ONE HUNDRED YEARS OF MACROMOLECULES: SOME VIGNETTES FROM HISTORY

ONE HUNDRED YEARS OF MACROMOLECULES
A SYMPOSIUM ORGANIZED BY SOMAIYA VIDYAVIHAR UNIVERSITY, MUMBAI
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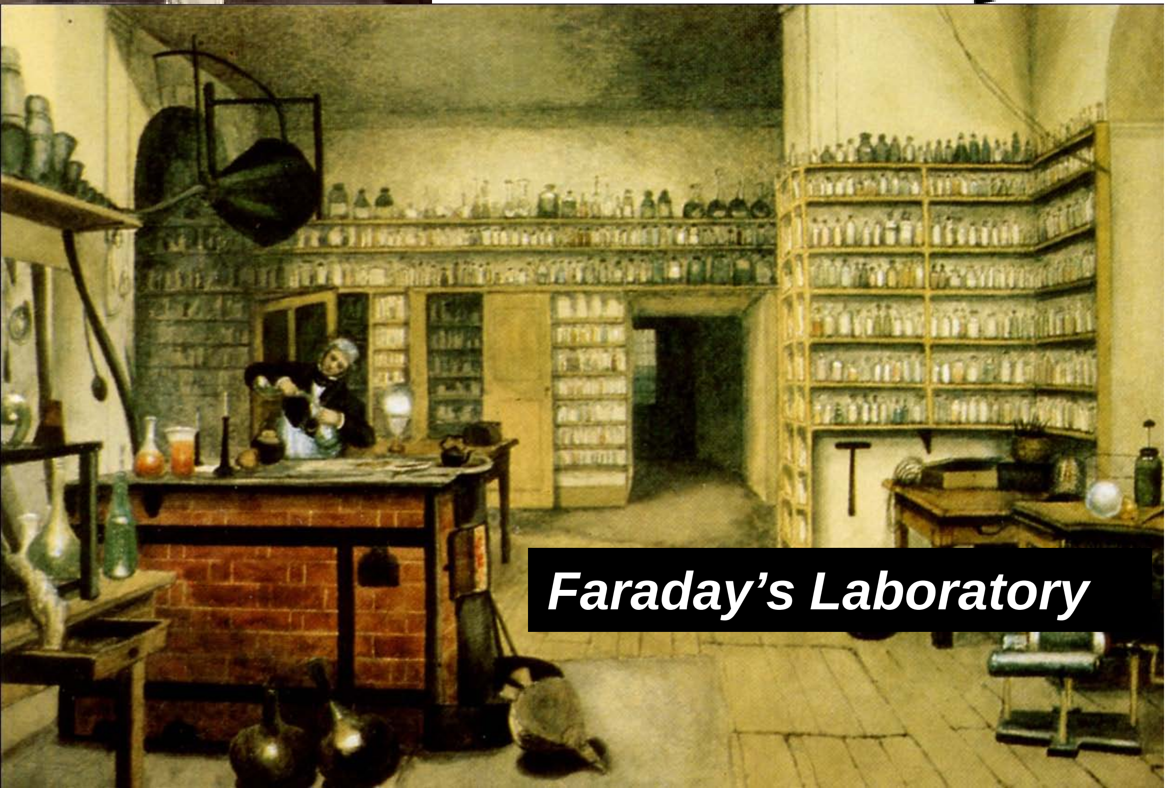
MICHAEL FARADAY
(1791- 1867)

M Faraday

The most influential scientist in the history of science



Faraday’s Laboratory

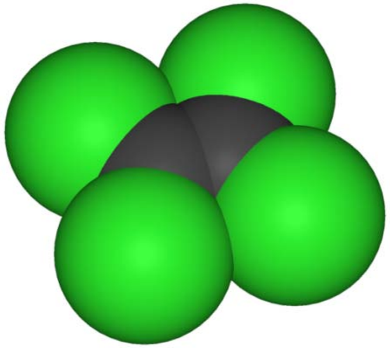
- One of the first scientists in the post – industrial revolution who established the methods of evidence based proof of hypothesis

- Contributed to both science and its applications; studied pollution of river Thames, developed the first optical glass, studied the chemistry of flames and established that fine dust of coal can combust spontaneously

MICHAEL FARADAY : A PIONEER IN CHEMISTRY

- Discovery of Benzene
- Laws of electrolysis; concept of anode, cathode, electrode and ions
- First demonstration of decomposition of magnesium sulfate by applying electrical potential; Design of a voltaic pile consisting of seven half penny pieces, seven discs of zinc and filter paper soaked in salt water (1812)
- First synthesis of hexa-chloroethane and tetrachloro-ethylene (1820)
- ***Identification of isoprene as a constituent of natural rubber , now known as poly(isoprene) (1826)***
- ***Determined the elemental composition of natural rubber; in his note book he also recorded in passing a reaction of rubber with sulfur***

Voltaic Pile



Tetrachloroethylene

Chemistry creates its own object. This creative power, similar to that of arts distinguishes it fundamentally from the other natural and historical sciences

Marcellin Bertholet, 1860

(1827- 1907)

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

BERTHOLET AND THE POLYMER HYPOTHESIS

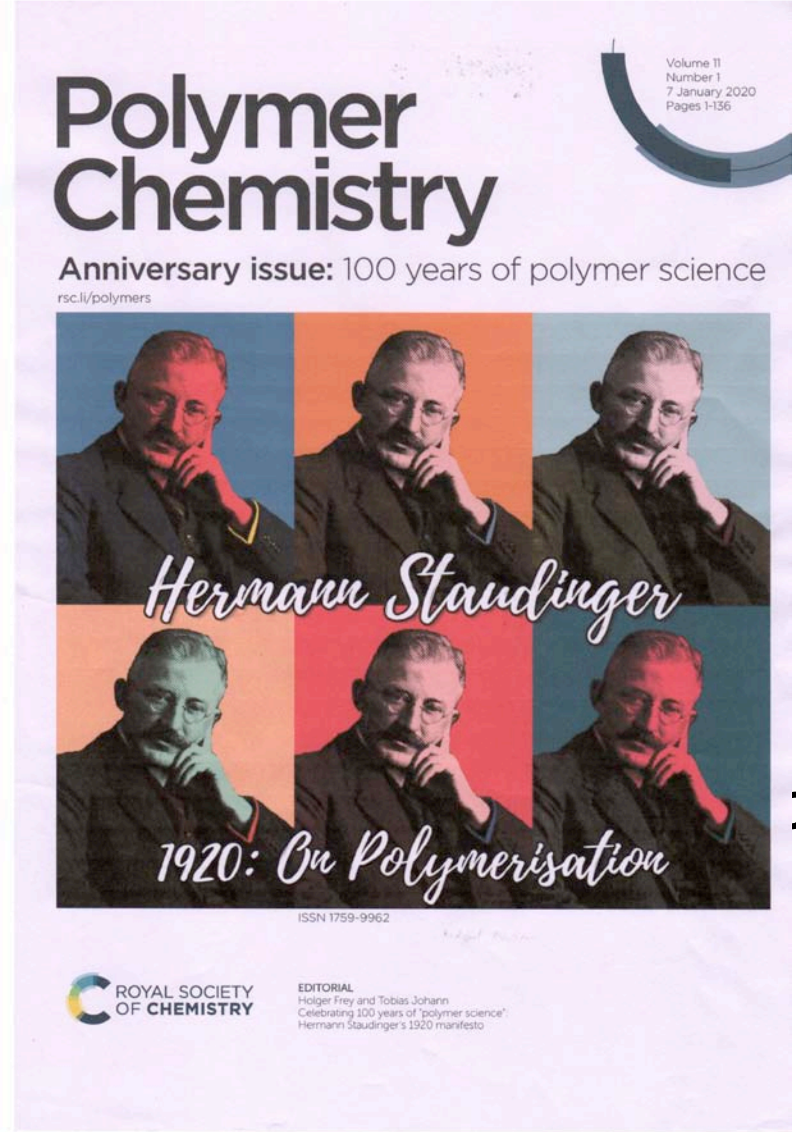
- Bertholet came to a remarkable understanding of the conversion of vinyl compounds into polymeric chain molecules. He reasoned that upon addition of an olefin to a chain with a terminal double bond, the unsaturation would be retained, so that there was no reason why long chains should not be produced. Bertholet isolated the dimer, trimer and tetramer of pentene.
- In 1853, Bertholet reported the thermal and catalytic polymerization of pinene ; 1869 he published his results on polymerization of ethylene, propylene, pentene and pinene.
- His prescience is all the more remarkable, because the only techniques available to him were, density and boiling point measurement and softening temperature of solids
- He presented his results in a long lecture titled “ la polymerie” presented at the Chemical Society of Paris in 1863

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)*

Ber. Dtsch. Chem. Ges., 53, 1073 , June 12, 1920

1073



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Hermann Staudinger
1920: On Polymerisation

ISSN 1759-9962

ROYAL SOCIETY OF CHEMISTRY

EDITORIAL
Holger Frey and Tobias Johann
Celebrating 100 years of "polymer science":
Hermann Staudinger's 1920 manifesto

*) A. 412, 295 [1917]; 404, 1 [1914].

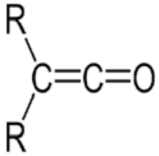
Berichte d. D. Chem. Gesellschaft. Jahrg. LIII. 71

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

Hermann Staudinger (1881-1965)
Nobel Laureate 1953

STAUDINGER : EARLY YEARS

- Volhard initiated him in chemistry; PhD in 1903 with Prof Vorlander in Halle
- Discovered ketenes as a new class of organic compounds in 1905 at Strasbourg during his habilitation with Thiele
- Began his scientific career at Karlsruhe in organic chemistry; discovered the Staudinger Reaction



- Appointed to the faculty of ETH, Zurich in 1912 as successor to Richard Willstatter
- Between 1910 -20, extensively studied chemical constituent of natural products (chrysanthemum flowers, pepper, coffee) and prepared chrysanthemic acids, pyrethrins, synthetic piperidine and furfurylthiol as a coffee flavour).
- One of his students from these days **Ruzicka** won the Nobel Prize in chemistry in 1939. Another was **Louis Hammet**, who will later on earn his fame as the founder of the discipline of " Physical Organic Chemistry". Another was **Henry Gilman** who laid the foundations of organometallic chemistry

STAUDINGER : EARLY YEARS

- Staudinger was a practitioner of mainstream organic chemistry, which was already a highly sophisticated and respected science, led by chemists such as Adolf von Baeyer, Emil Fischer, and Richard Willstatter. Although not yet 40, Staudinger was considered a leading organic chemist.

- About 1919, Staudinger decided to leave the safe and familiar field of synthetic organic chemistry to embark into the unknown field of large molecules. His pioneering spirit led him to break away from the typical thinking of traditional organic chemists and to advance new and revolutionary ideas.

- In 1926, he was appointed to a chair at Albert Ludwigs University in Freiburg, where he dedicated all his efforts to establishing and expanding the frontiers of polymer science. His research topics included natural rubber, cellulose, and synthetic polymers such as polyoxymethylene, polystyrene, and polyethylene oxide, which Staudinger considered to be model systems for the much more complex biopolymers.

MISCONCEPTIONS AND ARGUMENTS AGAINST THE EXISTENCE OF POLYMERS

- The major opposition to the concept of polymers came from the emergence of the concept of colloids
- Much of the behavior of polymers were identical to those observed in colloids, using the concepts of Thomas Graham. Miscellar self assembly of small molecules in the absence of covalent bond accounted for most of the properties of polymers
- Harries, between 1902 to 1907 proposed that natural rubber was composed of aggregates of dimethyl cyclooctadiene, held together by non covalent interactions (π – π) between the two double bonds
- Leading scientists of the day (example , Brill) argued that since a large molecule cannot be fitted into the crystallographic unit cell and, therefore, cannot exist. It was believed , based on some early evidence, that only compounds with molecular weight varying between 500-600 Daltons can fit into the dimensions of a unit cell

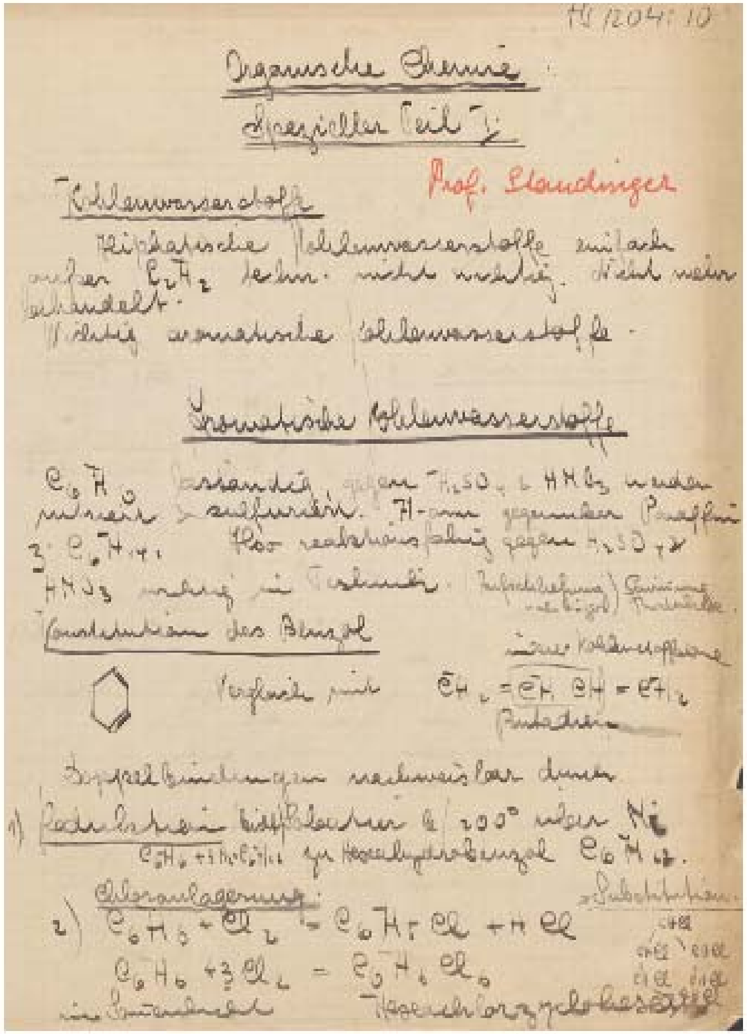
STAUDINGER AND THE ORIGIN OF MACROMOLECULAR CHEMISTRY

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

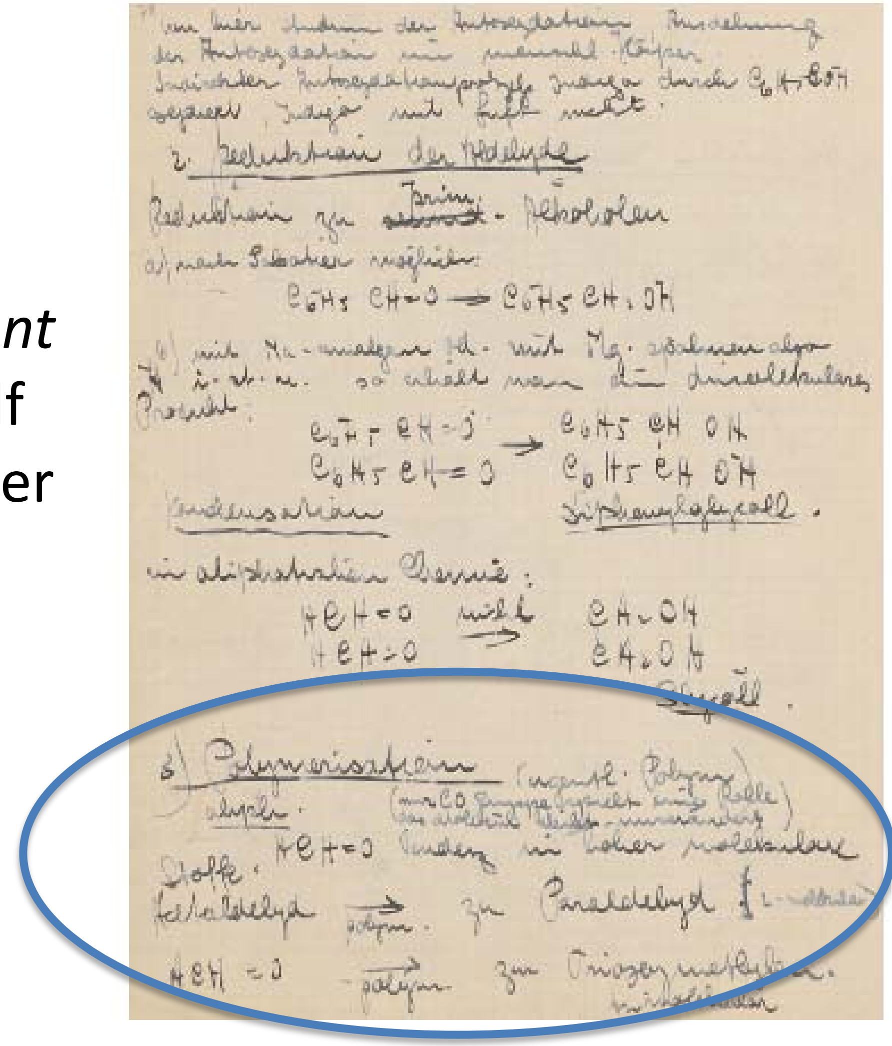
STAUDINGER AND THE ORIGIN OF MACROMOLECULAR CHEMISTRY

- First experimental evidence for existence of long chains came in 1922.Hydrogenation of natural rubber was not accompanied by the formation of volatile cyclic hydrocarbons *(Staudinger and Fritschi,Helv.Chim.Acta,5, 785 (1922)*
- The first definition of macromolecules: "For such colloid particles, in which the molecule is identical with the primary particle, and in which the individual atoms of this colloid molecule are linked together by covalent bonds, we propose for better differentiation the name **macromolecule** *(Staudinger,Ber.Dtsch.Chem.Ges.,57,1203(1924)*
- Much of the rigorous proof for the existence of macromolecules will come from physical measurements (viscosity measurements, molecular weight measurements by ultracentrifuge, osmometry and light scattering as well as X Ray diffraction)
- But being quintessentially an organic chemist, Staudinger was skeptical of physical measurements. Staudinger believed polymers to possess "rigid rod like structure", a belief he will not abandon for several years. When evidence began building up that polymers have flexible chains, Staudinger ignored them.

EXTRACT FROM THE NOTES TAKEN DURING STAUDINGER'S LECTURE IN ORGANIC CHEMISTRY , 1919



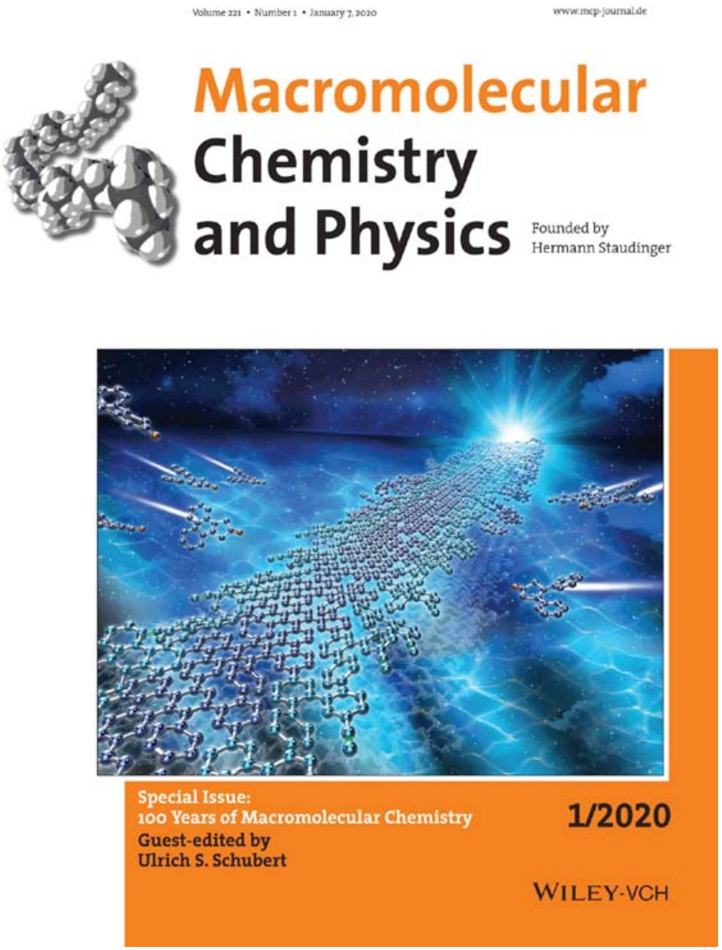
Student
Adolf
Krebser



STAUDINGER : A PROLIFIC WRITER

- Staudinger's research was published in more than 800 publications amounting to more than 10,000 printed pages. He summarized his research in his autobiography, *Arbeitserinnerungen (From Organic Chemistry to Macromolecules)* published in 1970. His collected works, entitled *Das Wissenschaftliche Werk von Hermann Staudinger (The Scientific Contributions of Hermann Staudinger)*, were edited by Magda Staudinger and published between 1969 and 1976.

- For many years, Staudinger's textbook, entitled *Die Hochmolekularen Organischen Verbindungen Kautschuk und Cellulose (The High Molecular Weight Organic Compounds Rubber and Cellulose)*, published in 1932 by Springer in Berlin, was the "bible" of many academic and industrial scientists. In 1947, Staudinger inaugurated the new journal *Makromolekulare Chemie* with Wepf & Company, publishers in Basel.



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Macromolecular Chemistry and Physics

Founded by Hermann Staudinger

Special Issue:
100 Years of Macromolecular Chemistry
Guest-edited by
Ulrich S. Schubert

1/2020

WILEY-VCH

INTERNATIONALER
HISTORISCHER MEILENSTEIN
DER CHEMIE

URSPRUNG DER
POLYMERWISSENSCHAFTEN

Albert-Ludwigs-Universität Freiburg
Baden-Württemberg
1926–1956

Dieses Gebäude ist nach Hermann Staudinger benannt, der in Freiburg von 1926 bis 1956 seine bahnbrechenden Forschungsarbeiten über Makromoleküle durchführte. Seine Theorien über die polymere Struktur von Fasern und Kunststoffen sowie seine späteren Untersuchungen von biologischen Makromolekülen bildeten die Grundlage für unzählige moderne Entwicklungen in den Material- und Biowissenschaften und für das rasante Wachstum der Kunststoffindustrie. Für seine Arbeit auf dem Gebiet der Polymere erhielt Staudinger 1953 den Nobelpreis für Chemie.

American Chemical Society

19. April 1999

GDCh

Gesellschaft Deutscher Chemiker

ACS International Historical Landmark of Chemistry : University of Freiburg

THE TALE OF TWO HERMAN(N)'S :
THE POLYMER PIONEERS

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

Herman Mark
(1895-1992)

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

Hermann Staudinger
(1881-1965)
Nobel Laureate 1953

HERMAN MARK AND INSIGHTS IN THE STRUCTURE OF POLYMERS

- Mark, along with Staudinger and Carothers should be be credited as a cofounder of Macromolecular Science

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

- With Polanyi , Mark began to explore the technique of Crystallography (X Ray and electron diffraction) for the study of organic molecules at Kaiser Wilhelm Institute, where at that time Fritz Haber was the director.

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

Mark presents his results in a meeting of the Society of German Natural Scientists at Dusseldorf in 1926 ; He says that important information can be obtained from unit cells and space groups, even if detailed molecular structures are not known; He proposes that in polymers "lattice forces are comparable to intramolecular forces and the entire crystallite behaves like a large molecule"

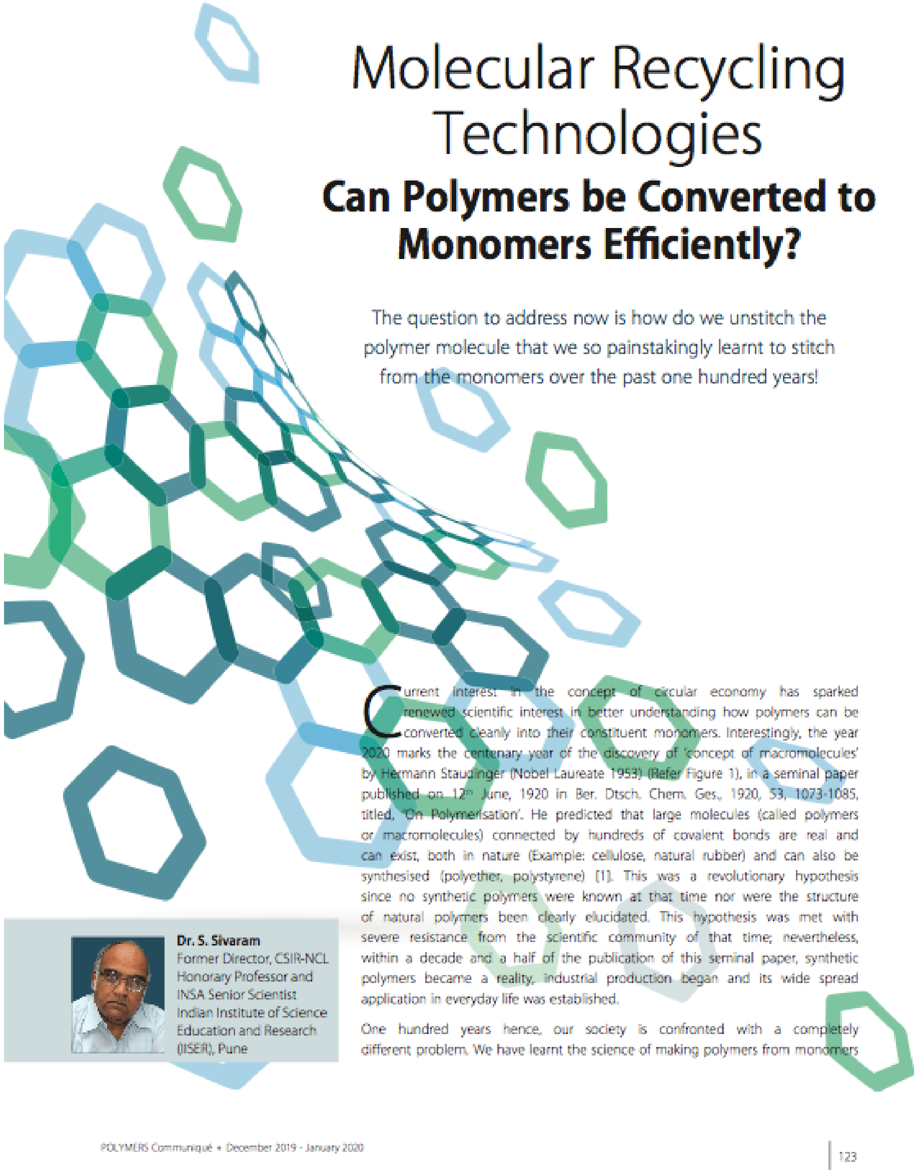
HERMAN MARK AND THE POLYMER INDUSTRY

- In 1926, Mark becomes the Director of research at IG Faben Industries in Ludwigshafen, a large producer of rayon and cellulose acetate. Here he develops the first commercial process for producing styrene
- Mark and Meyer solve the crystal structure of Cellulose in 1928, the first crystal structure of a polymer which reconciles the X-ray pattern with the chemical composition.
- Using X Ray, Mark establishes that natural rubber is a polymer of isoprene, namely, 1,4- polyisoprene and that isoprenes are in a *cis* configuration in the polymer chain

HERMAN MARK AND THE POLYMER INDUSTRY

- It is interesting that although Mark provided the most unequivocal support to the macromolecular hypothesis of Staudinger, he and Staudinger were not in good terms. Staudinger felt that macromolecular chemistry was his field and he looked upon physicists and physical chemists as interlopers, who stole his ideas.
- Mark left IG Farben in 1932 and returned to the University of Vienna . It was in Vienna that he along with Eugene Guth proposed the statistical theory of rubber elasticity and developed the Mark-Houwink relationship, relating dilute solution viscosity of a polymer solution to its molecular weight
- One of his famous students in Vienna was Max Perutz who went on to found the Medical Research Council at Cambridge which became a center of excellence in protein crystallography
- Mark helped Linus Pauling to build the first electron diffraction facility at Caltech, which ultimately led Pauling to delineate the “Nature of the Chemical Bond”

ONE OF THE CHALLENGES FOR THE NEXT CENTURY OF MACROMOLECULES



Molecular Recycling Technologies

Can Polymers be Converted to Monomers Efficiently?

The question to address now is how do we unstitch the polymer molecule that we so painstakingly learnt to stitch from the monomers over the past one hundred years!

Current interest in the concept of circular economy has sparked renewed scientific interest in better understanding how polymers can be converted cleanly into their constituent monomers. Interestingly, the year 2020 marks the centenary year of the discovery of 'concept of macromolecules' by Hermann Staudinger (Nobel Laureate 1953) (Refer Figure 1), in a seminal paper published on 12th June, 1920 in Ber. Dtsch. Chem. Ges., 1920, 53, 1073-1085, titled, 'On Polymerisation'. He predicted that large molecules (called polymers or macromolecules) connected by hundreds of covalent bonds are real and can exist, both in nature (Example: cellulose, natural rubber) and can also be synthesised (polyether, polystyrene) [1]. This was a revolutionary hypothesis since no synthetic polymers were known at that time nor were the structure of natural polymers been clearly elucidated. This hypothesis was met with severe resistance from the scientific community of that time; nevertheless, within a decade and a half of the publication of this seminal paper, synthetic polymers became a reality, industrial production began and its wide spread application in everyday life was established.

One hundred years hence, our society is confronted with a completely different problem. We have learnt the science of making polymers from monomers

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- For over one hundred years we have learnt how to stitch monomers together to make polymers

- Now we must begin to learn how to remove the stitches. We must understand how to convert polymers into monomers

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