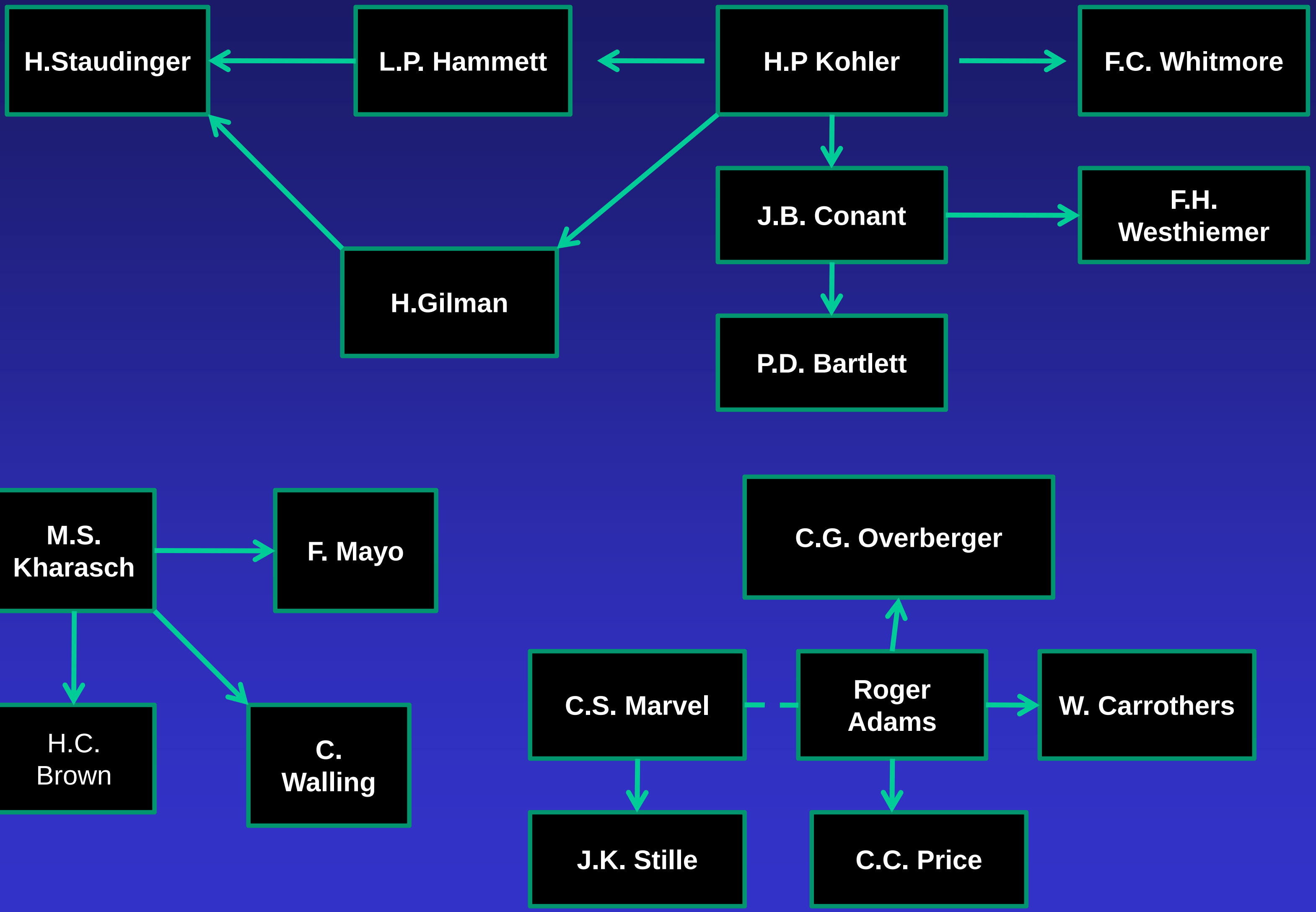
site-specific functional polymers

macromonomers

multifunctional

1950-2010
Celebrating Sixty Years of Science

THE NETWORK OF GREATNESS



H.Staudinger

L.P. Hammett

H.P Kohler

F.C. Whitmore

J.B. Conant

F.H. Westhiemer

H.Gilman

P.D. Bartlett

M.S. Kharasch

F. Mayo

H.C. Brown

C. Walling

C.G. Overberger

C.S. Marvel

Roger Adams

W. Carrothers

J.K. Stille

C.C. Price

POLYMER MATERIALS : HISTORY

- **Polymers were the product of post war renaissance in chemical industry driven by the promise of inexpensive petroleum derived feed-stocks**
- **The fifties and sixties saw the introduction of many polymers that changed the face of human civilization**
- **From early curiosities polymers became an indispensable part of our daily living and so ubiquitous that we no longer realize how addicted we are to polymer materials !**

The thermoplastic known as "high density polyethylene" (HDPE) was first produced commercially by Phillips Petroleum in 1955. It was given the tradename Marlex®. This new thermoplastic offered a good balance of mechanical properties, low specific gravity, electrical insulation, and chemical resistance. However, the material had few markets in those early years. Then came the Hula Hoop !

Richard Knerr and Artur Melin, founders of the Wham-O Company, were the architects of the biggest "fad" of all time – the "Hula Hoop". The Hula Hoop evolved from bamboo hoops previously used in Australia. At the peak of this craze in 1958, Wham-O was using 1,000,000 pounds of HDPE each week for Hula Hoop production.

Robin Day

***The British
designer of
Plastic Chairs;
An iconic design
when it was first
unveiled***

1967

Mr. McGuire: Come with me for a minute. I want to talk to you. I just want to say one word to you. Just one word

Ben: Yes, sir

Mr. McGuire: Are you listening ?

Ben: Yes sir, I am

Mr.McGuire: PLASTICS

Ben: Exactly how do you mean ?

Mr. McGuire: There is a great future in plastics. Think about it. Will you think about it?

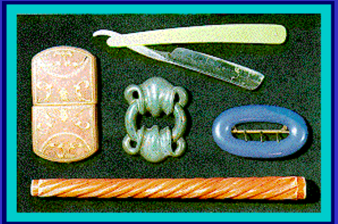
POLYMERS FULFILLING MATERIAL NEEDS OF SOCIETY…
(Global consumption exceeds 250 million tons)

Precursor 19th Century →
Semi Synthetics

- 1839 : Natural Rubber
- 1843 : Vulcanite / Gutta Percha
- 1856 : Shellac / Bois Durci
- 1862 : Parkesine
- 1863 : Celluloid
- 1894 : Viscose Rayon
- 1898 : Poly Carbonate

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

High Performance Plastics

THE POLYMER PYRAMID

PAI = TORLON® polyamide-imide

PK = KADEL® polyketone

PPSU = RADEL® R polyphenylsulfone

LCP = XYDAR® Liquid Crystal Polymer

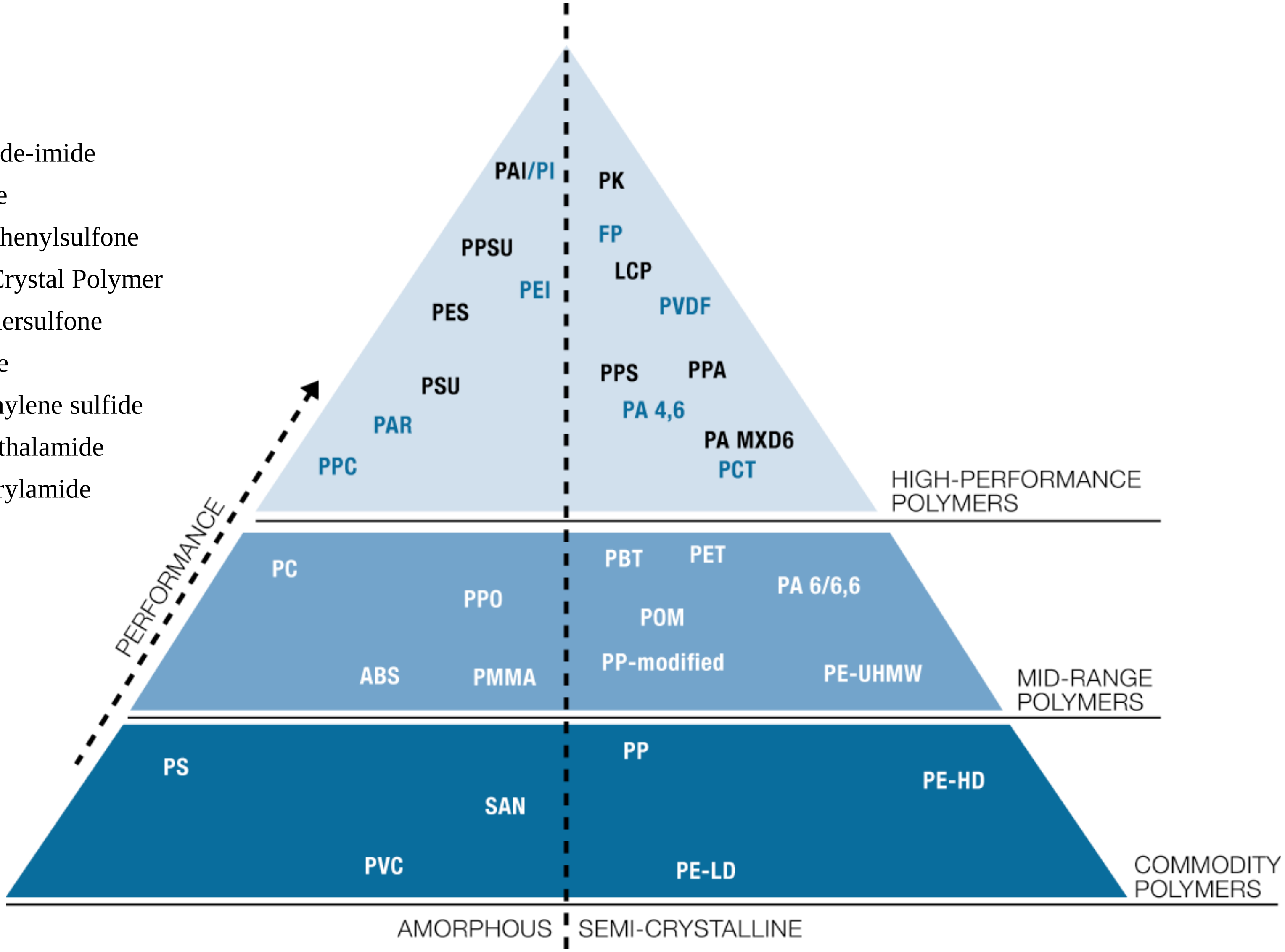
PES = RADEL® A polyethersulfone

PSU = UDEL® polysulfone

PPS = PRIMEF® polyphenylene sulfide

PPA = AMODEL® polyphthalamide

PA MXD6 = IXEF® polyarylamide



v was a historic achievement in
tionship between structure and

en structure and properties and this
provide a simple codification of the

ible to include all of the variations in
e most common polymers.

TANGRAM TECHNOLOGY Consulting Engineers

Tangram Technology
Periodic Table of Thermoplastics

Increasing performance →

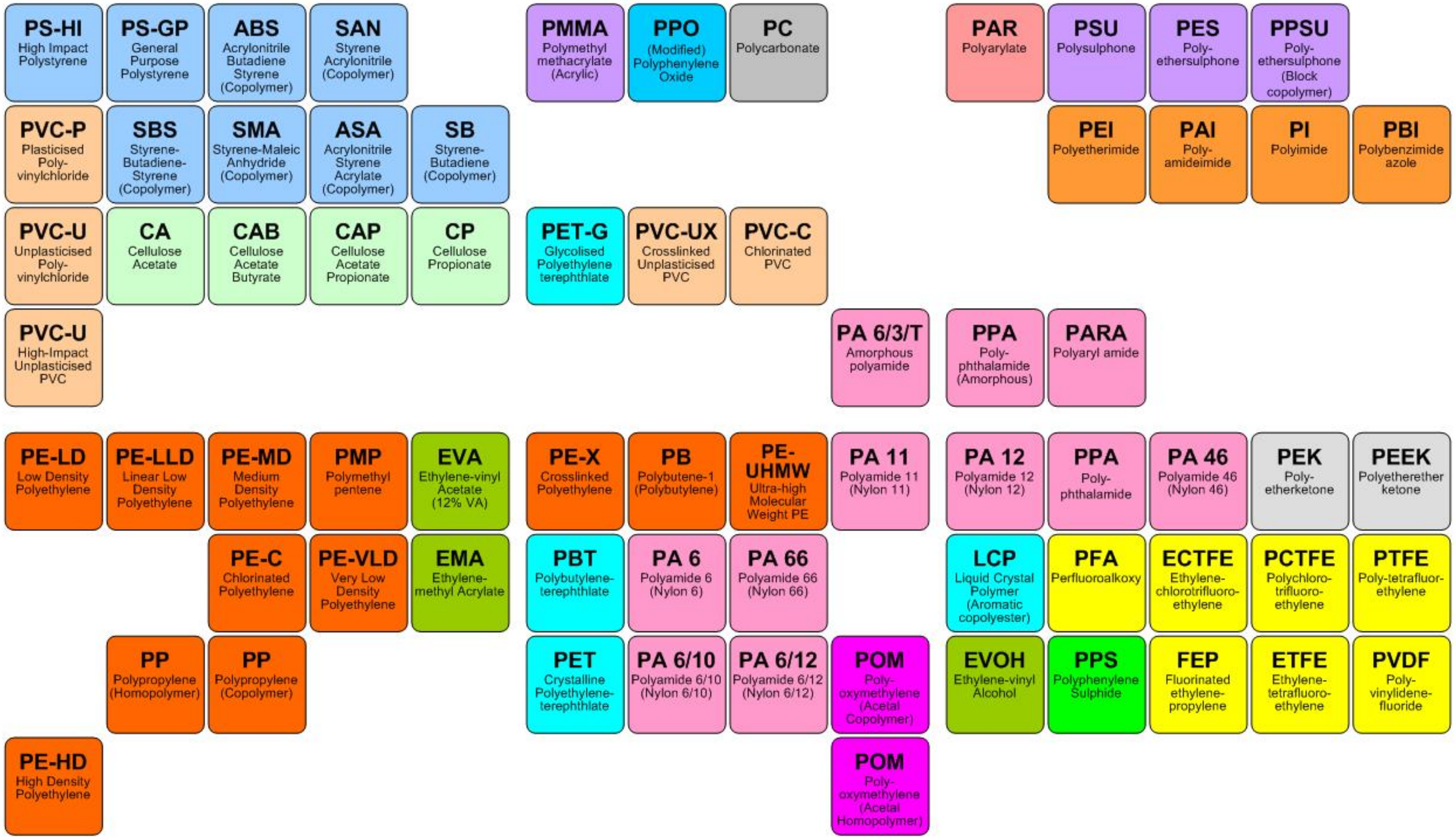
Amorphous | **Increasing crystallinity** ↓ | **Semicrystalline**

Random molecular orientation in both molten and solid phases.

General Characteristics
- Soften gradually.
- Generally transparent.
- Lower Tensile Strength and Tensile Modulus.
- Lower Density.
- Low Creep Resistance.
- High Dimensional Stability.
- Low fatigue resistance.
- Easy to bond using adhesives and solvents (high surface energy).

Random molecular orientation in molten phase, densely packed crystallites in solid phase.

General Characteristics
- Sharp melting point.
- Generally translucent or opaque.
- Higher Tensile Strength and Tensile Modulus.
- Higher Density.
- High Creep Resistance.
- Low Dimensional Stability.
- High fatigue resistance.
- Difficult to bond using adhesives and solvents (low surface energy).



	Commodity					**Engineering**				**Performance**				
Amorphous	**PS-HI** High Impact Polystyrene	**PS-GP** General Purpose Polystyrene	**ABS** Acrylonitrile Butadiene Styrene (Copolymer)	**SAN** Styrene Acrylonitrile (Copolymer)		**PMMA** Polymethyl methacrylate (Acrylic)	**PPO** (Modified) Polyphenylene Oxide	**PC** Polycarbonate		**PAR** Polyarylate	**PSU** Polysulphone	**PES** Poly-ethersulphone	**PPSU** Poly-ethersulphone (Block copolymer)	
	PVC-P Plasticised Poly-vinylchloride	**SBS** Styrene-Butadiene-Styrene (Copolymer)	**SMA** Styrene-Maleic Anhydride (Copolymer)	**ASA** Acrylonitrile Styrene Acrylate (Copolymer)	**SB** Styrene-Butadiene (Copolymer)						**PEI** Polyetherimide	**PAI** Poly-amideimide	**PI** Polyimide	**PBI** Polybenzimide azole
	PVC-U Unplasticised Poly-vinylchloride	**CA** Cellulose Acetate	**CAB** Cellulose Acetate Butyrate	**CAP** Cellulose Acetate Propionate	**CP** Cellulose Propionate	**PET-G** Glycolised Polyethylene terephthlate	**PVC-UX** Crosslinked Unplasticised PVC	**PVC-C** Chlorinated PVC						
	PVC-U High-Impact Unplasticised PVC								**PA 6/3/T** Amorphous polyamide	**PPA** Poly-phthalamide (Amorphous)	**PARA** Polyaryl amide			
Semicrystalline	**PE-LD** Low Density Polyethylene	**PE-LLD** Linear Low Density Polyethylene	**PE-MD** Medium Density Polyethylene	**PMP** Polymethyl pentene	**EVA** Ethylene-vinyl Acetate (12% VA)	**PE-X** Crosslinked Polyethylene	**PB** Polybutene-1 (Polybutylene)	**PE-UHMW** Ultra-high Molecular Weight PE	**PA 11** Polyamide 11 (Nylon 11)	**PA 12** Polyamide 12 (Nylon 12)	**PPA** Poly-phthalamide	**PA 46** Polyamide 46 (Nylon 46)	**PEK** Poly-etherketone	**PEEK** Polyetherether ketone
			PE-C Chlorinated Polyethylene	**PE-VLD** Very Low Density Polyethylene	**EMA** Ethylene-methyl Acrylate	**PBT** Polybutylene-terephthlate	**PA 6** Polyamide 6 (Nylon 6)	**PA 66** Polyamide 66 (Nylon 66)		**LCP** Liquid Crystal Polymer (Aromatic copolyester)	**PFA** Perfluoroalkoxy	**ECTFE** Ethylene-chlorotrifluoro-ethylene	**PCTFE** Polychloro-trifluoro-ethylene	**PTFE** Poly-tetrafluor-ethylene
		PP Polypropylene (Homopolymer)	**PP** Polypropylene (Copolymer)			**PET** Crystalline Polyethylene-terephthlate	**PA 6/10** Polyamide 6/10 (Nylon 6/10)	**PA 6/12** Polyamide 6/12 (Nylon 6/12)	**POM** Poly-oxymethylene (Acetal Copolymer)	**EVOH** Ethylene-vinyl Alcohol	**PPS** Polyphenylene Sulphide	**FEP** Fluorinated ethylene-propylene	**ETFE** Ethylene-tetrafluoro-ethylene	**PVDF** Poly-vinylidene-fluoride
	PE-HD High Density Polyethylene								**POM** Poly-oxymethylene (Acetal Homopolymer)					

KEY TO MAJOR POLYMER FAMILIES: Styrenes | Polyolefins | Vinyls | Cellulosics | Polyesters | Polyamides | Acrylics | Polycarbonates | Acetals | Polysulphones | Imides | Fluoropolymers

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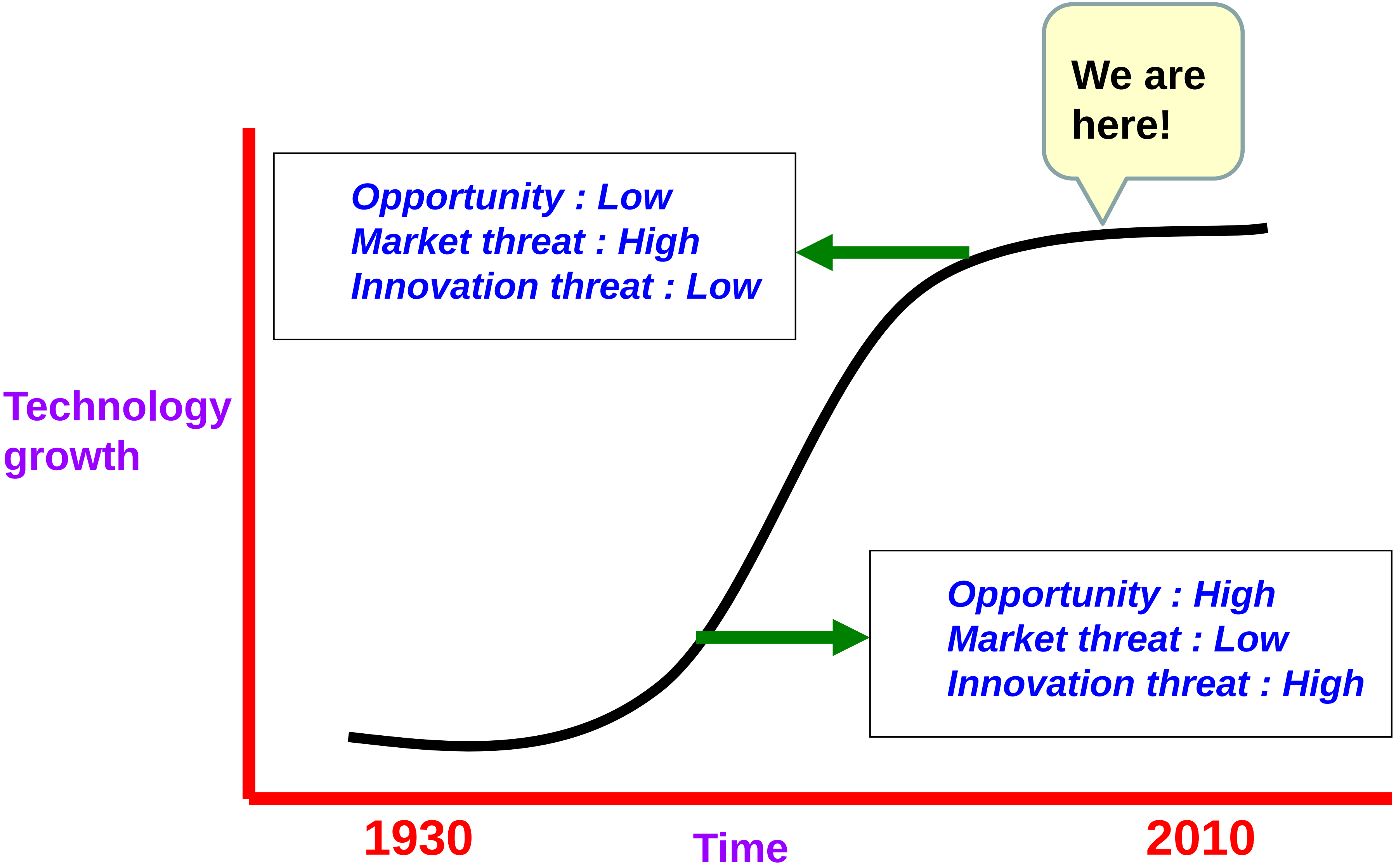


We are here!

Opportunity : Low
Market threat : High
Innovation threat : Low

Technology growth

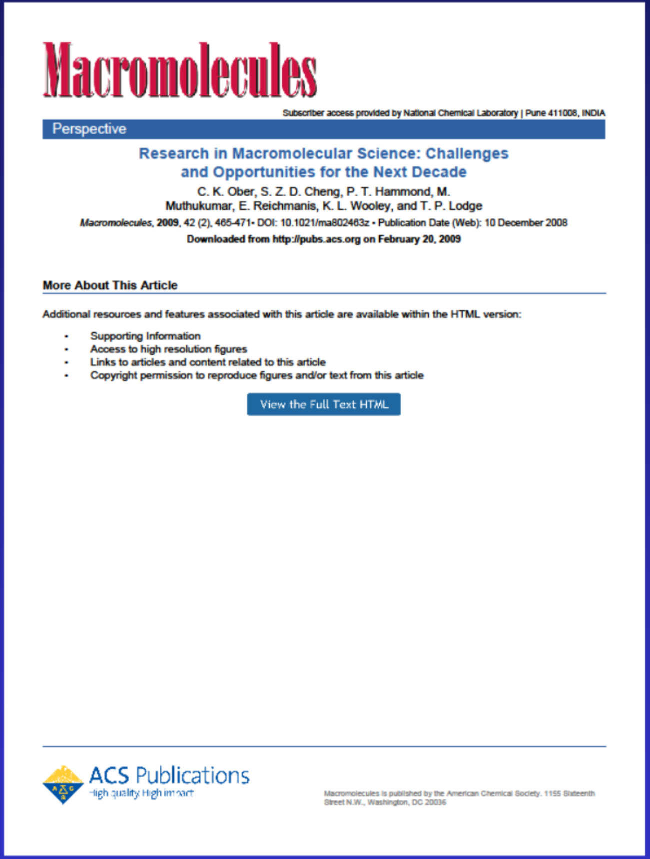
Opportunity : High
Market threat : Low
Innovation threat : High

1930

Time

2010

POLYMER SCIENCE : QUO VADIS



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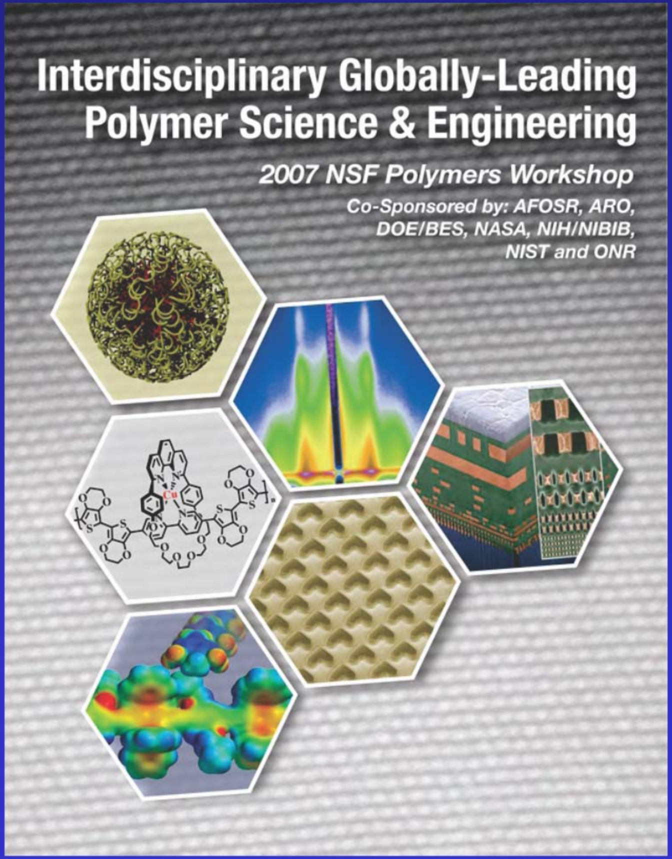

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