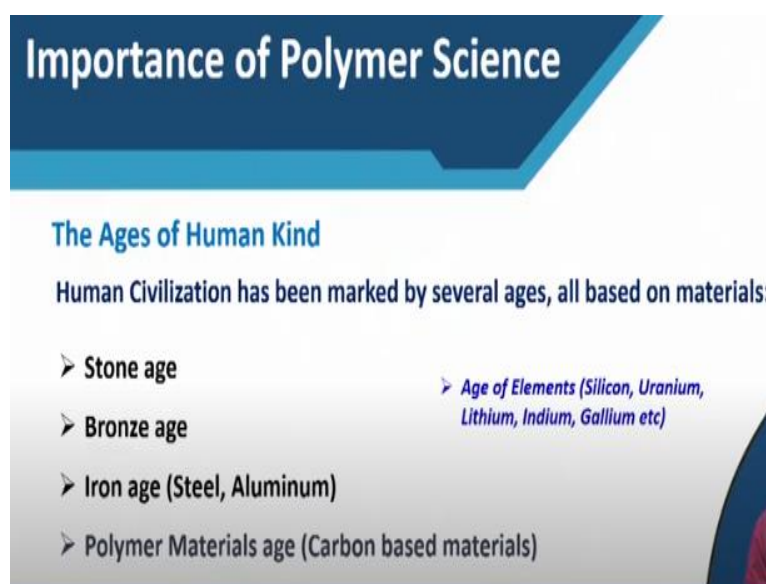


Introduction to Polymer Science
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Lecture - 01
Importance of Polymer Science and Brief Historical Background

Welcome to this course on introduction to polymer science and I am Dibakar Dhara from the Department of Chemistry, IIT Kharagpur. Today we will discuss about the importance of polymer science and I will just give brief historical background of polymer science.

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The slide features a dark blue header with the title 'Importance of Polymer Science' in white. Below the header, the text 'The Ages of Human Kind' is written in blue. A subtitle states 'Human Civilization has been marked by several ages, all based on materials:'. A list of ages follows, each preceded by a blue arrowhead: 'Stone age', 'Bronze age', 'Iron age (Steel, Aluminum)', and 'Polymer Materials age (Carbon based materials)'. To the right of the list, there is a blue arrowhead pointing to the text 'Age of Elements (Silicon, Uranium, Lithium, Indium, Gallium etc)'.

Now the first question of the course is about why we need to get introduced to polymer science. Thinking and going back about the ages of mankind, we will see that human civilization was marked by several ages, and those are all based on the materials which are mostly used for their day to day living and self defence. For example, we have the Stone Age, Bronze Age, Iron Age and now we have Polymer Age. Probably going forward we will have the age of elements, which includes silicon, uranium, lithium, and so on. However currently, we are in the age of polymers.

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“I am inclined to think that the development of Polymerization is, perhaps, the biggest thing that chemistry has done, where it has the biggest effect on everyday life”

Lord Alexander Todd (1907-1997)
President of the Royal Society of London
Nobel Laureate in Chemistry, 1957

Lord Alexander Todd, who was the President of Royal Society of London, and Nobel laureate in chemistry in 1957 once said that “I am inclined to think that the development of polymerization is, perhaps, the biggest thing that chemistry has done, where it has the biggest effect on everyday life”. Now it is known that polymers are one of the most important materials in our everyday life. Irrespective of different industries or various research areas, the basic understanding of polymers is very much essential for getting success in regular activities.

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Polymers are the materials of choice

- One of biggest success stories in new materials development over the last century
- Increasingly replaced conventional materials like wood, metals, stone or ceramics in several applications
- Especially in new material applications, polymers are now very often the materials of choice
- Polymers are everywhere
 - ❖ Plastics
 - ❖ Rubbers
 - ❖ Paints and surface coatings
 - ❖ Resins
 - ❖ Adhesives
 - ❖ Synthetic fibers
 - ❖ Specialty applications

Now why is there the age of polymers? Polymers are the materials of choice as of now and one of the biggest success stories in new materials developed over the last

century. Polymers have replaced and are increasingly replacing conventional materials like wood, metals, stone, or ceramics in more and more applications.

At present, when we think about any new material application, polymers are very often the choice of the material. If you think about plastics, rubber, paints, surface coatings, resins, additives, and several specialty applications, polymers are everywhere.

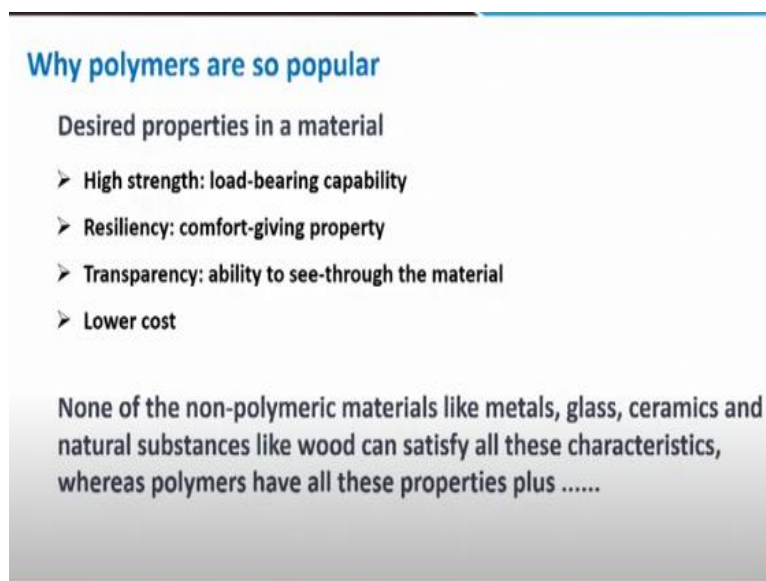
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Some photographs are shown on the areas where the polymers are used and we will find that if we get up in the morning and start brushing our teeth, we use a polymeric material and then get ready for going to our classes or colleges we will wear dresses, clothes, shoes, and these are all made of polymers. We will take a vehicle whether it is a cycle or a scooter or a car, will find many of the components in those vehicles are made up of polymers. And we can see from these photographs that, very commonly used materials are made up of polymers. For example, in several medical applications, you will find that plenty of applications products are made of polymers, which includes some of the applications where the polymers are not visible from outside. For example, a disposable or a biodegradable suture which is using for tying, stitching during operations, artificial heart valve, contact lenses, display devices. There are so many other applications where polymers are hidden inside the device. So basically, the polymers are either seen in applications or they can be also invisible. Hence, we

need to study the behavior of polymers and as a result, we need to get ourselves introduced to polymers sciences.

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Why polymers are so popular

Desired properties in a material

- High strength: load-bearing capability
- Resiliency: comfort-giving property
- Transparency: ability to see-through the material
- Lower cost

None of the non-polymeric materials like metals, glass, ceramics and natural substances like wood can satisfy all these characteristics, whereas polymers have all these properties plus

Why are polymers so popular? When we think about any material applications, we need that the materials should have high strength. That means, it should be able to bear a large amount of load. It should be resilient, which means it should give comfort, soft feeling, and preferably we can have materials that will have transparency, and of course if anybody wants to have all these properties at a lower cost. The conventional non-polymeric materials like metal, ceramics, glass, wood etc do not satisfy all these characteristics. For example, if you consider glass, they are having very high strength and can bear a high load but the problem is that it is brittle. So, we need to be very careful while using, otherwise glass breaks and there is a hazard involved in that.

To talk about metal, metals are very difficult to get in a transparent condition, and also prolonged use in ambient conditions results in corrosion. Besides of course, these materials are much heavy material. We want a material which would be light so that it can be carried easily and transport cost comes down. So, polymers give or satisfy all these properties.

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Other beneficial properties of polymers

- Durable: stable against hydrolysis and electrochemical corrosion
 - Lighter weight: excellent strength - weight ratio
 - Design flexibility: low-cost and low-energy processing, with high freedom of design and styling
 - Thermal and electrical insulator
 - Provides many options
 - Feedstock flexibility
 - ❖ Petroleum fractions
 - ❖ Natural gas
 - ❖ Coal
 - ❖ Agricultural and forest products and biomass as alternative
- Petrochemical industry

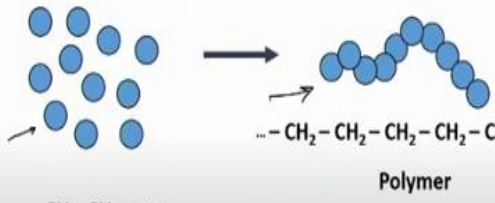
So, other beneficial properties of the polymers are that they are durable. The polymers are made of mainly carbon, along with hydrogen, oxygen. Most of the regular plastics or polymers which we use are hydrophobic in nature. As a result, they are resistant to hydrolysis and are stable against electrochemical corrosion. They are very light. So, if we consider the strength versus weight, the polymer gives the maximum strength versus weight ratio. For a given weight of the material, we can achieve high strength in polymers. Polymers give the design flexibility because the melting temperature or processing temperature of polymers is much lower. So, we can make products of polymers at a low cost and spending much lower energy and because of the easy melting of the polymers, a lot of polymeric products can be designed as per choice. So basically it gives you design flexibility. Polymers are generally thermal and electrical insulators which is a big advantage. Additionally, it gives feedstock flexibility as most polymers are made from petroleum fractions, though they can be also made from natural gases and coal. Some polymers can also be made from agricultural and forest products and biomass as an alternative resource. Mostly polymers are made from synthesized petroleum products. So that means, polymers are part of the petrochemical industry. So basically when we talk about polymer industries, we talk about petrochemical industries like we have Haldia Petrochemicals which produces polymers. We have Reliance Petrochemicals, which also produces polymers and there are similar other petrochemical companies producing polymers as well.

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Origin of Polymer Properties

What are Polymers?

Large molecules (macromolecules) – consist of many repeating structural units



$\text{CH}_2=\text{CH}_2$ Monomers



Polymer

... - $\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\dots$


Mainly based on organic compounds

So what is the reason for such good properties exhibited by polymers? For that, we just briefly know what are polymers. If we look at what polymers are, we know that polymers are large molecules, or macromolecules, which consist of many repeating structural units. So pictorially we can show that we have small repeating units which are linked with each other through covalent bonds to produce a large molecular weight. Polymers are mostly made from organic molecules that give light weight and other beneficial properties.

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Short Molecules	Long Molecules
	
<ul style="list-style-type: none">• Too short to entangle• Can separate easily• Behave independently	<ul style="list-style-type: none">• Completely entangled• Molecules can not easily move independently
<p>Bowl of Rice</p>	<p>Bowl of Noodles</p>

High MW help in providing superior properties like high tensile strength, impact resistant, toughness, melt viscosity, high melting temperature, etc.

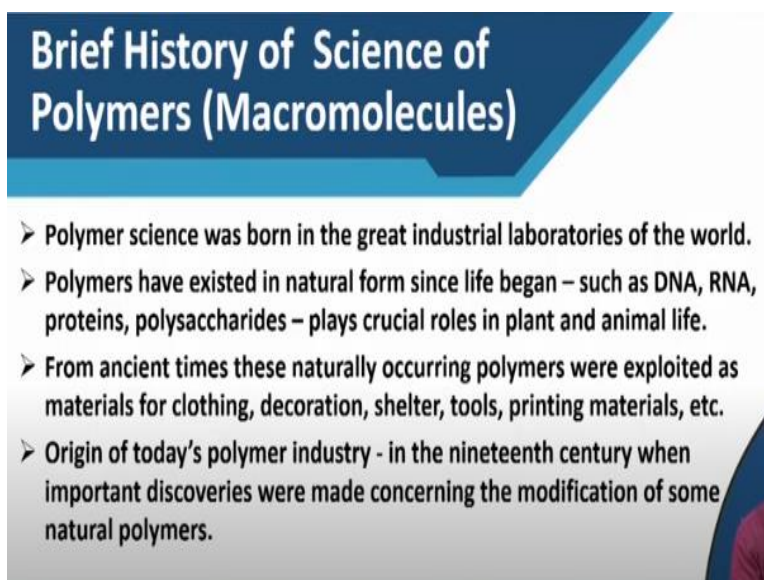


If we want to compare a small molecule and a polymer molecule, we imagine small molecules as grains of rice in a bowl. We can put a spoon and easily take out a spoon

of rice from it. That is possible because the rice grains are small, so they do not entangle with each other and we can easily separate them. The individual molecules, in this case, the rice grains, behave independently. They do not interfere with the movement of other molecules. Now when we compare polymeric molecules, because they are large, it is found that they are entangled like if we have a bowl of noodles. Then we put the spoon and want to take it out, we cannot take a single chain of noodles from the sample or the bowl. Because of the large length, they are entangled with each other. So polymer molecules are completely entangled and as a result the molecules cannot move independently.

Now this gives the advantageous properties like strength of the polymers and the toughness of the polymers. The polymer chains, as they are entangled, if you apply some force, they can easily dissipate the force and exhibit high strength and toughness and so on. The high molecular weight helps in providing superior properties like high tensile strength, impact-resistant, toughness, melt viscosity etc.

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Brief History of Science of Polymers (Macromolecules)

- Polymer science was born in the great industrial laboratories of the world.
- Polymers have existed in natural form since life began – such as DNA, RNA, proteins, polysaccharides – plays crucial roles in plant and animal life.
- From ancient times these naturally occurring polymers were exploited as materials for clothing, decoration, shelter, tools, printing materials, etc.
- Origin of today's polymer industry - in the nineteenth century when important discoveries were made concerning the modification of some natural polymers.

So we will now look at the brief history of polymers. As we already know that polymers are nothing but macromolecules. These two terms polymers and macromolecules are often used synonymously. Polymer science is unlike the normal or typical areas of physics and chemistry, where first there is a strong theoretical basis based on which the subsequent research and industrialization happened. Polymer science is the other way around. Initially, polymer science was born in the great industrial laboratories of the world. Before a basic understanding of polymers,

polymer-related industries were up and running. Polymers existed in natural form for a long time till life began. For example, in our body, we have DNA macromolecules like DNA, RNA, proteins, and polysaccharides, which play a crucial role in plants and animal life. You know from ancient times these naturally occurring polymers were exploited by man for making several items, like they were used for clothing, decoration, shelters, tools, and also for printing materials, etc.


So the origin of today's polymer industry happened in the 19th century when important discoveries were made, related to the modification of some of these natural polymers. So basically, the first research on polymers happened in the 19th century when people or scientists tried to modify, took these natural polymers, and modified them for making or improving their properties.

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Before 1907 – only modified natural materials

Material	Year	Discovered by
NATURAL RUBBER	1839	GOODYEAR -
VULCANITE	1843	HANCOCK .
GUTTA-PERCHA	1843	MONTGOMERIE
SHELLAC	1856	CRITCHLOW
BOIS DURCI	1856	LEPAGE
PARKESINE	1862	PARKES
XYLONITE	1869	SPILL
CELLULOID	1870	HYATT
CELLULOID PHOTOGRAPHIC FILM	1889	GOODWIN
VISCOSE	1892	CROSS, BEVAN & BEADLE
CELLULOSE ACETATE	1894	CROSS & BEVAN
CASEIN	1903	KUNTH
BAKELITE	1907	BAEKELAND

In 1907, first fully synthetic polymer "Bakelite" was invented by Leo H Baekeland from reaction of phenol and formaldehyde.
Commercial production: 1910




<http://plastiquarian.com>

Some of the examples of those research are shown here. For example, if we talk about Goodyear, who found that heating natural rubber with sulfur increases the elasticity of the natural rubber and also tackiness, which is very beneficial for use of natural rubber. Later, Hancock and Goodyear found that if we use a large amount of sulfur and heat with natural rubber we can make very hard rubber which is called vulcanite. And later Hancock was granted a patent in England and then Charles Goodyear's brother Nelson Goodyear was granted a patent in the US in 1851 for vulcanite. There was also cellulose nitrate, or nitrocellulose, used for several applications like celluloid and celluloid photographic films and so on.

Before 1907, there was a lot of research that happened for the modification of these natural polymers but in 1907 the first fully synthetic polymers were invented by Leo H. Baekeland by reaction of phenol with formaldehyde, and the product was called Bakelite. And it went to commercial production in 1910. So Bakelite was the first fully synthetic polymer invented by Leo H. Baekeland from the reaction of phenol and formaldehyde.

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The Dawn of the Chemical Industry: The Manufacture of Bakelite



Leo H Baekeland (1863-1944)

- Leo Baekeland was trying to invent a substitute for Shellac, then wholly supplied by India to the world
- In the process he made the first man made polymeric material, beginning the age of plastics
- Heat resistant and insulating
- He founded a company called Bakelite Corporation in 1910 to manufacture the product

US Patent # 942,699; December 7, 1909

So he was granted US patent in 1909, following which in 1910 this product was commercialized. He was trying to invent a material that was a substitute for Shellac, which was then solely supplied from India to the world. In the process, he made the first man-made polymeric material, which started the age of plastics or polymers. The material was heat resistant and insulating and he founded a company called Bakelite Corporation in 1910 to manufacture this product. Till now, during these inventions and also modification of these natural polymers, there was no understanding about the nature of the polymers.

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The Concept of “Macromolecules”

- Polymer industry was running well without proper understanding of the nature of polymers.
- For over a century, scientists believed that the polymers consisted of physically-associated aggregates of small molecules like micelles of surfactants.
- In 1920, Hermann Staudinger, then professor of organic chemistry at the Eigenössische Technische Hochschule in Zurich, first conceived that polymers are made of very large molecules containing large sequence of simple chemical units linked together by covalent bonds.

The polymer industry was running well without a proper understanding of the nature of polymers. And for over a century, scientists believed that the polymers consisted of physically associated aggregates of small molecules like micelles or surfactants. Only in 1920 Hermann Staudinger, a professor of organic chemistry at ETH Zurich, first conceived that the polymers are made of very large molecules containing a large sequence of simple chemical units linked together by a covalent bond. So, this is the first time somebody conceived that polymers are large molecules that were made of by linking the repeating units by covalent bonds.

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Hermann Staudinger: Father 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 intuition and imagination, he proposed that polymers were composed of large number of repeating units linked together by covalent bonds (“Über Polymerisation”; Ber. Dtsch. Chem. Ges., 53, 107, 1920). At that time he had no experimental evidence for his hypothesis.
- *2020: The Year of Polymers – 100 Years of Macromolecular Chemistry*
- The scientific community was very reluctant to admit the existence of extremely large compounds with molecular weights exceeding 5000. Instead, micelle-type aggregates, as observed for soap molecules, were considered to account for the unusual properties of such materials. Moreover, some scientists were convinced that the size of a molecule could never exceed the size of the unit cell, as measured by X-ray crystallography.
- Staudinger persevered in spite of being criticized by the scientific community.



Hermann Staudinger
(1881-1965)





That is the reason why Hermann Staudinger is considered as the father of macromolecular chemistry. So he propounded the revolutionary concept that macromolecules can be formed by linking a large number of small molecules using covalent bonds. He could not give experimental evidence to prove the fact. So basically, from his intuition and imagination, he proposed and published a paper titled *Über Polymerization* in the journal in 1920. That is the year, which has been considered as the start or beginning of macromolecules as a science. This year 2020 is the 100th year of macromolecular chemistry and that is the reason this year has been celebrated by many chemical societies and chemists across the globe as 100 years of macromolecular chemistry.

However, it was not easy for him to convince the scientific community. The contemporaries were very reluctant to admit the existence of extremely large molecules with molecular weight exceeding 5000. As mentioned earlier, they believed that these polymers are nothing but micelle-type aggregates as observed for soap molecules which accounts for the unusual properties of these polymeric materials like high viscosity and so on. Moreover, some scientists were convinced that the size of a macromolecule or molecule could not, could never exceed the size of the unit cell as measured by X-ray crystallography. But Staudinger did not give up. He tried and convinced the rest of the scientific community and to do that he performed additional experiments.

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Hermann Staudinger: Father of Macromolecular Chemistry

- Staudinger, following the scientific tradition of classical organic chemistry, presented sound experimental evidence to support the existence of high molecular weight polymers
- Staudinger's hydrogenation experiments on natural rubber showed that hydrogenated rubber was very similar to normal unsaturated rubber.
- During the late 1920s, Staudinger provided additional evidence based on viscometry to confirm that molecular weights remained unchanged during chemical modification of polymers.
- Despite the impressive experimental evidence, Staudinger continued to encounter very strong opposition from eminent scientists of the period, notable amongst them, Emil Fischer and Heinrich Wieland, both were Nobel prize winners
- By the end of the 1920s and during the 1930s, Staudinger's macromolecular concept found increasing acceptance by other chemists especially due to work of Herman Mark and Wallace H. Carothers. *Staudinger was finally awarded Nobel Prize in 1953.*







He used the traditional classical organic chemistry experiments to support the existence of high molecular polymers. His experiments on the hydrogenation of natural rubber did not show any dissimilar properties to normal hydrogenated, unsaturated rubber. During the late 1920s, Staudinger provided additional evidence based on viscometry to confirm that the molecular weights remain unchanged during the chemical modification of polymers. Despite these impressive experiments, Staudinger continued to encounter very strong opposition from eminent scientists of that period. Some of the noted among them were Emil Fischer and Wieland and both were Nobel Prize winners.

A young scientist who is proposing something from imagination and intuition, which was opposed by the Nobel laureates, must be a genius as he fought for convincing others about his concept that polymers are indeed made up of large macromolecules. But at the end of the 1920s and during the 1930s Staudinger's macromolecular concept found increasing acceptance by other chemists. That was especially due to the work by Herman Mark and Wallace H. Carothers and finally, in 1953, Staudinger was awarded the Nobel Prize for his discovery of his work on macromolecular chemistry.

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Pillars of Macromolecular Chemistry

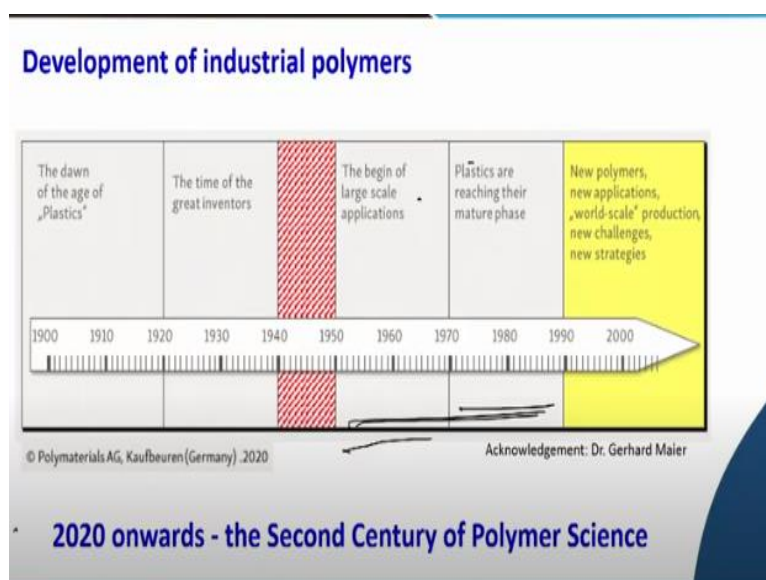
			Developed fundamental understanding, both theoretical and experimental, in the physical chemistry of macromolecules
Herman F Mark (1895-1992)	Wallace H Carothers (1896-1937)	Paul J Flory (1910-1985)	
X Ray Crystallography of Macromolecules to show that a molecule could be larger than its unit cell (1926-28)	Confirmed the existence of molecules of extremely high molecular weight, but led as well to the development of nylon, the first totally synthetic fiber used in consumer products.	1974 Nobel Prize in Chemistry	

We need to talk about other pillars of macromolecular chemistry. Herman F. Mark was a crystallographer, who helped Staudinger to convince that the molecules can have a molecular weight of more than 5000 or it can be larger than a unit cell. So basically, he was one of the stalwarts who helped Staudinger to convince the scientific

community that polymers are indeed large molecules. William H. Carothers confirmed the existence of molecules of extremely high molecular weight and he led and developed the first fully synthetic fiber which are used for consumer products. He first invented linear polymers from condensation polymers and used them for making polyamides.

Later Paul J. Flory developed a fundamental understanding of both theoretical and experimental physical chemistry of macromolecules. So basically Staudinger along with these three other scientists Herman F. Mark, Wallace H. Carothers, and Paul J. Flory should be considered as the pillars of macromolecular chemistry.

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Now following this understanding, there was plenty of activities among scientists for developing new polymers. Also, there was large-scale polymer production happening during the 1950s to 1970s and which continued till the 1990s. So basically, in this time-frame, the polymers were discovered which was facilitated by the cheap availability of petrochemicals.

Now, when we move forward to the new millennium and beyond 2020 polymer sciences are looking for newer applications or more specialized applications for polymers. So basically from 2020 onwards, we have the second century of polymer sciences.

So in the next lecture, we will talk more about polymers as a whole, give the bird's eye picture of the polymer as a product and then talk about what is the problem of polymers and what are the present research needs for polymer science.