



NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 302

COURSE TITLE: POLYMER CHEMISTRY I

CHM 302: POLYMER CHEMISTRY I [2 UNITS]

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COURSE GUIDE

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1. Introduction

Polymer Chemistry 1 is a two units compulsory organic chemistry course. The course code is CHM 302 and is available to all students offering B.Sc Chemistry in the School of Science and Technology, NOUN. Polymer chemistry is a special field of organic chemistry that studies the **formation, structures, reactions, modifications and properties of polymers**, as well as its **degradations** and **recycling**. They can be natural or synthetic polymers. Polymer Chemistry has since grown from studying natural to synthetic polymers paving way to obtaining new polymers with greater uses and applications, serving us in our basic needs of **food, clothing and shelter**, to others like giving physiological aids to the blind, crippled, dumb, aids for heart problems and so on; protective wears, insulators, domestic and industrial appliances etc. There are two basic chemical reactions by which polymers are formed: addition chain-growth polymerizations and condensation step-growth reactions. The polymers are of variable structures which determine their specific properties. The reactions are continually receiving modifications for improvements and productions of high quality polymers. It is important to stress that properties of polymers are determined greatly by its structures, and what makes them special is the very large giant size of polymers having amu of up to millions and more.

2. Learning outcomes (aims and objectives)

The course is aimed at sensitizing learners with

- (a) basic information on polymers as giant molecules formed from joining of units called monomers; the method by which it occurs is called polymerization reactions.
- (b) the big sizes of polymers' structures determine its properties and importance.
- (c) today, polymer compounds are very important to our modern life and developments. Many new innovations are being introduced to studies of polymers, which are not only studied in chemistry, but also polymers are studied in other fields like Engineering, Pharmaceutical, Medicine, Agriculture etc.

3. Course requirements (course materials, study units, text books, assignment file e.t.c.)

The course material contains six modules [1-6]. There are all together fifteen study units distributed within the six modules. The following textbooks are recommended for the six modules. Other relevant references and literature are listed at the end of each study unit along with these:

- T.L. Brown; H.E. LeMayJr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International p. 499-513.
- P.Y. Bruice (2007): Organic Chemistry. 5th Edition. Pearson Education Inc. p. 1232-1257.
- R.T. Morrison and R.N. Boyd (2008): Organic Chemistry. Macromolecules. Polymers and Polymerization. 6th Edition. Prentice-Hall of India, (PHI) Private Ltd., p. 1077-1096.
- I.L. Finar (2008). Organic Chemistry Vol.1 6th Edition Pearson Education. P.114-118.
- L.G. Wade,Jr and M.S. Singh (2008). Organic Chemistry 6th Edition. Pearson Education p. 330-363.
- Philip Matthews (2004). Advanced Chemistry- Polymers; Polymers and Industry p.879-897.
- M. Clugston and R. Flemming (2000). Advanced Chemistry- The Polymerization of Ethene, The mechanism of polymerization, Revisiting Polymerization 1&2. p. 514-517.

The student activities in red, numbered from A, are to be attempted fully by learners. Their attempts are to be submitted in files at the centers nearest to them for progress monitoring and assessments.

4. Information about assessment (assignment and examination, grading etc)

Assessments will be collated and graded on assignments [student activities in red], observations, recordings, inferences, attempts of TMAs [TMAs are in green, they must be well attended to], and final written examination on the course on specified days.

5. Course overview (how many units, modules etc)

There are six modules in this course, comprising of fifteen study units distributed within the six modules. Module 1 has three units 1-3; Module 2 has two units 1&2; Module 3 has four units 1-4; Each of Modules 4, 5 and 6 has two units 1&2 each. As much as possible compounds are expressed in their IUPAC form; Units are expressed in S.I. units.

6. Strategies for studying the course (tutors & tutorials)

The pattern of presentation of CHM 302 course material is very simple and practical. Familiar and everyday examples of polymers around us are quoted. Questions asked from learners have most of their answers from the study units they are placed. Learners should have their writing materials near them when studying this course, for jottings and attempting simple exercises within each study units. This will foster coherence. Some part of studying this course will require you consult the internet to gain assess to websites, and important information on polymer chemistry. Also take note of words that are bolded. Analogies and problem-solving approaches are utilized to make the course more practical and aid fast understanding of learners.

7. Summary

We have discussed the Course Guide. It introduced these macromolecules as many units called monomers joining to form the whole called polymer, by method of polymerization reactions. The aims and objectives of the course have been stated with the course requirements. Information has been given about assessments and the course overview as consisting of six modules 1-6. There are fifteen study units within this course (CHM 302). To fully understand and participate in this course, basic strategies for studying the course have been stated.

Course Material contains six Modules with fifteen units distributed within the six modules. Each unit has at least two standard TMAs at the end of it written in green. At the end of each logical and short question are detailed answers to the TMAs in blue, all are at the end part of the course material.

COURSE MATERIAL

FOR

CHM 302: POLYMER CHEMISTRY I [2 UNITS]

Course Outline:

The nature of Polymer nomenclature; Outline of sources of raw materials for polymers; Polymerization process, condensation polymerization in details; Solubility and solution properties of polymers; Structures and properties of polymers; Fiber forming polymers.

PRE-AMBLE

Polymer is derived from the Greek words: '*Poly* meaning many, and *meros* meaning parts.' Polymer therefore implies **MANY PARTS**. The parts are units called **monomers**. How does the many parts form the whole? Polymers are formed by processes of **POLYMERIZATION**.

COURSE MATERIAL

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Module 1: Nature of Polymers and their Nomenclature

Unit 1: Introduction to Polymer Chemistry and Nomenclature

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1.0 Introduction

Polymer is derived from the Greek words: '*Poly* meaning many, and *meros* meaning parts.' Polymer therefore implies **MANY PARTS**. The parts are units called **monomers**; hence polymers are derived from large number of repeating units called **monomers**. The process by which this is achieved is called **polymerization**. Some are biopolymers because they are naturally occurring, while many are synthetic polymers. Many important products which make us comfortable are polymers.

2.0 Objectives

At the end of this unit you should be able to

- define polymer
- show that polymers are obtained by polymerization reaction
- give the general formula of polymers, and names
- appreciate the diverse uses of polymers and some distinct scientists that contributed to establishing polymer chemistry
- give highlights on the work and findings of specific scientist that contributed to polymer chemistry
- know that all polymers are macromolecules, but not all macromolecules are polymers

3.0 Introduction

A **polymer** (from Greek means: much, many and part) is a large molecule (macromolecule) composed of repeating structural units typically connected by covalent chemical bonds. The term '*polymer*' refer to large class of natural and synthetic materials with varieties of properties. We will be concerned in polymer Chemistry with the structures, properties and preparations of important polymers. How to obtain them should be paramount in mind.

3.1 General Information on Polymers

Polymers are **giant organic compounds** composed of many repeating units called **monomers**, with high relative molecular masses ranging from not less than several hundreds, to thousands or even millions. They are also referred to as **macromolecules**, but not all macromolecules are polymers! General molecular formula of polymers is usually represented as $[-\text{monomer(s)}-]_n$ where 'n' is a range of large numbers that are not fixed. Polymers can be obtained from nature (Natural polymers), and they are also synthesized (Synthetic polymers). The reaction that leads to the formation of polymers is called **polymerization**. Natural polymers, also known as biopolymers include natural rubber (latex), nucleic acids, proteins, polysaccharides, wool, silk and cotton. For example, natural rubber has a molecular weight of 12,000; starch, 40,000; and proteins, 1000-1,000,000. Processes of polymerization involve simple processes of addition, condensation and cyclization reactions, to more complex and combined reactions.

Polymer compounds are very useful in day-to-day activities of man. Useful polymers are utilized in cosmetics, paints, clothing and wears, agricultural implements, plastics and rubber, vulcanization, wrappers, furniture, compact discs, photographic films, parts of automobiles, soles of shoes, packs, glues, toys, bottles and flasks, electrical insulators and so on. Polymer products also serve as physiological aids to the crippled, people with heart problems, providing hearing and vision aids, protective wears and goggles, industrial and domestic appliances.

Activity A: Why are all polymers macromolecules, while all macromolecules are not polymers?

Answer: Macromolecules without repeating units called monomers, though with large molecular weights [10^2 s to 10^6 s] are not polymers. If macromolecules are not formed by the process of polymerization reaction between monomers, they are not polymers.

3.2 Polymer nomenclature

There are multiple conventions for naming polymer substances. Many commonly used polymers, such as those found in consumer products, are referred to by a common or trivial name. The trivial name is assigned based on historical precedent or popular usage rather than a standardized naming convention. Both the American Chemical Society and IUPAC have proposed standardized naming conventions; the ACS and IUPAC conventions are similar but not identical. Examples of the differences between the various naming conventions are given in the table below:

Table 1: 1 Common, ACS and IUPAC Names of Polymers

Common Name	ACS Name	IUPAC Name
Polyethylene	Polyethylene	Polyethene
Poly (ethylene oxide) or (PEO)	poly(oxyethylene)	poly(oxyethene)
Poly (ethylene terephthalate) or (PET)	poly (oxy-1,2-ethanedioxy-carbonyl phenylenecarbonyl)	poly (oxyetheneoxyterephthaloyl)
Nylon	poly[amino(1-oxo-1,6-hexanediy)]	poly[amino(1-oxohexan-1,6-diy)]

In both standardized conventions, the polymers' names are intended to reflect the monomer(s) from which they are synthesized rather than the precise nature of the repeating subunit. For example, the polymer synthesized from the simple alkene ethene is called polyethylene, retaining the -ene suffix even though the double bond is removed during the polymerization process:

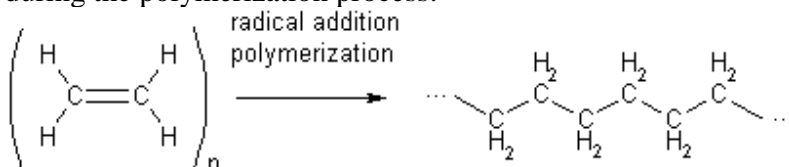
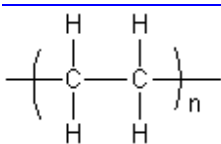


Fig 1: The polymerisation of ethene into poly(ethene)



3.3 Some distinct Polymer Scientists

Earlier in the 19th century many scientists like *Alexander Parke*, *John Wesley Hyatt*, *Louis Chardonnet*, *Hermann Staudinger* synthesized many useful polymers. Before this time *Jons Jakob Berzelius* formed the word **polymer** meaning in Greek language 'many parts'. They showed that polymers are long chains of monomers linked together. Not until recently is much appreciation given to studies on **Polymer Chemistry**, which is a major aspect of studies on **Material Science**.

3.3.1 Alexander Parkes who was born on 29th December 1813, and lived till 29th June 1890 a native of Birmingham, England. He was a metallurgist and invented the first thermoplastic celluloid based on nitrocellulose with ethanol as solvent. He called it 'Parkesine' the first man-made plastic. The material anticipated many of the modern aesthetic and utility uses of plastics. It was first exhibited at the 1862 London International Exhibition. A. Parkes has a total of 66 patents on developing processes and products related to electroplating and plastic. Some of his outstanding works are summarized thus:

In 1850 he developed and patented the Parkes process for economically desilvering lead, also patenting refinements to the process in 1851 and 1852.

In 1855 he developed Parkesine - the first thermoplastic - a celluloid based on nitrocellulose with the solvent ethanol. This material, exhibited at the 1862 London International Exhibition, anticipated many of the modern aesthetic and utility uses of plastics.

In 1866 he set up The Parkesine Company in London for bulk low-cost production. It was not, however, a commercial success as Parkesine was expensive to produce, prone to cracking and highly flammable. The business closed in 1868.

Parkes' material was developed later in improved form as Xylonite by his associate D. Spill, who brought a patent infringement lawsuit against J.W. Hyatt who developed celluloid in the U.S. It was ultimately unsuccessful because in 1870, the judge ruled that it was Parkes who was the true inventor due to his original experiments.

Remembrance of Parkes are made at many locations. Plastics Historical Society put up a blue plastic plaque in 2002 in his home town Dulwich, London. He was commemorated

by The Birmingham Civic Society who erected a blue plaque in 2004 on the original Elkington Silver Electroplating Works.



The blue plaque on the old Birmingham Science Museum

3.3.2 John Wesley Hyatt

He lived November 28, 1837 to May 10, 1920 an American inventor, who contributed to the development of celluloid with his brothers, and began producing in 1872. He also invented the Hyatt filter, a means of chemically purifying water while it is in motion; a widely used type of roller bearing; a sugarcane mill superior to any previously used; a sewing machine for making machine belting; and a substitute for ivory in the manufacture of billiard balls and other articles. Hyatt's eventual result was a commercially viable way of producing solid, stable nitrocellulose, which he patented in the U.S. in 1869 as "Celluloid" (US patent 50359; now a genericized trademark). In 1870 Hyatt formed the Albany Dental Plate Company (later renamed the Celluloid Manufacturing Company) to produce billiard balls, false teeth and piano keys,^[1] among other products.

In parallel, a third English inventor, Daniel Spill, had independently developed essentially the same product, which he patented in the UK as "Xylonite". Spill later pursued Hyatt in a number of costly court cases between 1877 and 1884. The eventual decision was that the true inventor of celluloid was Parkes, but that all manufacturing of celluloid could continue, including Hyatt's. Hyatt's other patented inventions include roller bearings and a multiple-stitch sewing machine.

3.3.3 Louis Chardonnet

L. Chardonnet is a French chemist who lived 1839 to T1924. He invented rayon and produced artificial silk from nitrocellulose.



The French chemist L.M.H.B. Chardonnet, who invented rayon.

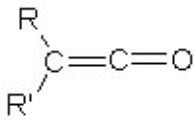
Louis-Marie-Hilaire Bernigaud, comte de Chardonnet, was born in Besancon, France. He is credited with having developed artificial silk, which came to be known as rayon. Around 1860s Chardonnet, originally trained as an engineer, assisted Louis Pasteur in an effort to save the French silk industry from an epidemic affecting silkworms. In 1878, while working in a photographic darkroom, Chardonnet accidentally overturned a bottle of nitrocellulose. When he started to clean up the spill, he saw that the nitrocellulose had become viscous due to evaporation. As he wiped it, he noticed long, thin strands of fiber resembling those of silk. Chardonnet began to experiment further with the nitrocellulose. He worked with the silkworm's food, mulberry leaves, turning them into a cellulose pulp with nitric and sulfuric acids, and stretched the resulting pulp into fibers. This fiber, cellulose nitrate, could be used in garments, but it was highly flammable. Some garments made of this early artificial silk reportedly burst into flame when a lit cigarette was nearby. Chardonnet solved this problem by denitrating these fibers with ammonium sulfide, which reduced the flammability of the material without sacrificing its strength. Chardonnet received his first patent for artificial silk in 1884 and began manufacturing the material in 1891. In 1924 artificial silk came to be known as rayon.

3.3.4 Hermann Staudinger

Hermann Staudinger (23rd March 1881 to 8th September 1965), is a German chemist from Worms who demonstrated the existence of macromolecules which he characterized as polymers. For this work he received the 1953 Nobel Prize in Chemistry. He is also known for his discovery of ketenes and of the Staudinger reaction.

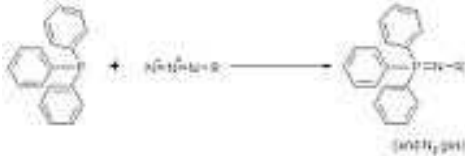


After he got his Ph.D. from the University of Halle in 1903, Staudinger took a position at University of Strasbourg where he discovered the ketenes.



Ketene [R,R' = H or alkyl]

Ketenes are synthetically-important intermediate for the production of yet-to-be-discovered antibiotics like penicillin and amoxicillin. In 1907, Staudinger began an assistant professorship at the Technical University of Karlsruhe where he successfully isolated a number of useful organic compounds (including a synthetic coffee flavoring) as more completely reviewed by Mülhaupt. In 1912, Staudinger commenced studies that led to discovery of the Staudinger reaction at the Swiss Federal Institute of Technology in Zurich, Switzerland. One of his earliest discoveries came in 1919, when he and colleague Meyer reported that azides react with triphenylphosphine to form phosphazide and gaseous nitrogen by way of the reaction commonly referred to as the Staudinger reaction with a high yield of phosphazide.



At Zurich, Staudinger while here started research in the chemistry of rubber, measuring high molecular weights by the physical methods of Raoult and van't Hoff. Contrary to prevailing ideas as stated below. Staudinger proposed in a landmark paper published in 1920 that rubber and other polymeric substances such as proteins, starch and cellulose are long chains of short repeating molecular units linked by covalent bonds some are in a head-to-tail fashion. In other words, polymers are like chains of paper clips, made up of small constituent parts linked from end to end thus:



This period, leading organic chemists like Heinrich Wieland and Emil Fischer believed that the measured high molecular weights were only apparent values caused by the aggregation of small molecules into colloids. At first the majority of Staudinger's colleagues also refused to accept the possibility that small molecules could link together covalently to form high-molecular weight compounds. Mülhaupt aptly noted that this is due in part to the fact that molecular structure and bonding theory were not fully understood in the early 20th century.

Evidences which supported Staudinger's hypothesis came-up in the 1930s. High molecular weights polymers were confirmed by membrane osmometry, and also by Staudinger's measurements of viscosity in solution. X-ray diffraction studies of polymers by Herman Mark provided direct evidence for long chains of repeating molecular units. Also the synthetic work led by Carothers demonstrated that polymers such as polyesters and nylon could be prepared by well-understood organic reactions.

Staudinger's elucidation of the nature of high-molecular weight compounds which he termed *Makromoleküle* tremendously led to the birth of the studies of polymer chemistry. Staudinger himself saw the potential for this science long before it was fully realized. "It is not improbable," Staudinger smartly commented in 1936, "that sooner or later a way

will be discovered to prepare artificial fibers from synthetic high-molecular products, because the strength and elasticity of natural fibers depend exclusively on their macromolecular structure – i.e., on their long thread-shaped molecules.” Staudinger founded the first polymer chemistry journal in 1940, and in 1953 received the Nobel Prize in Chemistry for “his discoveries in the field of macromolecular chemistry.” His pioneering research has afforded the world myriad plastics, textiles, and other polymeric materials which make consumer products more affordable, attractive, and fun.

Activity B: Download from the internet the polymer invented and processes of three of above mentioned scientists.

3.4 Introduction to more classifications and nomenclature of Polymers

Polymers can be classified into types depending on their chemical mode of formation or on their physical properties and forms.

Based on their physical nature we have the following polymers: elastomers, fibers, resins, plastics, plasticizers, thermoplastics, thermosetting, nylons, polyesters, acrylonitriles.

Polymers can be grouped depending on their chemical nature as: (i) Type of reaction leading to their formation- addition polymers, and condensation polymers; (ii) Type of functional group in monomers, number and their linkages- bifunctional, trifunctional polymers, linear, cross-linked polymers, homopolymers, copolymers and terpolymers. Each of these groupings will be well explained in the next two units, and in module 5.

Activity C: Give brief explanation on each of the groupings of polymers listed in 3.4 above, based on the physical and chemical natures as stated above.

4.0 Conclusion

Polymers are long chains of monomers linked up by polymerization to form high molecular weight macromolecules of several hundreds to thousands and a times millions, which are very useful to man. Names of simple polymers usually reflect the type of monomer(s) they are formed from. Not less than four distinct polymer chemists are discussed.

5.0 Summary

In this unit we have learnt that

1. polymers are obtained by polymerization
2. in the process of polymerization, repeating units called monomers join together/ link up to form large macromolecules of high molecular weights [10^2 s - 10^6 s]
3. general formula of polymers are $[-\text{monomer(s)}-]_n$
4. polymers have diverse uses and some scientists contributed to studies of polymer chemistry, which is very important in material science
5. all polymers are macromolecules, but not all macromolecules are polymers
6. we live in an age of polymers. Most of the polymers formed are very essential for our survival and comfort.

6.0 Tutor-Marked Assignment (TMA)

TMA

1. Justify with not less than TEN/10 reasons why polymer chemistry is important to us.
2. Highlight/ summarize the works and findings (inventions) of three named scientists who contributed to the study of polymer chemistry out of the followings: Henri Braconnot; Leo Baekeland; Wallace Carothers; Giulio Natta; Karl Ziegler; Paul Flory.
3. Classify polymers based on their (a) physical properties (b) chemical nature

7.0 References/Further Readings

- T.L. Brown; H.E. LeMay Jr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International p. 499-513.
- P.Y. Bruice (2007): Organic Chemistry. 5th Edition. Pearson Education Inc. p. 1232-1257.
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- I.L. Finar (2008). Organic Chemistry Vol.1 6th Edition Pearson Education. P.114-118.
- L.G. Wade, Jr and M.S. Singh (2008). Organic Chemistry 6th Edition. Pearson Education p. 330-363.
- Philip Matthews (2004). Advanced Chemistry- Polymers; Polymers and Industry p.879-897.
- M. Clugston and R. Flemming (2000). Advanced Chemistry- The Polymerization of Ethene, The mechanism of polymerization, Revisiting Polymerization 1&2. p. 514-517.
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- Everton Clive (1986). The History of Billiards and Snooker (The Story of Billiards and Snooker, 1979) Haywards Heath, UK: Partridge Pr. p.11.
- Helmut Ringsdorf (2004). "Hermann Staudinger and the Future of Polymer Research Jubilees - Beloved Occasions for Cultural Piety". *Angewandte Chemie International Edition* 43 (9): 1064–1076. [doi:10.1002/anie.200330071](https://doi.org/10.1002/anie.200330071).
- Heinrich Hopff (1969). "Hermann Staudinger 1881-1965". *Chemische Berichte* 102 (5): XLI. [doi:10.1002/cber.19691020502](https://doi.org/10.1002/cber.19691020502).

Unit 2: Physical Groupings of Polymers with their Nomenclature.

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- 3.7 Natural rubber
- 3.8 Synthetic Rubber
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References/ Further Readings

1.0 Introduction

Polymers can be grouped depending on either their physical properties or based on their chemical nature. We will consider the names of polymers based on physical groupings and present reasons for such.

2.0 Objectives

At the end of this unit you should

- understand each of the physical groups of polymers
- know examples of each group
- give reasons for such names
- be able to give basic properties of each in terms of rigidity, strength of intermolecular forces and amount of cross links.

3.0 Physical Groupings of Polymers

Names ascribed to polymers based on their physical properties afford them to be grouped as elastomers, fibers, resins, plastics, plasticizers, thermoplastics, thermosetting, nylons, polyesters, acrylonitriles and so on. Some of these will be discussed below.

3.1 Elastomers

Elastomers are rubber or rubber-like polymers with high degree of elasticity. The name 'Elastomers' is coined because of their elastic properties. They can be stretched much more than thrice their original length, and on release go back to their normal shape. Molecules of the polymer line-up on stretching and when released are not extended nor aligned, but go back to their initial random conformation which is favored by their entropy overcoming their enthalpy, along with their long polymer chain with few cross links, all affords them not to be very rigid. Also they do not have much tendency to glide from a molecular layer over the other i.e. with resistance to plastic flow. Elastomers are without polar groups or sites for hydrogen bonding. Examples include rubber.

3.2 Fibers

Fibers are thin, long, threadlike, elongated polymers, which can be easily pulled (with tensile strength). They can be woven and spun, to impart strength on materials. When drawn the polymeric material is stretched, fiber molecules are lined-up permanently. This tendency is supported by the strong intermolecular attractions and is responsible for enthalpy overcoming entropy, unlike in Elastomers. Natural fibers include wool, cotton and silk. Rayon one of the first useful fibers synthesized in 1865 is an example of fibers that are long silk-like shining strands. They were improved on by Louis Chardonnet and introduced to Paris in France in 1891. The word 'rayon' is from ability of the fiber to shine. Another example of synthetic fiber is vinyon, a copolymer of chloroethylene and ethenyl ethanoate. It has great strength but of limited uses because of its low softening temperature of 65⁰C.

Activity A: With equations only show the linear arrangement of copolymer formed between monomers chloroethene and ethenylethanoate.

3.3 Resins

Resins are transparent or translucent lustrous soft solid polymers, which are not usually molded. They are highly cross-linked forming rigid and irregular three-dimensional structures, hence referred to as 'space-network polymers'. Molecules are gigantic with heavy covalent bonds, which do not soften on heating, but may become harder, due to formation of extra cross-links. This is why they are also referred to as '**thermosetting** polymers'.

Activity B: Present the alternative names for following polymers: resins, fibers, Elastomers, natural rubber.

3.4 Plastics

Plastics are another, which are more solid polymers, they are molded polymers. A good example is celluloid one of the first plastic material invented by the British scientist A. Parke, in 1856, from mixing nitrocellulose and camphor; it was used widely for producing piano keys and billiard balls. It was too volatile with the presence of the nitro group, and so was modified removing the nitro group. It served as a reprieve for elephants as well as replaced the scarce ivory. It was important as film for motion pictures.

3.5 Thermoplastics

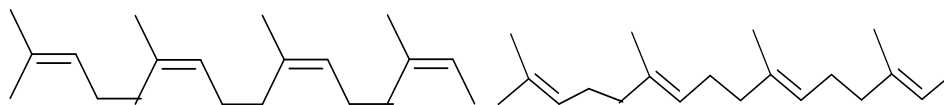
Polymers with or without cross-links but are hard at room temperature are called thermoplastics. They are with weak binding forces between chains. When heated because they are more flexible, they easily soften. But on cooling it gets reversed. Hence they are moulded when soft in liquid form. They are subject to plastic flow, have much weaker attractive forces and soluble in organic solvents. Teflon is a stable thermoplastic with high softening point at 327⁰C. It is utilized in making non-stick cooking utensils.

3.6 Thermosettings

They could be made from low molecular weight compounds and could be semi-fluids. But on heating the chains become highly cross-linked with high covalent bonds, very rigid materials which reduce drastically their mobility. This is why thermosettings are not used widely; they are usually obtained crystalline, hard, plain and insoluble. Once they are set, they cannot be worked into another shape. They can only be heated to destroy their shape before building the shape one is interested in.

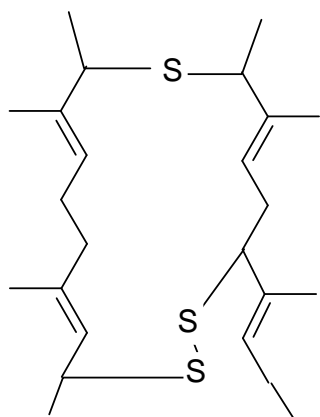
3.7 Natural rubber

Rubber is naturally obtained as latex, a white fluid which oozes out of wounded bark of rubber tree [*Hevea brasiliensis*]. It is a polymer of the diene: 2-methyl-1,3-butadiene [$-(C_5H_8)_n-$] which is isoprene units, the building blocks of regular terpenes. Hence it is also referred to as polyisoprene or better still as polyterpene. There can be as much as 5000 isoprene units in a molecule of rubber. It is a good example of homopolymer. Natural rubber exists as two isomers (cis- and trans- forms).



Structures of cis- and trans-poly methyl-1,3-butadiene

The cis- isomer (cis-methyl-1,3-butadiene/ cis-polyisoprene) has more elastic properties. 1,4-polymerization of the isoprene molecules affords the double bonds to be in the cis-form. The 1,4-polymerization give the cis- isomer which is more stable. The trans-isomer is called gutta-percha (trans- poly methyl-1,3-butadiene/ trans- polyisoprene). It is non-elastic, very useful as coverings and for under water cables and golf-balls. The raw natural rubber has very few crosslinks between the polymeric chains. This is why it is like thermoplastics which softens and sticks on heating, but on cooling gets hardened and brittle. Vulcanization remove this problem by heating raw rubber with Sulphur to form S-linkages [see diagram below] between the polymeric chains. This was first put forward by C.Goodyear in 1838. He heated raw rubber with 8% sulphur [See below]. Today more cold cures in vulcanization exist. This includes (i) use of 2½% solution of disulphide chloride and carbon disulphide; (ii) addition of accelerators in vulcanization makes possible the vulcanization process to take place at lower temperatures. At most temperatures properties of vulcanized rubber have higher tensile strength and elasticity, and are more durable.

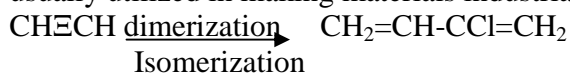


S-linkages in vulcanized rubber

The durability of rubber materials can be improved upon by addition of additives like antioxidants that prevent auto oxidation. For example aldehyde-phenylamine condensations and addition also have accelerating action.

3.8 Synthetic rubber

Synthetic rubber has been made by some scientists from derivatives of 1,3-dienes other than isoprene. One of the earliest is from polymerization of 2-chloro-1,3-butadiene also called chloroprene, which can be obtained from dimerization of ethyne, followed by its subsequent isomerization in HCl. The polymer neoprene has great resistance for chemicals and autooxidation, but is more expensive to manufacture. Hence it is not usually utilized in making materials industrially.



Poly[2-chloro-1,3-butadiene] also called neoprene rubber, is more flexible and elastic.

Another is **buna rubber** invented in Germany around 1930, which takes its name from the main starting materials in its polymerization reaction. 1,3-butadiene its monomer is polymerized using sodium (natrium) as the catalyst.

Cold rubber or SBR (derivative of buna) is another example of synthetic rubber invented to replace unavailability of natural rubber during World War II. It is a copolymer of 1,3-butadiene and phenyl ethylene in ratio 7:3. The mechanism is a free-radical copolymerization.

They are all-purpose synthetic rubber, which can be vulcanized just as for natural rubber and are highly durable than other synthetic rubbers, use for producing tyres industrially.

Hardness of the rubber can be altered by increasing the amount of phenyl ethylene in the copolymer. Other examples include nylons, polyesters, plasticizers, stabilizers.

4.0 Conclusion

Names of physical groups of polymers are very much related to the nature and properties of each, from which the names are coined. Such include their elasticity, durability, strength, textures, elongations, tensile abilities, softness and hardness.

5.0 Summary

In this unit we have

- highlighted the basic physical groupings of polymers, with their nature and properties.
- related their names to indicate some of their features.
- considered practical examples of such physical groups, their preparations and importances.

6.0 Tutor-Marked Assignment (TMA)

1. Name some natural polymers.
2. Name some synthetic polymers.
3. Differentiate between natural rubber and synthetic rubber.
4. State five physical groups of polymers, with two examples each.
5. Indicate three named physical groups that have their names directly coined from specific features of the group.
6. give the names of common polymers and products they are put in use for.

7.0 References/Further Readings

- T.L. Brown; H.E. LeMayJr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International p. 499-513.
- P.Y. Bruice (2007): Organic Chemistry. 5th Edition. Pearson Education Inc. p. 1232-1257.
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Unit 3: Chemical Groupings of Polymers with their Nomenclature.

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- 2.0 Objectives
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 - 3.2 Condensation Polymers
 - 3.3 Types of Monomers
 - 3.4 Cross-linked Polymers
 - 3.5. Stereochemistry
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References/ Further Readings

1.0 Introduction

Polymers can be grouped based on their chemical properties. These we will be considered in details in Modules 3 to 5.

2.0 Objectives

At the end of this unit you should be

- familiar with basic groupings of polymers based on their chemistry
- able to identify monomers as monofunctional or bifunctional, and so on
- to differentiate between homopolymers, copolymers and terpolymers
- able to give alternating names of addition and condensation polymers, as chain-growth and step-growth

3.0 Main Content

The two types of polymerizations lead to the formation of ‘addition polymers’ and ‘condensation polymers’. Type of functional groups and number of functional groups in the monomer determines the chemical groupings polymers would have and be.

3.1 Addition polymers

The polymerization is common among unsaturated monomers, and there is no loss of smaller units, as in the formation of condensation polymers. It is also referred to as **chain-growth polymerization**. Common monomers are the unsaturated olefin compounds. They form vinyl polymers. Addition polymerization occurs in the following patterns of reactions:

1. Radical and non-radical addition polymerization,
2. Cationic addition polymerization;
3. Anionic addition polymerization;
4. Catalyzed and uncatalyzed addition polymerization;
5. Ring opening polymerization.

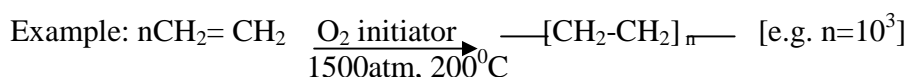
Each is characterized by occurrence of three steps in the mechanism of the reaction- the initiation, propagation and termination stages. [See Module 3].

3.2 Condensation polymers

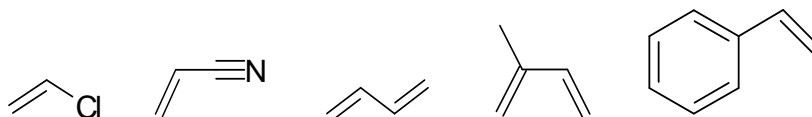
Formation of condensation polymers involves the linking of monomers with loss of smaller units like H₂O, CO₂, NH₃ molecules. It is also referred to as **step-growth polymerization**. The monomers involved are usually saturated. Polyamides and polyesters are good examples condensed polymers. [See Module 3].

3.3 Based on functional group(s) and number of types of monomers that form the polymer.

The number of functional groups present in the monomer (s) as well as number of types of monomers that join to form the polymer is important in classifying polymers. Linear polymers with simpler structures are formed from a type of monomer that has a single functional group. They are referred to as **homopolymers**. Examples include natural rubber [poly isoprene], polythene and polypropene.



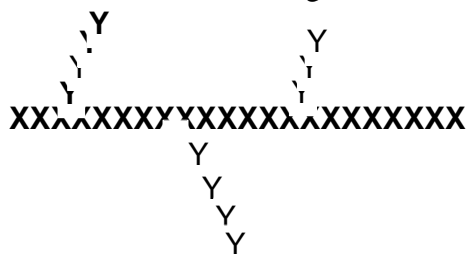
Polymers are referred to as bifunctional when two functional groups are on each monomer that forms it e.g. vinyl halides [with halogen alpha to double bond], acrylonitriles [with nitrile and double bond], 1,3-butadienes [with two double bonds], isoprene [2-methyl-1,3-butadiene], phenyl ethene [styrene].



Activity A: Identify each of the following bifunctional monomers by matching with the appropriate names. Also identify functional groups on each.

Many times more than a type of monomer is involved in producing a polymer. Polymers formed from only two types of monomers are called **Copolymers**. They are diversified by different arrangements of the monomers. The following copolymers are known based on the pattern of arrangements i.e. linkages of the two types of monomers in the structure of each polymer [NB: **X** and **Y** represent each of the monomer types]:

- (i) Linear alternating copolymer: There is frequent and regular alternation between the two monomers. i.e. **X-Y-X-Y-X-Y-X-Y-X-Y-X-Y-X-Y-X-Y-X-Y-**
- (ii) Statistical copolymers: The two monomers are randomly distributed depending on each monomer's reactivity. This also indicates its alternative name 'random copolymer'. i.e. **Y-Y-X-Y-X-X-X-X-X-Y-Y-Y-X-Y-X-Y-**
- (iii) Blocks: Sequence is observed in the copolymer with substantial blocks of each monomer type. i.e.
-Y-Y-Y-X-X-X-X-X-Y-Y-Y-X-X-X-X-X-Y-Y-Y-X-X-X-X-X-Y-Y-Y
- (iv) Grafted copolymer: Here blocks of the monomers are grafted on backbone of the other as branches. e.g.



Many useful and important products are results of different copolymers, like food wrappers, sporting equipments and wears, films etc. More complex polymers formed from not less than three different monomers include **terpolymers**.

Complexity in the structure of polymers formed increases with increase in number of monomers involved, and also with increase in number of functional groups in each monomer.

Activity B: What are trifunctional polymers? Give examples.

Activity C: Identify the monomer(s) in each of the following polymers: polypropene, polytetrafluoroethene.

3.4 Cross-linked polymers

Allylic positions on polymers with double bonds are very reactive. Their reactions lead to formation of bridges between molecules. This is called cross-linkings. A good example is what we discussed on vulcanization of rubber, where sulphur is heated with natural rubber to form cross-linkings, leading to improvements, in the use of the polymer. Cross-linkings afford polymers to be crystallizable (since molecules lie close together and strong), of high melting point. The crystallite region is destroyed when polymer molecules are heated.

3.5 Based on the stereochemistry

Polymers can be grouped as syndiotactic, isotactic, and atactic polymers based on their stereochemistry. [p.1040M&B]

Branchings on optically active polymers like methyl groups and their random arrangements called alignment determine its stereochemistry, and its nature and properties. For example in poly-2-methyl propene the following situations can be seen:

- (a) When all the methyl groups alternate uniformly, it is the **syndiotactic form**.
- (b) If all the methyl groups are on one side of the structure, it is the **isotactic form**. It is usually formed by the non-radical mechanism.
- (c) For the non-uniform alternation of the methyl groups, it is the **atactic form**. It is obtained by the radical method.

4.0 Conclusion

The chemical groupings of polymers are of two types: Addition chain-growth, and condensation step-growth. Stages of reactions in the former are highly related and involve three steps [initiation, propagation and termination], while the stages in condensation are independent, with the elimination of smaller units like H₂O, CO₂ and NH₄ during the process.

Other chemical properties use for describing polymers include functional groups present, types of monomer(s) in the polymer, stereo chemical arrangements in the molecule and cross linkings.

5.0 Summary

In this unit we learnt that

- methods of forming polymers are mainly addition chain-growth and condensation step-growth polymerizations, which are involved in chemical classifications of polymers.
- addition polymerization can go by radical or ionic [cationic or anionic] mechanism. Each is characterized by three stages- initiation, propagation and termination stages.
- condensation polymerization involves steps that are independent and simple molecules are given out.
- polymers can be bifunctional, trifunctional, homopolymer, copolymer and terpolymer depending on functional group(s) in monomer(s).
- stereo chemically polymers could be syndiotactic, isotactic and atactic.
- Cross links occur usually at allylic (unsaturated) positions on molecules of the polymer. They affect some of the physical properties of the polymer.

6.0 Tutor-Marked Assignment (TMA)

1. Will cross-links be possible in polyalkanes? Give reasons for your answers.
2. With structures show syndiotactic, isotactic and atactic forms of poly2-chloropropene.
3. Use structures only to differentiate between the four copolymers- random, block, linear and grafted.
4. In a tabular form differentiate between addition chain-growth and condensation step-growth polymerizations.

7.0 References/Further Readings

- T.L. Brown; H.E. LeMayJr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International p. 499-513.
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Module 2: Sources of Raw Materials for Polymers

Unit 1: Raw Materials from Economic Sources are Industrial Methods of Producing Polymers

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- 1.0 Introduction
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 - 3.2 Polyethylene
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 - 3.4 Some products of Polymerization
 - 3.5 Sources of raw Polymers materials in Nigeria
 - 3.6 Non-economic Polymers
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References/ Further Readings

1.0 Introduction

Industrial production of polymers is based on how they can be economically obtained. Many important polymers are synthesized for economic reasons such as higher yields and durability. Starting materials are the raw materials from which polymers are made. They also include feasibility of conditions for producing them and the total cost of production to make it fit and meet the purpose for which they are made. We will be considering some examples.

2.0 Objectives

At the end of this unit you should be able to

- know some sources of raw materials and be more acquainted with general methods of producing each
- appreciate why some raw materials and methods are preferred to others in producing polymers
- identify available raw materials in Nigeria for chemical industries that produce polymer products and the likes
- understand basic principles behind recycling, which is a major source of raw materials for production of polymers
- understand differences between industrial productions and laboratory synthesis of polymers

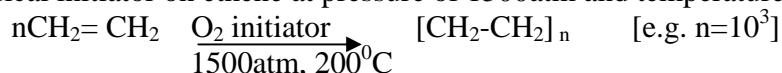
3.0 Main Content

Industrial production of polymers involves cheapest methods of producing them, which embraces both cheap sources of the raw materials and feasibility with economic conditions of producing them.

3.1 Preferred methods are choices of economic sources of obtaining starting materials for the preparation of polymers. Producing them cheaply and efficiently is a major concern for the companies that manufacture them. A good illustration will be the manufacturing of polyethylene from ethylene. There are many methods for producing polythene for domestic and commercial purposes with some differences in their properties. Polyethylene is important for making nylon bags, disposable wraps, water bags and bottles, beach chairs etc. Composition of polyethylene looks simple, but it is not all that easy to produce. It is an addition chain-growth polymerization reaction. The preferred should involve less stringent and outrageous conditions of high pressure and temperature. Also the softening temperature should be high. The density should be high, with appropriate textures [e.g. crystallizability, rigidity, softness, crispy feels, amorphous nature etc].

3.2 We will outline the established methods of producing polyethylene and give justification(s) for each, to serve as illustration:

(i) Process of high pressure [ICI] technique involve minute amount of oxygen as free radical initiator on ethene at pressure of 1500atm and temperature of 200⁰C.



The polymeric chain produced is of low density of 0.92g/cm³ and has methyl branching.

(ii) Phillips process occurs between 150-180⁰C and 30-35atm, with chromium III oxide as catalyst and mixture of SiO₂ and Al₂O₃ in ratio 9:1, by ionic mechanism. There is methyl branching on the polymeric chain formed with higher density of 0.96g/cm³, with softening temperature of 130-136⁰C. The conditions are a little less stringent than the high pressure technique and product is of higher density.

(iii) Zeigler process occurs at 50-75⁰C and 2-7atm, which is quite moderate. TiCl₄ and Al(CH₃)₃ act as catalyst as ethene is passed into it. Dilute acids decompose the catalysts after reaction is completed, followed by separation of the product by filtration. Polymerization is by ionic mechanism. Product obtained has moderate high density of 0.945cm³, with softening temperature of 120-128⁰C.

The last two methods are preferred; the polymer formed is of high density as all ionic mechanism, with molecules regularly packed and closer, hence more rigid and crystalline. They have high tensile strength, high softening temperatures.

Activity A: Which will you prefer as an industrialist to produce polythene between Phillips and Zeigler's process? Justify your answer.

Activity B: Find out details of PVC methods of producing polymers.

3.3 Varieties of plastics

Plastics are very important as containers. They come in varieties, and are constantly recycled after use. Recovery and recycling provide increasing amounts of some chemicals. As environmental concerns increase, these operations will probably become an important source of materials used in the manufacture of certain polymers.

On plastics are fastened recycling symbol which could be with abbreviations of the kind of polymer used in its production, and number at the middle. They are usually placed under the plastic container. These are indicating the type of polymer used in producing the plastic, hence knowledge of the composition of each plastic product can be known to guide in recycling plastics made from the same polymer. The number also indicates the ease of recycling. Lower numbers implies they can easily be recycled. Below are varieties of polymers used in manufacturing plastic materials:

Table 2:1 Varieties of Polymers used in Manufacturing Plastic Materials

Polymer	Abbreviation	Recycling number	Plastic material
Polyethylene terephthalate	PET/ PETE	1	Cups, jugs, buckets, bowls, chairs, plates, vase, etc
High density polyethylene	HDPE	2	
Polyvinylchloride[PVC]	V/ PVC	3	
Low density polyethylene	LDPE	4	
Polypropylene	PP	5	
Polystyrene	PS	6	
For all other plastics	FAOP	7	

Sources: T.L. Brown; H.E. LeMayJr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International, p.501; P.Y. Bruice (2007): Organic Chemistry. 5th Edition. Pearson Education Inc. p.1239.

3.4 Polystyrene [poly phenyl ethylene] the polymer obtained from chain-growth polymerization reactions of phenyl ethylene gives important products like toothbrushes, disposable food containers, packagings, toys, egg cartons, cups and insulators. The polymer is pumped with abundance of air to produce materials utilized in house construction.

3.5 Basic raw materials for producing polymers are their monomers. Most of the polymers produced are further worked on to make important finished products we use constantly. Some of which have been mentioned earlier, another list of monomers and the polymers they form with the common final materials they are put can be found in Module 3. Examples include polypropylene, PVC, teflon, nylon, dacron, orlon, rayon, vinyon.

3.6 Evidences and practical examples of sources of raw materials for polymers in Nigeria.

Nigeria is highly populated, the 11th in the world and most populous in Africa. She is endowed with vast amounts of varieties of natural resources such as petroleum, minerals and agricultural products. Report of the **Vision 2010** committee in 1997 indicate that the manufacturing sector of the nation should be able to contribute about 24% to the average annual GDP [Gross Domestic Products], which is still below 10% now. It is therefore the aim of the committee to maximally utilize our natural resources and raw materials into finished products for exportations to build up our economy. Presently the country is not very buoyant in raw materials for producing polymer products. The followings are lay-out of basic raw materials available in Nigeria utilized by the manufacturing sector of the country.

Table:2.2 Raw materials in Nigeria

S/N	Item	Occurrence	Location	Estimated reserve [tonnes]	Comments
1	Copper	Sulphides, oxides	Bauchi	undetermined	Exploration is extended to Plateau granites.
2	Lead and zinc	Sulphides	Ebonyi Bauchi	2-2.5 million undetermined	Commercial exploitation ceased during civil war.
3	Tin	Oxides	Plateau	200,000	Very well developed, but urgent need to discover new deposits.
4	Aluminium	Oxide	Gongola, C/River	underdetermined	Accelerated exploration programmes urgently required, for all nation's need are imported.
5	Bauxite	Oxides and hydroxides	Gongola, C/River	undetermined	The sole source of Al for our industries, presently imported.
6	Clay	Silicates	Eastern states	billions	Deposits exceed domestic need.
7	Gypsum	Sulphates	Gombe,	Estimated to be	FG ban on

			Taraba, Borno, Sokoto, Benue	very large	importation, has pick-up tempo on exploration and exploitation. To reach minimum of 50% by 2010.
8	Limestone	Carbonate	Enugu, Bendel, Ogun, Gombe, Sokoto, C/River, Abia	billions	Major raw material for cement. Reserve exceeds present industrial needs including use in steel plants.
9	Asbestos	Silicate	Kaduna	small	Detail studies desirable.
10	Coal and lignite	Native	Enugu, Abia, Benue, Nasarawa, Plateau, Gombe	350 million, still to be fully investigated	On very strong footing. But Nigerian coal is non-cooking.
11	Bitumen	Petroleum	Edo, Ogun, Ondo, Lagos, Abakaliki, Anambra, Abia, Ebonyi	Above 42.7 billion barrels	

Sources: (1) Prof. D.M. Orazulike (2002). THE SOLID MINERAL RESOURCES OF NIGERIA: MAXIMIZING UTILIZATION FOR INDUSTRIAL AND TECHNOLOGICAL GROWTH. Inaugural Lectures Series. P.299-343.
(2) Prof I.B. Odeyemi (2001). MINERALS AND MAN: AN INSEPARABLE DUO. Inaugural Lectures Series. P.572.

Resources from solid minerals include (i) iron and iron-alloy metals (ii) non-ferrous industrial metals (iii) precious metals (iv) metal fuel and (v) industrial minerals.

There are six cement plants in Nigeria.

Activity A: List the six Nigerian Cement Industries.

WAPCO Lagos; BCC Gboko; ACC Gombe; Nigercem Nkalagu; Bcc Ltd Okpella; CCNN, Sokoto.

3.7 Expensive/ non-economic methods of producing polymers

These are usually laboratory preparations, where costing and gains are not really put into considerations. The major aim is to show and prove that a method can work, or a polymer can be produced experimentally. Medical applications of polymers and in drugs which are determinants of life are good examples of polymers that are obtained by expensive methods of production. Many times, such are specially demanded for or Government

sponsor the production of the polymers. Such examples include 'Life science products' which are usually produced with very high specifications and are closely scrutinized by government agencies such as the Food and Drug Administration. Crop protection chemicals, about 10 percent of this category, include herbicides, insecticides, and fungicides.

Specialty chemicals are another category of relatively high valued, rapidly growing chemicals with diverse end product markets. Typical growth rates are one to three times GDP with prices over a dollar per pound. They are generally characterized by their innovative aspects. Products are sold for what they can do rather than for what chemicals they contain. Products include electronic chemicals, industrial gases, adhesives and sealants as well as coatings, industrial and institutional cleaning chemicals, and catalysts. Coatings make up about 15 percent of specialty chemicals sales, with other products ranging from 10 to 13 percent.

4.0 Conclusion

Manufactured polymers are economically based. Industrial production of important polymers relies on the sources of its raw materials, along with feasible conditions. Total cost of production must be cheap for the purpose(s) for which they are made for. Recycling affords cheap sources of raw materials.

5.0 Summary

In this unit we have

- considered the raw materials for producing important polymers like polyethylene, as well as the conditions that suit their industrial productions.
- justified and given reasons for preference of a method over another.
- understood some of what is entailed in industrial production of important polymers.

6.0 Tutor-Marked Assignment (TMA)

1. Compare and contrast between Zeigler and Phillips process of obtaining polythene.
2. Provide the abbreviations for the following important industrial polymers, and give examples of appropriate product materials that they can be formed into.

Polymer	Abbreviation	Material
Polyethylene terephthalate	?	?
High density polyethylene	?	?
Polyvinylchloride[PVC]	?	?
Low density polyethylene	?	?
Polypropylene	?	?
Polystyrene	?	?

3. What are the major raw material requirements for the manufacturing of cement?
4. What are specialty chemicals? State their features.

5. Present ways to persuade government of your country to recycle plastics. What incentives would be necessary and what collection methods would you suggest could be used?

7.0 References/Further Readings

- T.L. Brown; H.E. LeMayJr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International p. 499-513.
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Unit 2: Chemical Industries are Important Sources of Raw Materials in Polymer Chemistry

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1.0 Introduction

From the chemical industry, valuable raw materials for the production of important polymers and their products are obtained on large scale, such as the inorganics (chlorides, alkalis, sulfuric acid, sulfates) and fertilizers (potassium, nitrogen, and phosphorus products) as well as segments of catalysts, pigments, and propellants, fine chemicals used in producing high purity inorganics on a much smaller scale. Many of these inorganics are use for or act as catalysts, acids, bases, decolorizers, plasticizers and so on. The **chemical industry** comprises the companies that produce industrial chemicals. It is central to modern world economy, converting raw materials (oil, natural gas, air, water, metals, and minerals) into more than 70,000 different polymer products.

2.0 Objectives

At the end of this unit you should

- be familiar with specific raw materials obtained from chemical industries
- understand that safety is important in industrially produced chemicals, hence need to follow legislative orders on it

3.0 Main Content

The chemical industry involves the use of chemical processes such as chemical reactions and refining methods to produce a wide variety of solid, liquid, and gaseous materials.

Most of these products are used in manufacturing other items, with smaller number of them used directly by consumers. The polymer industry utilizes most of these as raw materials [organics, petroleum, oils, fats, waxes, inorganics and metals] for the production of important polymers.

3.1 The chemical industry adds value to raw materials by transforming them into the chemicals required for the manufacture of consumer products like the useful polymers. Since there are usually several different processes that can be used for this purpose, the chemical industry is associated with intense competition for new markets. It is made up of companies of different sizes, including several giants that are engaged in the transformation of some very basic raw materials into final products, as well as medium-size or small companies that concentrate on very few of these steps. The closer to the raw material, the larger the scale of operations; such "heavy" chemicals are usually manufactured by continuous processes. At the other extreme in terms of scale are the firms that manufacture "specialties," mostly in batch processes, from "intermediates" that correspond to chemicals which have already gone through several steps of synthesis and purification.

Industrial production of chemicals was usually based on running reactions that were known to yield the desired products on much larger scales. Success in these endeavors lay much more in the experience and skill of their practitioners than the application of solid chemical principles. This led to serious problems of control and the generation of noxious by-products. The introduction of the Leblanc process in the northwest of England led to a general public outcry against the dark and corrosive smoke that covered the surrounding countryside. The Alkali Act, passed in response in 1863, represents the first legislation that established emission standards.

3.2 Some starting materials from chemical industry for polymers

Sodium carbonate may be mined directly; its use may be preferred over a manufactured product. It is used mainly in the glass industry. Sodium silicates may be derived from sodium carbonate and in their finely divided form, silica gel, may be used in detergents and soaps. Sodium hydroxide has many different uses in the chemical industry. Considerable amounts are used in the manufacture of paper and to make sodium hypochlorite for use in disinfectants and bleaches. Chlorine is also used to produce vinyl chloride, the starting material for the manufacture of polyvinyl chloride (PVC) an important polymer, and in purification of water. Hydrochloric acid may be prepared by the direct reaction of chlorine and hydrogen gas or by the reaction of sodium chloride and sulfuric acid. It is used as a chlorinating agent for metals and organic compounds. Bromine is used in water disinfection; bleaching fibers and silk; and in the manufacture of medicinal bromine compounds and dyestuffs. Basic chemicals [e.g. crude petroleum,

natural gas, air, metal in ores, mining fields etc] represent the starting point for the manufacture of industrial chemicals. Some of them are in combined states, compounds, while few are in their elemental forms like sulphur. They are usually one step away from the raw materials and are produced on a very large scale employing continuous processes. The unit price of these products is relatively low, and producing them cheaply and efficiently is a major concern for the companies that manufacture them. Sulfur, nitrogen, phosphorus, and chloralkali industries are the main producers of basic inorganic chemicals, and they will often sell them to other industries as well as using them in the manufacture of their own end-products. The basic principles for their production and major uses are indicated here for each of these industries.

Titanium dioxide is by far the most important titanium compound. It can be purified by dissolving in sulfuric acid and precipitating the impurities. The solution is then hydrolyzed, washed, and calcinated. Alternatively, ground rutile is chlorinated in the presence of carbon and the resulting titanium tetrachloride is burned in oxygen to produce the chloride. Titanium dioxide is found in nature in three crystal forms: anastase, brookite, and rutile. Its extreme whiteness and brightness and its high index of refraction are responsible for its widespread use as a white pigment in paints, lacquers, paper, floor covering, plastics, rubbers, textiles, ceramics, and cosmetics.

3.3 Coal and petroleum are important sources of raw materials

Chemicals in the bulk petrochemicals and intermediates are primarily made from liquefied petroleum gas (LPG), natural gas, and crude oil. Their sales volume is close to 30 percent of overall basic chemicals. Typical large-volume products include ethylene, propylene, benzene, toluene, xylenes, methanol, vinyl chloride monomer (VCM), styrene, butadiene, and ethylene oxide. These chemicals are the starting points for most polymers and other organic chemicals as well as much of the specialty chemicals category.

Other derivatives and basic industrials include synthetic rubber, surfactants, dyes and pigments, turpentine, resins, carbon black, explosives, and rubber products and contribute about 20 percent of the basic chemicals' external sales. Inorganic chemicals (about 12 percent of the revenue output) make up the oldest of the chemical categories. Products include salt, chlorine, caustic soda, soda ash, acids (such as nitric, phosphoric, and sulfuric), titanium dioxide, and hydrogen peroxide. Fertilizers are the smallest category (about 6 percent) and include phosphates, ammonia, and potash chemicals.

The raw materials for polymer production come from petroleum and less from coal. These two fossil fuels are the main energy sources in the U.S. Consequently, polymers and energy are linked through these raw materials. Because the amounts of these fossil fuels are limited, particularly petroleum, the items made of polymers derived from petroleum may have a limited lifetime.

3.4 Organics and pharmaceuticals

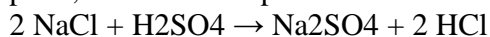
Polymers and plastics, especially polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene and polycarbonate comprise about 80% of the industry's output worldwide. Chemicals are used to make a wide variety of consumer goods, as well as thousands inputs to agriculture, manufacturing, construction, and service industries. The chemical industry itself consumes 26 percent of its own output. Major industrial polymers include rubber and plastic products, textiles, apparel,

petroleum refining, pulp and paper, and primary metals. Chemicals is nearly a \$3 trillion global enterprise, and the EU and U.S. chemical companies are the world's largest producers. **Basic chemicals**, or "commodity chemicals" are a broad chemical category including polymers, bulk petrochemicals and intermediates, other derivatives and basic industrials, inorganic chemicals, and fertilizers. Typical growth rates for basic chemicals are about 0.5 to 0.7 times GDP. Product prices are generally less than fifty cents per pound. Polymers, the largest revenue segment at about 33 percent of the basic chemicals dollar value, include all categories of plastics and man-made fibers. The major markets for plastics are packaging, followed by home construction, containers, appliances, pipe, transportation, toys, and games. The largest-volume polymer product, polyethylene (PE), is used mainly in packaging films and other markets such as milk bottles, containers, and pipe. Polyvinyl chloride (PVC), another large-volume product, is principally used to make pipe for construction markets as well as siding and, to a much smaller extent, transportation and packaging materials. Polypropylene (PP), similar in volume to PVC, is used in markets ranging from packaging, appliances, and containers to clothing and carpeting. Polystyrene (PS), another large-volume plastic, is used principally for appliances and packaging as well as toys and recreation. The leading man-made fibers include polyester, nylon, polypropylene, and acrylics, with applications including apparel, home furnishings, and other industrial and consumer use. The principal raw materials for polymers are bulk petrochemicals.

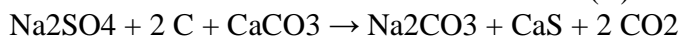
3.5 Inorganics

Many of today's large companies started as producers of inorganics. Industrial inorganic chemistry includes subdivisions of the chemical industry that manufacture inorganic products on a large scale such as sulfur, nitrogen, phosphorus, and chloralkali. Industries produce them as their main products of basic inorganic chemicals, and often sell them to other industries as well as use them in the manufacture of their own end-products. Examples: (i) Air contains molecular nitrogen and oxygen. They may be separated by liquefaction and fractional distillation along with inert gases, especially argon.

(ii) Salt or brine can be used as sources of chlorine and sometimes bromine, sodium hydroxide, and sodium carbonate. Industrial Revolution marks the origin of the chemical industry. Sulfuric acid [tetraoxosulfate VI acid] and sodium carbonate [sodium trioxocarbonate IV] were among the first chemicals produced industrially. "Oil of vitriol" (as sulfuric acid was known) played an important role in the manipulation of metals, but its production on an industrial scale required the development of materials that would resist attack. Sodium carbonate was obtained in its anhydrous form, "soda ash," from vegetable material until the quantities produced could no longer meet the rapidly expanding needs of manufacturers of glass, soap, and textiles. The Royal Academy of Sciences of Paris, in 1775, had to establish a contest for the discovery of a process based on an abundant raw material, sodium chloride. Nicolas Leblanc's method was put forward for the preparation of soda by converting salt into sulfate thus though he did not win the prize, but Leblanc's process is associated with the birth of industrial chemistry.



The sulfate is converted to soda with charcoal (C) and chalk (CaCO₃)



Sulfuric acid was an essential chemical for dyers, bleachers, and alkali manufacturers. Its production on a large scale required the development of lead-lined chambers that could resist the vapors which were formed when sulfur was burned with nitrates.

This process was wasteful and emitted corrosive gases. It improved only in the mid-nineteenth century when towers to recycle the gases were finally introduced. The transportation of sulfuric acid was dangerous, and alkali manufacturers tended to produce their own as a result. This marked the beginning of the diversification and vertical integration that are characteristic of the chemical industry.

Sulfuric acid was also used in the manufacture of superphosphates, which were produced as fertilizers on a large scale by the mid-nineteenth century. By that time, a solution was found for the complex engineering problems that had hampered the use of the alternative process to produce soda.

Ernest Solvay, a Belgian chemist, designed a tower in which carbon dioxide reacted efficiently with solid salts. The Solvay process had enormous advantages over the Leblanc process: It did not generate as much waste and pollution; its raw materials, brine and ammonia, were readily available (the latter from gasworks); less fuel was used, and no sulfur or nitrate was involved. In spite of its higher capital costs, it was rapidly adopted and soon became the major source of alkali.

Another major process used in the manufacture of inorganic chemicals is the catalytic conversion of nitrogen and hydrogen to ammonia. The German chemist Fritz Haber first synthesized ammonia from nitrogen and hydrogen in 1909. Four years later, together with another German, Carl Bosch, he modified the process for the commercial production of ammonia. The Haber (or Haber–Bosch) process represented a technological breakthrough since it required a very specialized plant to handle gases at high pressures and temperatures.

(iii) From mineral ores metals such as iron, aluminum, copper, or titanium as well as phosphors, potassium, calcium, and fluorine are obtained. Saltpeter was once an important source of nitrogen compounds, but today most ammonia and nitrates are produced synthetically from nitrogen gas in the air.

Inorganic chemicals such as chlorine, produced at this plant in Louisiana, are used in the manufacturing of several chlorides, including PVC and hydrochloric acid.

(iv) Sulphur occurs in underground deposits and can be brought to the surface by compressed air after it is melted by superheated steam. Increasing quantities of sulfur are recovered from petroleum and natural gas where they are impurities. The following table 1 summarizes some important sources of inorganic chemicals as raw materials and what they are utilized for.

Table 2: 3 U.S. production of minerals in 2001.

U.S. PRODUCTION OF MINERALS IN 2001

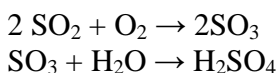
Source	Thousands of Tons	Examples of Uses
Phosphate rock	37,706	Fertilizers, detergents
Salt	49,723	Chlorine, alkali production
Limestone	20,617	Soda ash, lime
Sulfur	10,144	Sulfuric acid production
Potassium compounds	1,323	Caustic potash, fertilizers

U.S. PRODUCTION OF MINERALS IN 2001

Source	Thousands of Tons	Examples of Uses
Sodium carbonate	11,356	Caustic soda, cleaning formulations

Source: The Chemical Industry. Retrieved from "http://en.wikipedia.org/wiki/Chemical_industry"

Sulfuric Acid and Sulfates: Sulfuric acid has long been the chemical that is manufactured in the largest quantities on a world scale. Its production is often linked to a country's stage of development, owing to the large number of transformation processes in which it is used. It plays important roles in most processes of polymerization. Sulfuric acid is manufactured from elemental sulfur. Mining was the main source for this element, which was obtained from sulfide-containing ores or in very pure form from underground deposits by the Frasch process (injection of superheated steam and air into drillings and the separation of the mixture that rises to the surface). The large-scale consumption of petroleum and natural gas has changed this scenario since sulfur occurs as an impurity in most fossil fuels and must be removed before the fuels are processed. These fuels are presently the main source of sulfur, and their relative importance tends to increase with more rigorous controls on emissions. It is manufactured in three stages



Since the reaction of sulfur with dry air is exothermic, the sulfur dioxide must be cooled to remove excess heat and avoid reversal of the reaction.

Most plants use reactors with various stages in order to cool the stream for the catalytic step. Conversion by a vanadium pentoxide catalyst deposited on a silicate support is the critical step in the process, in which the gaseous stream is passed over successive layers of catalyst. The gas mixture is then passed through an absorption tower. Oleum, the product, is a concentrated solution of sulfuric acid containing excess sulfur trioxide.

As an inexpensive source of acid, a large amount of the sulfuric acid that is produced is used for the manufacture of other mineral acids. It is also used to produce sulfates, such as ammonium sulfate (a low-grade fertilizer), sodium sulfate (used in the production of paper), and aluminum sulfate (used in water treatment), as well as organic sulfates (used as **surfactants**). Sulfuric acid is also a good catalyst for many reactions, including the transformation of ethanol into ethylene or ethyl ether (Table 2).

Table 2:4 U.S. production of inorganic chemicals in 2001.

U.S. PRODUCTION OF INORGANIC CHEMICALS IN 2001

Chemical	Thousands of Tons
Sulfuric acid	40,054
Ammonia	13,046
Sodium chloride	12,019
Phosphoric acid	11,605
Sodium hydroxide	10,687
Nitric acid	7,823
Ammonium sulfate	2,556
Titanium dioxide	1,463

U.S. PRODUCTION OF INORGANIC CHEMICALS IN 2001

Chemical	Thousands of Tons
Aluminum sulfate	1,165

Source: The Chemical Industry. Retrieved from "http://en.wikipedia.org/wiki/Chemical_industry"

3.6 Metals are chemicals in a certain sense. They are manufactured from ores and purified by many of the same processes as those used in the manufacture of inorganics. However, if they are commercialized as alloys or in their pure form such as iron, lead, copper, or tungsten, they are considered products of the metallurgical industry. They play major roles as catalysts in the polymerization reactions to produce important polymers.

4.0 Conclusion

Raw materials for polymers though important, are not among the top basic chemicals produced world wide. Every year, the American Chemistry Council tabulates the U.S. production of the top 100 basic chemicals. In 2000, the aggregate production of the top 100 chemicals totaled 502 million tons, up from 397 million tons in 1990. Inorganic chemicals tend to be the largest volume, though much smaller in dollar revenue terms due to their low prices. The top 11 of the 100 chemicals in 2000 were sulfuric acid (44 million tons), nitrogen (34), ethylene (28), oxygen (27), lime (22), ammonia (17), propylene (16), polyethylene (15), chlorine (13), phosphoric acid (13) and diammonium phosphates (12).

5.0 Summary

In this unit we have seen that

- the chemical industry has shown rapid growth for more than fifty years.
- the fastest growing areas have been in the manufacture of synthetic organic polymers like plastics, fibers and elastomers.
- the chemical industry has been concentrated in three areas of the world, Western Europe, North America and Japan (the Triad). The European Community remains the largest producer area followed by the USA and Japan.
- in Europe, especially Germany, the chemical, plastics and rubber sectors are among the largest industrial sectors.
- instrumental in the changing structure of the global polymer chemical industry has been the growth in China, India, Korea, the Middle East, South East Asia, Nigeria, Trinidad, Thailand, Brazil, Venezuela, and Indonesia.

6.0 Tutor-Marked Assignment (TMA)

1. With two examples each state the raw materials for production of specific polymers obtained from chemical industries, which are (a) organics (b) from petroleum (c) inorganics

2. What are 'basic chemicals'?

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Module 3: Processes of Polymerization;

Unit 1: Synthetic polymerization

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- 1.0 Introduction
- 2.0 Objectives
- 3.0 Main Contents
 - 3.1 General information on polymerization
 - 3.2 The two Polymerizations
 - 3.3 Designing of synthetic Polymers
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
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1.0 Introduction

The process of polymerization has made possible diversifications and obtaining important polymers in more economic and higher yields, with improvements. Varieties of polymers which are important to man and of better qualities have been made available through syntheses. There are two basic patterns of polymerization

- Addition polymerization and
- Condensation polymerization

2.0 Objectives

At the end of this unit you should be able to

- fathom the two basic patterns of polymerizations as addition and condensation polymerizations
- know the alternative names for addition and condensation polymerizations
- understand that modifications are involved in polymerization reactions to suite the desired polymer products

3.0 Main Content

Synthetic polymer materials like nylon, teflon, polyethylene and silicone have formed the basis for a burgeoning polymer industry. In recent times there have been significant developments in rational polymer synthesis. Most commercially important polymers today are entirely synthetic and produced in high volume on appropriately scaled organic synthetic techniques. Synthetic polymers today find application in nearly every industry and area of life. Polymers are widely used as adhesives and lubricants, as well as structural components for products ranging from children's toys to aircraft. They have been employed in a variety of biomedical applications ranging from implantable medical devices to controlled drug delivery. Polymers such as poly (methyl methacrylate) find application as photoresist materials used in semiconductor manufacturing and dielectrics for use in high-performance microprocessors. Recently, polymers have also been employed as flexible substrates in the development of organic light-emitting diodes for electronic displays. All are possible through the two basic patterns of polymerizations: addition and condensation polymerizations.

3.1 Synthetic polymers are equally important to man as natural polymers, if not even better. They afford much more diversifications and varieties of polymers with better qualities, greater uses and applications than from natural sources.

The process of polymerization can proceed in two general ways: addition and condensation polymerizations, depending upon the types of monomers used. These two main methods of generating synthetic polymers are

- addition polymerization and
- condensation polymerization

Addition polymers (chain-growth polymers), have one monomer simply adding to the next. This process is continuous to form chains of the monomers in the polymer. For example chains of polyethylene can have 10,000-20,000 ethylene units. **Condensation polymers** (step-growth polymers), are made from two different monomers or bifunctional monomers. They are joined together with the elimination of a small molecule, like water, ammonia and carbon IV oxide. Nylon and polyester are examples of condensation polymers.

3.2 The two polymerization reactions are continuous chain reactions to obtain the very high molecular weight polymers. Each has its characteristic features; which will be discussed in the next three units. Their alternative names are thus: Addition polymerization is 'Chain-growth polymerization', its chain reactions can be radically or ionic ally initiated, followed by propagation and termination stages with no loss of molecules. Also their monomers are unsaturated; Condensation polymerization is also called 'Step-growth polymerization', its continuous reactions involve loss of small units

like H₂O, CO₂, NH₃ molecules during the condensation of its monomers. More characteristic features of each will be considered soon.

3.3 Polymers are designed synthetically to meet specific needs and desired impressions. No too fast rules exist on methods of carrying out polymerization reactions to obtain useful industrial polymers of choice. Manufacturers of important industrial polymers never make available the detailed outlines of their methods. Many times it looks so simple, but the reality of conditions for carrying them out, may be too demanding or non-practicable to be observed. The following may guide in designing synthetic polymerization reactions to produce the desired products, and so should be taken into cognizance in the production of the appropriate polymer:

- Texture, shape and impressions to be met.
- Starting materials and raw materials involved in the polymerization reactions.
- Paths of reaction and type of catalyst(s) involved, in terms of nature and amount.
- Temperature and pressure at which the polymerization reactions occur.
- Different stages involved in the syntheses.
- Control measures and precautions to be observed so as to have the desired products.
- Timings and durations of each stage in the polymerization reactions.
- Knowledge of the mechanisms of the reactions [radical or ionic polymerization].

4.0 Conclusion

Polymerization is the process by which polymers are made from its monomers. The two methods of generating synthetic polymers are 'addition chain-growth' and 'condensation step-growth' polymerizations to give varieties of quality polymer products that are very useful to man. It is suffice to know a major challenge: Newer methods such as plasma polymerization do not fit neatly into either category. Synthetic polymerization reactions may be carried out with or without a catalyst.

5.0 Summary

In this unit we have

- stated the two basic methods of polymerizations as addition chain-growth and condensation step-growth polymerizations.
- presented the alternative names of addition polymerization as chain-growth, and condensation polymerization as step-growth.
- mentioned basic feature to differentiate between the two methods of polymerizations.
- outlined things to take cognizance of in the production of appropriate polymers.

6.0 Tutor-Marked Assignment (TMA)

1. Give the two basic methods of polymerization. Present their alternative names.
2. Mention five things that should guide you in designing the polymerization reaction that will give you the desired polymer.
3. State the differences between the two basic methods of polymerization.

7.0 References/Further Readings

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Unit 2: Addition Chain-growth Polymerization Reactions

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- 3.2 Addition Monomers
- 3.3 Products of addition Polymerization
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1.0 Introduction

We have earlier discussed that **Polymers** are “giant molecules” formed from repeating units (*poly* = many and *mer* = parts). The individual units are called **monomers**; thousands of these are linked together to form a polymer molecule. “Giant molecules” have high molecular weight [10^3 s to 10^6 s amu].

2.0 Objectives

At the end of this unit you should be able to

- understand more details on addition chain-growth polymerization and give its features

- give examples of addition reactions of polymers
- predict polymer products of specific monomers undergoing addition

3.0 Main Content

It would be important to write out equations to show addition chain-growth polymerization reactions as monomers add-up without loss of molecules, which involves the double bonds on the monomers. Vinyl derivatives are very appropriate for these.

3.1 In addition polymerization reactions the monomers are unsaturated [with double or triple bonds]. During the course of the reaction, for example in the case of polymerization reaction of ethylene, at the double bond the pi electrons are released to form new C-C bonds with two other molecules of ethylene. [i.e. the double bond initially with pi and sigma bonds, is broken so that the two electrons in the pi are now utilized in forming new C-C single bonds with two other ethylene molecules, leaving only the sigma bond of the initial double bond in place. This is repeated on every unsaturated bond; hence all appear as single bond in the polymer product, like a chain. Addition chain-growth polymerization gives rise to direct integral multiple of the monomer units with same percentage composition of elements in the total monomers which make it up.

3.2 Monomers are usually made of carbon and hydrogen atoms. Hetero atoms like oxygen, nitrogen and halogen atoms can be present. Good examples of monomers are ethylene molecule, $\text{CH}_2 = \text{CH}_2$, vinyl chloride, $\text{CH}_2 = \text{CHCl}$, vinyl acetate and $\text{CH}_2 = \text{CHCO}_2 \text{CH}_3$. **Addition polymers** are formed by monomers just “adding on” to each other without loss of atoms. All monomers forming addition polymers have C=C bonds (carbon-carbon double bonds). In addition polymerization, the unsaturated monomers are coupled through their multiple bonds. These double bonds open up as the monomers join in chains 1000 to 10,000 units long. For example, ethylene molecules can join together (under the proper conditions of temperature, pressure, and catalyst) to form polyethylene (polyethene):

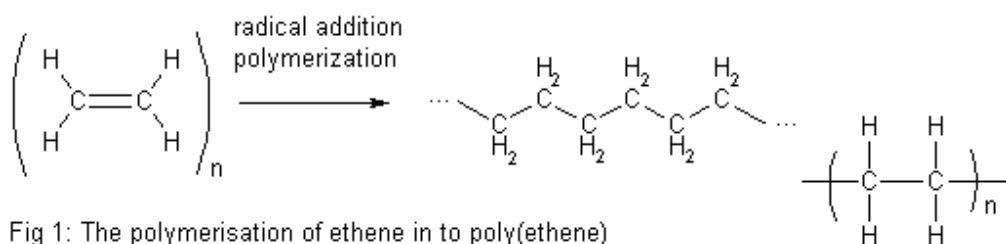


Fig 1: The polymerisation of ethene into poly(ethene)

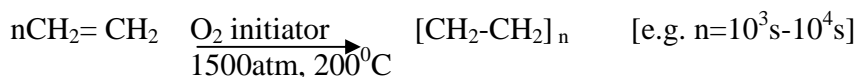
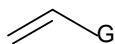


Table 3:1 Examples of vinyl monomers

Derivatives of ethylene serve as monomers in many chain-growth polymerization reactions. They are called vinyl compounds with general formula:



*whole structure is presented $\text{CH}_2=\text{CCH}_3\text{COOCH}_3$

Activity 1: (a) Show the addition chain-growth polymerization reactions of two of the above vinyl monomers. (b) What are the common uses the polymer is applied for?

3.3 The reaction gets initiated when reactive molecules are first formed by either formation of a radical or ion (cation or anion). Each of these will be examined in the following unit 3. More examples of addition polymers include polymethyl methacrylate (Lucite or Plexiglass), Teflon, polyvinyl alcohol, polystyrene, polyvinyl chloride (PVC), polyacrylonitrile (Orlon), and natural rubber.

4.0 Conclusion

Addition polymers are formed from the addition of one monomer to another monomer

Examples of G	Monomer	Polymer formed	Applications of the polymer
H	ethene/ ethylene	polyethene/ polyethylene	toys, plastic bags, films, disposable bottles,
Cl	vinyl chloride	polyvinyl chloride [PVC]	squeeze bottles, pipes, sidings, floorings.
CN	acrylonitrile	Polyacrylonitrile [Orlon]	blankets, rugs, simulated furs, yarns, apparels, orlon/ acrilan materials.
phenyl [Ph]	styrene	Polystyrene	toys, packages, cartons of eggs, clear and hot drink cups.
CH_3 [methyl]	propylene [propene]	polypropylene [polypropene]	carpeting and upholstery, molded caps, butter tubs.
$\text{CH}_3 \text{COO}$	vinyl acetate	polyvinyl acetate	adhesives, latex paints.
All H=F, and G=F	Tetrafluoroethylene	Polytetrafluoroethylene	Heat-resistant coatings
Methyl methacrylate*	Methyl methacrylate	Polymethyl methacrylate 45	Glass substitutes, jewelry
OH	Vinyl alcohol	Polyvinyl alcohol (PVA)	Glues

Unit 3: Mechanisms in Addition Chain-Growth Polymerization Reactions [Radical and Ionic Addition Polymerizations]

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- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References/ Further Readings

1.0 Introduction

There are three basic mechanisms by which addition chain-growth polymerization can occur. They could be radical or cationic or anionic. The structure of the monomer and the initiator determines which will occur. Each of them occurs by three stages:

- (i) Initiation stage, which commences the polymerization by forming the reactive molecule which can be radical or cationic or anionic. This is where the three basic mechanisms take their names.
- (ii) Propagation stage: where the growth of the chain continues. Lastly is
- (iii) Termination stage: Here the chain stops growing and the reaction is terminated.

2.0 Objectives

At the end of this unit you should be able to

- understand the three basic mechanisms [radical, cationic & anionic] in addition polymerization reactions
- identify the three stages [initiation, propagation and termination] in each of the mechanisms
- predict propagation sites in each reactive molecule
- write basic chemical equations to illustrate details of all the addition polymerization reactions
- know that the anionic mechanism results into formation of living polymers

3.0 Main Content

Addition chain-growth polymerization occurs by three basic mechanisms. They are radical, cationic and anionic mechanisms. Each involves three stages, which are initiation (caused by an initiator, which usually will not alter the properties of the polymer), propagation (always with propagating site at the end of the most recent unit added) and the termination stage

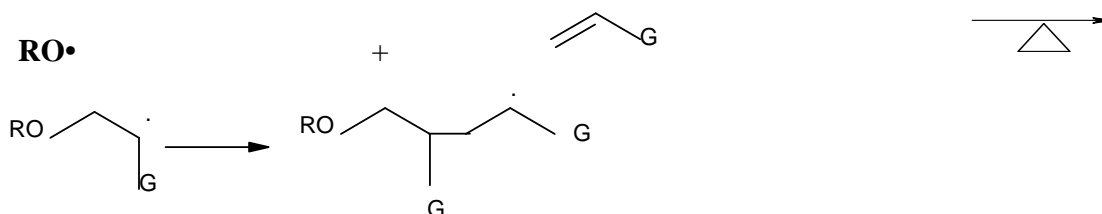
3.1 Radical addition chain-growth polymerization:

Usually an **initiator** is used to start the addition chain-growth polymerization reaction. The initiator is a compound that can convert the monomer into a free radical (a substance that contains an unpaired electron). When free radicals react with a double bond, a chain reaction occurs, which could theoretically continue as long as there is monomer material present. This is because the radical molecules are very reactive.

There is homolytic breaking of the initiator to form a radical which adds to the vinyl monomer, changing it also into a radical [active molecule]. Equation below show how the initiator forms radicals. [**RO•** is a generalized symbol for a free radical initiator, which usually does not alter the properties of the polymer formed since it is not in significant amount].



The radical reacts with the monomer to give another radical of it which adds to other monomers, process repeated over and over, so the chain keeps growing i.e. propagates, with the radical at the end of the most recent unit added, known as the propagating site.



Activity 2: Show the propagating site in the above dimmer.

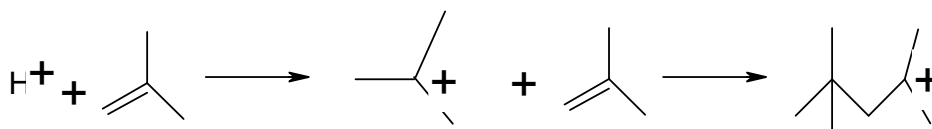
At last the chain-growth reaction stops once the propagating site is no more available, there is no formation of other free radicals. The stage is referred to as 'termination stage'. These may be caused by any of the followings:

- i. two radicals combine at the propagating sites
- ii. disproportionation of two radicals occurs as one radical oxidizes to alkene [loses an H to the second], and another gets reduced to the alkane by accepting the H.
- iii. combines with an impurity at the propagating site.

Another case is the **'chain transfer'** where another molecule AB combine with a growing chain such that A. terminates it, and B. is left to initiate growth of another chain. Here growth of the chains are being controlled. The readiness of molecule AB to homolytically split is influential here. Steric controls and nature of other on it are also important here. Most alkenes and vinyl compounds undergo radical addition polymerizations.

3.2 Cationic addition chain-growth polymerization:

It is an electrophilic addition reaction. An electrophile initiates this polymerization reaction. It could be a proton $[H^+]$, which add to the vinyl molecule to turn it to a cation. Lewis acid and base e.g. BF_3 and H_2O is usually involved in producing the proton that adds to the unsaturation hence initiates the formation of the reactive cation. This now adds to other monomers, process repeated over and over, so the chain keeps growing i.e. propagation stage, with the positive charge at the end of the most recent unit added, known as its propagating site.



Activity 3: Identify the cationic propagating site in the above dimmer.

Termination of the cationic addition chain-growth reaction can be caused by any of the following:

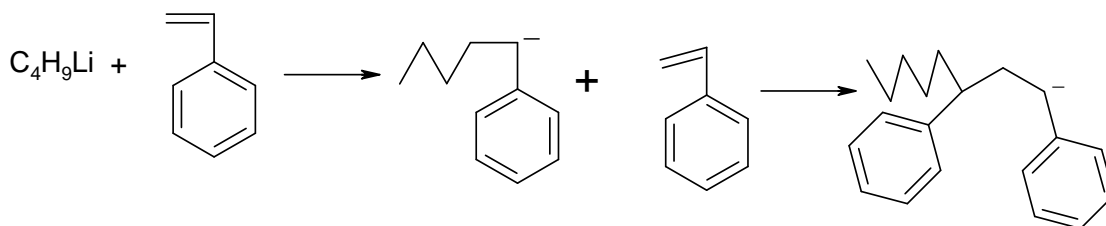
- i. loss of a proton to form unsaturation [double bond] at the end of the chain.
- ii. nucleophile adds to the cationic propagating site to form saturated polymer chain.
- iii. when there is chain transfer reaction with the solvent

Structure of the monomer determines whether rearrangement will occur or not, this is towards retaining more stability. Rearrangements may occur depending on the stability of the carbocation formed. [Recall that tertiary C^+ is most stable than secondary C^+ , and primary C^+ is least stable]. Monomers that undergo cationic addition reactions include styrenes, methyl vinyl ethers, and 2-methyl propene.

3.3 Anionic addition chain-growth polymerization:

Nucleophile [usually a strong base e.g. butyllithium and sodium amide] initiates this polymerization by adding to the alkene to form a reactive anion, a carbanion. Alkenes are generally electron rich, so reluctant to addition of electrons, but presence of electron withdrawing groups [e.g. carbonyls and amides] that decrease density of electrons on the alkene foster it for nucleophilic reactions. The reactive anion [carbanion] formed add to other monomers, passes the negative charge to the extreme newly added monomer which now carries the carbanion. The process is repeated over and over, so the chain keeps growing i.e. propagation stage, with the negative charge at the end of the most recent unit

added, known as its propagating site. Common monomers that undergo anionic addition chain-growth reactions include methyl methacrylate, styrene, acrylamide, and acrolein.



Termination of the anionic addition chain-growth polymer occurs by any of the followings:

- i. a chain transfer reaction with solvent which donates a proton at the end of chain.
- ii. impurities in the reaction mixture reacting with it.
- iii. Propagation of chain terminates when all the monomers have fully participated in the reaction to form the chain, leaving no monomer unreacted and the propagating site still available for reactions if more monomers are added. What is formed is called a **'living polymer'**.

Termination never occurs by loss of protons as in cationic or by disproportionation and radical combination. A good example is glue a polymer of methyl methacrylate that demonstrates this effect when poured in between fingers, and it tends to gum the fingers together. This implies that nucleophilic group from the skin triggers the living polymer to continue chain formation reaction. Ability to continue forming covalent bond with the surface of material it is poured on makes it to glue-up/ join.

The type of substituent on the vinyl group determines which of these three mechanisms the addition chain-growth polymerization will occur. The following polymers are by addition polymerization: polymethyl methacrylate (Lucite, or Plexiglass), Teflon, polyvinyl alcohol, polystyrene, polyvinyl chloride (PVC), polyacrylonitrile (Orlon), and natural rubber

4.0 Conclusion

Radical, cationic and anionic are basic mechanisms occurring in addition chain-growth polymerization. Each of these involves three stages: initiation, propagation and termination.

5.0 Summary

In this unit we have learnt that

- addition chain-growth polymerization involves three basic mechanisms: radical, cationic and anionic, and we studied features of each, and identified their propagating sites.
- each of the three mechanisms occur in three stages: initiation, propagation and termination stages.
- the initiator doesnot alter the properties of the polymer.
- cationic is electrophilic addition polymerization, while anionic is nucleophilic addition reaction.
- 'living polymers' are formed in anionic addition chain-growth polymerization reactions.

6.0 Tutor-Marked Assignment (TMA)

1. Justify the influence of initiators on the properties of a polymer.
2. From which monomer(s) is this polymer formed? $-\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2-$
3. Show the cationic addition chain-growth polymerization of 2-methylpropene
4. Use equations to show each of the three possible causes of termination of chain-growth in (a) radical addition (b) cationic addition (c) anionic addition

7.0 References/Further Readings

- T.L. Brown; H.E. LeMay Jr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International p. 499-513.
- P.Y. Bruice (2007): Organic Chemistry. 5th Edition. Pearson Education Inc. p. 1232-1257.
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Unit 4: Condensation Step-growth polymerization reactions

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- 1.0 Introduction
- 2.0 Objectives
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 - 3.2 Thermoplastics and thermo sets
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1.0 Introduction

Step reactions are involved which are independent of each other and does not involve no chain-carrying free radicals or ions like cations and anions. The monomers have more than a functional group. During the polymerization small molecules such as NH_3 , HCl , CO_2 or H_2O is lost. We will also see that properties of the polymers are function of the arrangements and links/ bonding in it, determining also its shapes.

2.0 Objectives

At the end of this unit you should be able to

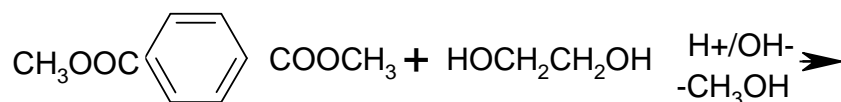
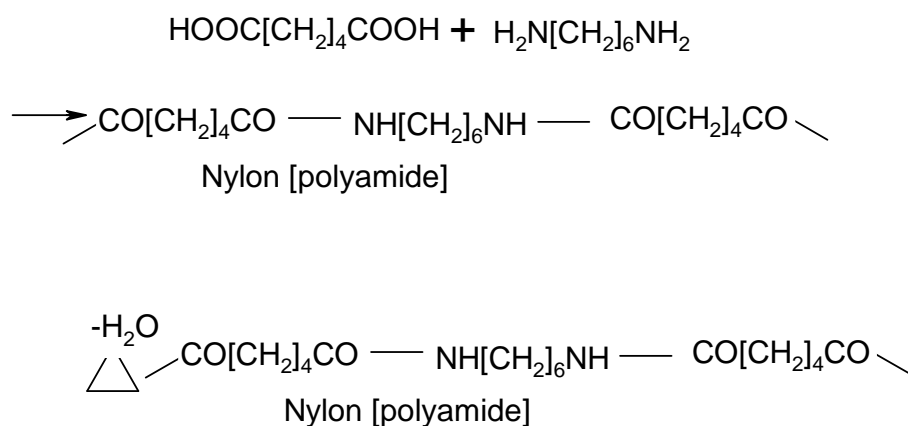
- give details of condensation step-growth polymerization as step reactions that are independent of each other with loss of small molecules like H_2O , CO_2 , HCl and NH_3

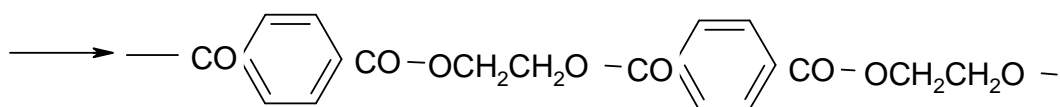
- know that monomers involved in condensation reactions have more than a functional group
- express properties of condensation polymers as function of the arrangements and links with bonding in it, which also determine its shapes and uses.

3.0 Main Content

The condensation step-growth reactions are independent of each other. Chain-carrying free radicals or ions like cations and anions are not involved. Small molecules like NH_3 , HCl , CO_2 or H_2O are liberated during condensation.

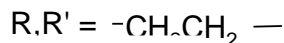
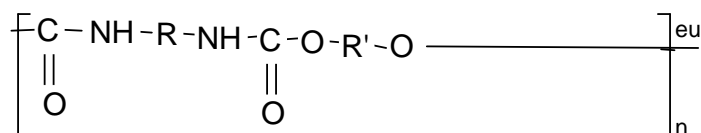
3.1 Condensation polymers are formed when the monomers react with each other so that a small molecule, such as H_2O , CO_2 , NH_3 or HCl , is eliminated as a product each time a monomer reacts with another monomer. This is where the name of condensation polymerization is derived. There must be at least two functional groups on each reacting monomer in order for the reaction to continue to form a chain; hence a linear polymer is formed as in nylon and dacron. For monomers with more than two functional groups i.e. with more than two sites for reaction, a highly cross-linked polymer is formed as in resins like glyptal a polyester. After every elimination, reacting groups are available for more condensations. Other examples of condensation polymers are polyurethane foam, epoxy glue and resins, peptides and proteins. The formation of nylon (polyamide) and dacron (polyester) are shown.





Dacron [polyester]

Condensation polymers include polycarbonate, polyethylene terephthalate and polyurethane. **Polycarbonates** are important as shatterproof eyeglass lenses, CDs, DVDs, bulletproof windows and green houses. **Polyethylene terephthalates** are polyesters, important as apparels, soft-drink bottles, tire cords and magnetic tapes. **Polyurethanes** are another condensation polymer utilized for foam furniture stuffing, spray-on insulation, automobile parts, footwear and water-protective coatings. They contain urethane groups {RNHCOOR'}, which are formed from the reaction of isocyanate {RN=C=O} and an alcohol {R'OH}. E.g. reaction of toluene-2,6-diisocyanate and ethylene glycol in the presence of a blowing agent {N₂ or CO₂} gives polyurethane foam. This condensation reaction is unique because there is no liberation of small molecule here, unlike others. They are also examples of block copolymers. Polyurethanes has the following general structure:



Polyurethane

3.2 Polymers are produced as long chains that sometimes have connections between them due to involvements of wider variety of functional groups on the monomer. If the chains are *not* connected to one another, the polymer typically can be melted and reshaped repeatedly. These polymers are called **thermoplastics**. Examples are polyethylene, nylon, and polyester, polyvinyl chloride, and polystyrene. But if the long chains are joined together with cross-links, the material becomes extremely rigid; once formed, these polymers do not soften or melt when heated. The polymers are **thermosets**. Bakelite and related polymers of the condensation polymerization of phenol and methanal [with loss of water molecules] are thermo sets of quite old synthetic polymers, but still have very important uses. More examples are the plastics used to manufacture bowling balls, handles on kitchen utensils, Formica table tops, and some modern auto bodies to lessen weight, compared to if it had been totally made of metals.

In the formation of **thermoplastics**, they have individual chain arrangements that determine their physical properties. It could be in both ordered crystallizable [arrangements are more orderly] and amorphous noncrystallizable forms. Regularity with close fittings of the molecules of the polymer permits the crystallizables to have strong forces like hydrogen bondings, dipole-dipole attractions and van der Waals forces with less heat content (low enthalpy). But lack of randomness constitutes unfavorable entropy

for the polymer. A balance is strike between this two, hence polymers form solids made of regions of crystallinity called crystallites, which are embedded in amorphous materials. They are liable to cracking. At room temperature the plastics are hard, but soften on heating so that it can be molded. The chains can easily slip over each other at fairly high temperature to give different shapes of most of the materials we constantly use e.g. toys, plates of switches, combs, casings etc.

Thermo set polymers are highly rigid with much cross-links. The cross-links are responsible for its rigidity, the more the harder.

4.0 Conclusion

Condensation polymerization involve step reactions that are independent of each other with loss of small molecules like H_2O , CO_2 , NH_3 and HCl . Condensation polymers are important materials with divers physical structures like thermosettings, thermoplastics and copolymers.

5.0 Summary

In this unit we have learnt that

- condensation step-growth polymerization are step reactions that are independent of each other with loss of small molecules like H_2O , CO_2 and NH_3
- monomers involved in condensation reactions have more than a functional group
- properties of condensation polymers are function of the arrangements and links with bonding in it, this also determine its shapes and uses.

6.0 Tutor-Marked Assignment (TMA)

1. What is a condensation (step-growth) polymer?
2. Write an equation for the formation of the condensation polymer formed between toluene-2,6-diisocyanate and ethylene glycol.
3. Use equations only to illustrate the following, showing the structures:
In the polymerization of PET polyester, the monomers are terephthalic acid ($\text{HOOC-C}_6\text{H}_4\text{-COOH}$) and ethylene glycol ($\text{HO-CH}_2\text{-CH}_2\text{-OH}$) but the repeating unit is $-\text{OC-C}_6\text{H}_4\text{-COO-CH}_2\text{-CH}_2\text{-O-}$, which corresponds to the combination of the two monomers with the loss of two water molecules.

7.0 References/Further Readings

- T.L. Brown; H.E. LeMayJr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International p. 499-513.
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Module 4: Solubility and Solution Properties of Polymers;

Unit 1: Solubility Properties of Polymers

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- 3.7 Non –aqueous solvent and their solubility
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1.0 Introduction

Solubility properties of polymers are dependent on conditions like temperature, pressure, polarity and surface area. Equations are also used in describing solubility of polymers for industrial, technological and pharmaceutical uses. Examples include Hildebrand, Hansen, Gibb's, Henry's and Flory-Huggins.

Solubility describes the property of solid, liquid or gaseous substances called solute to dissolve in solvent to form a homogeneous solution. The solubility of a substance strongly depends on the nature of solvent used as well as on temperature and pressure. The extent of the solubility of a substance in a specific solvent is measured as the saturation concentration, where adding more solute does not increase the concentration of the solution. Solvents are generally a liquid, which can be pure substance or mixture. Commonly spoken of are solid solutions, but rarely do we speak of gas solutions, instead is vapour-liquid equilibrium. Extent of solubility widely ranges, from fully/ perfectly soluble (like ethanol in water), to poorly soluble, as in AgCl in H₂O. The term insoluble implies it is poorly or not at all soluble compounds in the solvent.

Under certain conditions the equilibrium solubility can be exceeded to give a so-called supersaturated solution, which is metastable.

Polymers are not usually in gaseous form, not usually volatile, though their monomers from which they are formed may be.

2.0 Objectives

At the end of this unit you should be able to

- concisely describe solubility properties of polymers
- state factors responsible for the determination of solubility of polymers
- differentiate between solubility and solvolysis
- compare solubility of organic compounds [which polymers are] and inorganic/ polar compounds
- understand expressions of solubility

3.0 Main Content

Solubility is a dynamic equilibrium, meaning that solubility results from the simultaneous and opposing processes of dissolution and phase separation (e.g. precipitation of solids). Solubility equilibrium occurs when the two processes proceed at a constant rate.

Solubility is used also in some fields where solute is altered by solvolysis [reactions with the solvent; reaction of substances with solvent and in solvent]. For example, most metals and their oxides are said to be "soluble in hydrochloric acid," whereas the aqueous acid degrades solids to irreversibly give soluble products. It is also true that most ionic solids are degraded by polar solvents, but such processes are reversible. In those cases where the solute is not recovered upon evaporation of the solvent, the process is referred to as **solvolysis**. The thermodynamic concept of solubility does not apply directly to solvolysis. Furthermore, the solubility of a solute and the composition of its soluble components depend on pH. In general, solubility in the solvent phase can be given only for a specific solute which is thermodynamically stable, and the value of the solubility will include all the species in the solution.

3.1 Factors determining solubility

Solubility is defined for specific phases. For example, the solubility of two polymorphs in water is expected to differ, even though they have the same chemical formula. The solubility of one substance in another is determined by the balance of intermolecular forces between the solvent and solute, and the entropy change that accompanies the

solvation. Factors such as **temperature** and **pressure** will alter this balance, thus changing the solubility.

Solubility of a given solute in a given solvent typically depends on **temperature**. Many solids dissolved in liquid water, with solubility increasing with temperature up to 100 °C. In liquid water at high temperatures, like when approaching the critical temperature, the solubility of ionic solutes tends to decrease due to the change of properties and structure of liquid water; the lower dielectric constant results in a less polar solvent. Gaseous solutes exhibit more complex behavior with temperature. As the temperature is raised, gases usually become less soluble in water, but more soluble in organic solvents.

The temperature dependence when occasionally few solutes become less soluble in water as temperature increases is sometimes referred to as "retrograde" or "inverse" solubility. But the solubility of organic compounds which most polymers are, are nearly always increasing with temperature. The technique of recrystallization, used for purification of solids, depends on a solute's different solubilities in hot and cold solvents. A few exceptions exist, like certain cyclodextrins.

Effects of **pressure** are as follows: For condensed phases (solids and liquids), the pressure dependence of solubility is typically weak and usually neglected in practice. Pressure dependence of solubility does occasionally have practical significance. An instance is in the precipitation fouling of oil fields and wells by calcium sulphate (which decreases its solubility with decreasing pressure) can result in decreased productivity with time.

Solubility may also strongly depend on the presence of other species dissolved in the solvent i.e. ligands in liquids. Solubility will also depend on the excess or deficiency of a common ion in the solution, a phenomenon known as the **common-ion effect**. To a lesser extent, solubility will depend on the ionic strength of solutions. The last two effects can be quantified using the equation for solubility equilibrium.

For a solid that dissolves in a redox reaction, solubility is expected to depend on the **potential** (within the range of potentials under which the solid remains the thermodynamically stable phase).

The metastable super saturated solubility also depends on the physical **size** of the solid or droplet of the solute or, moreso on the specific or molar surface area of the solute. It can be quantified on solubility equilibrium. For highly defective solids, solubility may increase with the increasing degree of disorderliness. Both of these effects occur because of the dependence of solubility constant on the Gibbs energy of the crystal. The last two effects, although often difficult to measure, are of practical importance. For example, they provide the driving force for precipitate aging (the solid size spontaneously increases with time).

Polarity is another factor affecting solubility. We usually say in solubility that "like dissolves like". The statement shows that a solute will dissolve best in a solvent that has a similar polarity to itself. This view is too simple, since it ignores many solvent-solute interactions, but it is a useful rule of thumb. For instance, a very polar (hydrophilic) solute like urea is very soluble in highly polar water, less soluble in fairly polar methanol, and practically insoluble in non-polar solvents such as benzene. In contrast, a non-polar or lipophilic solute like naphthalene is insoluble in water, fairly soluble in methanol, and

highly soluble in non-polar benzene. Liquid solubilities also generally follow this rule. Lipophilic plant oils, such as olive oil and palm oil, dissolve in non-polar solvents like alkanes, but they are less soluble in polar liquids like water. Synthetic chemists often exploit differences in solubilities to separate and purify compounds from reaction mixtures, using the technique of liquid-liquid extractions. Insolubility and spontaneous phase separation does not mean that dissolution is disfavored by enthalpy. It is opposite in the case of water and hydrophobic substances. Hydrophobic hydration is reasonably exothermic and enthalpy alone should be favoring it. It appears that entropic factors — the reduced freedom of movement of water molecules around hydrophobic molecules — lead to an overall hydrophobic effect.

3.2 Solubility of gaseous substances

Gaseous solutes exhibit more complex behavior with temperature. As the temperature is raised, gases usually become less soluble in water, but more soluble in organic solvents. Henry's law helps in quantifying solubility of gases in solvents. The solubility of a gas in a solvent is directly proportional to the partial pressure of that gas above the solvent. This relationship is written as:

$$p = kc$$

where k is a temperature-dependent constant (e.g. dioxygen (O_2) in water at 298 K has $769.2L \cdot atm/mol$), p is the partial pressure (in atm), and c is the concentration of the dissolved gas in the liquid (mol/L).

3.3 Rate of dissolution

Dissolution is not automatically an instantaneous process. It is fast when salt and sugar dissolve in water but much slower for a tablet of paracetamol or larger solids. These observations are the consequence of two factors: the rate of solubilization is determined by the solubility product and the surface area of the material. The speed at which a polymer dissolves may depend on its crystallinity or lack thereof in the case of amorphous solids and the surface area (crystallite size) and the presence of polymorphism. Many practical systems illustrate this effect, for example in designing methods for controlled drug delivery. Critically, the dissolution rate depends on the presence of mixing and other factors that determine the degree of under saturation in the liquid solvent film immediately adjacent to the solid solute crystal. In some cases, solubility equilibria can take a long time to establish (hours, days, months, or many years; depending on the nature of the solute and other factors). In practice, it means that the amount of solute in a solution is not always determined by its thermodynamic solubility, but may depend on kinetics of dissolution (or precipitation).

The rate of dissolution and solubility should not be confused as they are different concepts, kinetic and thermodynamic, respectively. The solubilization kinetics, as well as apparent solubility can be improved after complexation of an active ingredient with cyclodextrin. This can be used in the case of drug with poor solubility.

3.4 Expressing solubility

Solubility is commonly expressed as a concentration, either by mass (g of solute per kg of solvent, g per dL (100 mL) of solvent), molarity, molality, mole fraction or other similar descriptions of concentration. The maximum equilibrium amount of solute that can

dissolve per amount of solvent is the solubility of that solute in that solvent under the specified conditions. The advantage of expressing solubility in this manner is its simplicity, while the disadvantage is that it can strongly depend on the presence of other species in the solvent (for example, the common ion effect). **Solubility constants** are used to frequently describe saturated solutions of ionic compounds of relatively low solubility. The solubility constant is a special case of equilibrium constant. It describes the balance between dissolved ions from the salt and undissolved salt. The solubility constant is also "applicable" (i.e. useful) to precipitation, the reverse of the dissolving reaction. As with other equilibrium constants, temperature can affect the numerical value of solubility constant. The solubility constant is not as simple as solubility; however the value of this constant is generally independent of the presence of other species in the solvent.

The **Flory-Huggins** solution theory is a theoretical model for describing the solubility of polymers. Hansen Solubility Parameters and the Hildebrand solubility parameters are empirical methods for the prediction of solubility. It is also possible to predict solubility from other physical constants such as the enthalpy of fusion.

Partition coefficient (Log P) is a measure of differential solubility of a compound in hydrophobic solvents like octanol and a hydrophilic solvent like water. The logarithm of these two values enables compounds to be ranked in terms of hydrophilicity (or hydrophobicity).

3.5 Applications of solubility

Solubility is of fundamental importance in a large number of scientific disciplines and practical applications, ranging from ore processing, to the use of medicines, and the transport of pollutants, now to polymer chemistry. Solubility is often said to be one of the "characteristic properties of a substance," which means that solubility is commonly used to describe the substance, to indicate a substance's polarity, to help to distinguish it from other substances, and as a guide to applications of the substance.

Solubility of a substance is useful when separating mixtures. A mixture of sodium chloride and silica may be separated by dissolving the sodium chloride in water, and filtering off the undissolved silica. The synthesis of chemical compounds, by the milligram in a laboratory, or by the ton in industry, both make use of the relative solubility of the desired product, as well as unreacted starting materials, by-products, and side products to achieve separation. Also in the synthesis of benzoic acid from phenylmagnesium bromide and dry ice, benzoic acid is more soluble in an organic solvent such as CH_2Cl_2 or $[\text{C}_2\text{H}_5]_2\text{O}$, and when shaken with this organic solvent in a separatory funnel, will preferentially dissolve in the organic layer. This process is known as liquid-liquid extraction. It is an important technique in synthetic chemistry.

3.6 Organic compounds and solubility

Polarity is based on the principle that *like dissolves like*, is the usual guide to solubility with organic systems. For example, petroleum jelly will dissolve in gasoline because both petroleum jelly and gasoline are hydrocarbons. It will not, on the other hand, dissolve in alcohol or water, since the polarity of these solvents is too high. Sugar will not dissolve in gasoline, since sugar is more polar in comparison with gasoline. A mixture of gasoline and sugar can therefore be separated by filtration or extraction with water.

3.7 Non-aqueous solvents and their solubility

Most publicly available solubility values are those for solubility in water. References for solubility in non-aqueous solvents are not too common.

3.8 Solid solutions

This term is often used in the field of metallurgy to refer to the extent that an alloying element will dissolve into the base metal without forming a separate phase. The solubility line (or curve) is the line (or lines) on a phase diagram which give the limits of solute addition. That is, the lines show the maximum amount of a component that can be added to another component and still are in solid solution. In the solid's crystalline structure, the 'solute' element can either take the place of the matrix within the lattice (a substitutional position, for example: chromium in iron) or can take a place in a space between the lattice points (an interstitial position, for example: carbon in iron).

In microelectronic fabrication, solid solubility refers to the maximum concentration of impurities one can place into the substrate.

3.9 Incongruent dissolutions

Many substances dissolve congruently, i.e., the composition of the solid and the dissolved solute stoichiometrically match. However, some substances may dissolve incongruently, whereby the composition of the solute in solution does not match that of the solid. This solubilization is accompanied by alteration of the "primary solid" and possibly formation of a secondary solid phase. However, generally, some primary solid also remains and complex solubility equilibrium establishes. This kind of solubility is of great importance in geology, where it results in formation of metamorphic rocks.

4.0 Conclusion

Polymers solubility properties depend on conditions like temperature, pressure, polarity and surface area

5.0 Summary

In this unit we have learnt

- about solubility properties of polymers
- factors responsible for the determination of solubility of polymers
- the differences between solubility and solvolysis
- about solubility of organic compounds [which polymers are] and inorganic or polar compounds, and their comparisons
- the expressions of solubility

6.0 Tutor-Marked Assignment (TMA)

1. Describe the state of saturation in solubility.
2. Differentiate between solubility and solvolysis.
3. List and highlight factors that affect solubility of a solute in a solvent.
4. What determines the rate of solubilization of a solute?

7.0 References/Further Readings

- T.L. Brown; H.E. LeMay Jr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International p. 499-513.
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Unit 2: Solution Properties of Polymers

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- 3.0 Main Contents
 - 3.1 Cholesteryl Benzoate
 - 3.2 Principles Liquid crystal operate
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 - 3.5 More examples of Solution properties
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References/ Further Readings

1.0 Introduction

Liquid crystals when heated have structure of solids but with freedom of movements as in liquids at sharp transition temperatures. The different alignments of liquid crystal molecules are responsible for the different orders. These solution properties are utilized in our modern electronic devices like calculators, cellular phones, laptops, mobile media players

2.0 Objectives

At the end of this unit you should

- know the principles behind operations of liquid crystals
- present some of the importance and applications of liquid crystal phases

- be able to relate different orders and alignments of liquid crystal molecules

3.0 Main Content

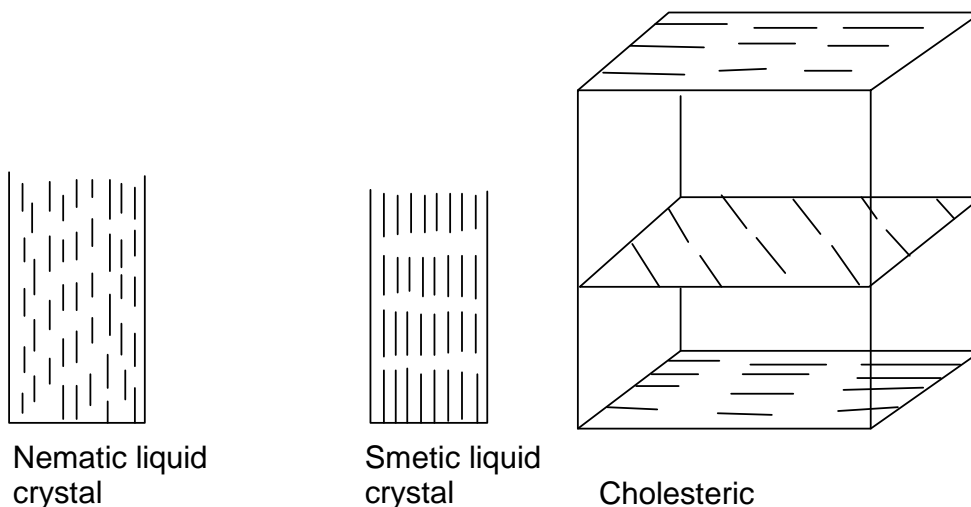
Solids normally pass directly from solid to liquid phase on heating. Instead of this some substances like polymers when heated pass through an intermediate liquid crystalline phase that has structure of solids but with freedom of movements as in liquids. The partial orderliness in it makes it very viscous and has properties of both liquid and solid phases. Region in which they exhibit above property is marked by sharp transition temperature. We will be considering molecular principles of liquid crystals with special optical properties.

3.1 F. Reintzer a botanist (1888) was the first to observe this while handling organic compound: cholesteryl benzoate, which on heating melted at 145°C to a viscous milky liquid. But on reaching 179°C the liquid became clear. On cooling it reversed. i.e. it turns viscous and milky at 179°C , while the liquid solidifies at 145°C . Today this phenomenon is called '**liquid crystal**'. Most of our modern electronic devices are based on these technologies: liquid crystal displays (LCDs) and light-emitting diodes (LEDs).

3.2 The principles liquid crystal operates

For polymers, they pass through intermediate liquid crystalline phase that has both structures of solids as well as freedom of motion like liquids; it can be accounted for by their partial ordering, hence the sharp transition temperature they have. The weak intermolecular forces that hold the molecule together in liquid crystal are easily affected by temperature, pressure and electrical field changes.

There are different types of the liquid crystalline phases, depending on the orientation and alignments. Polymers have long, elongated, rodlike molecules, with polar groups atimes [e.g. C=O, C=N, COOH, R-O-R, OH, CONH, C-X]; hence with intermolecular forces [H-bondings, van der Waals forces and dipole-dipole attractions]. In ordinary situation polymers are oriented randomly. [NB: Lengths of the molecules are greater than their widths]. But the liquid crystalline phases have different orderings. The different alignments of liquid crystal molecules are responsible for the different orders. They can be illustrated thus:



Nematic

Smectic

Cholesteric

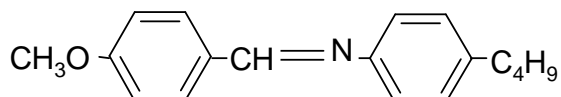
Nematics have its molecules in one dimensional ordering, aligned along their long axes as handful of pencils with non-aligned ends. Smectic molecules have two dimensional orderings, molecules are aligned along their long axes and in layers. Molecules of cholesteric are in successive layers. Their orientation is at characteristic angles to adjacent layers, hence no repulsive interactions and gives a screwlike axis.

3.3 Some importance and applications of solution properties of polymers

The liquid crystal displays (LCDs) in some of our modern electronic devices like calculators, cellular phones, laptops, mobile media players utilize the solution property. They have wide applications in temperature and pressure sensors, as well as displays of electrical devices of the above mentioned and wireless devices. They are utilized in monitoring devices e.g. the cholesteric liquid crystal is used in monitoring temperature changes in situations where conventional methods are not possible. Like taking skin temperature of infants; detecting hot spots in micro-electronic circuits, that can signal presence of flaws.

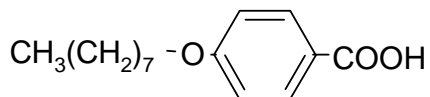
3.4 Some molecules of liquid crystals

(i)



[Changes between solidification-viscous liquid] at 21-47⁰C

(ii)



[Changes between solidification-viscous liquid] at 108-147⁰C

(iii) Dow Industrial Specialty Polymers in Electronics Applications

Activity A: Find out details of (iii) Dow Industrial Specialty Polymers in Electronics Applications

3.5 More examples

(i) Solutions of the polymer polyvinyl alcohol (PVA) and polyvinyl acetate can be made into gels by addition of a borax solution. Borax cross-links the polymer chains, to give interesting properties of gels.

(ii) "Slime" is a polyvinyl alcohol polymer.

(iii) "Glue" is a polyvinyl acetate polymer.

4.0 Conclusion

Some polymers can pass through different types of liquid crystalline phases, which are utilized in modern devices like calculators, cellular phones, laptops, portable media players etc.

5.0 Summary

In this unit we have learnt

- the principles on which liquid crystals operate.
- some of the importance and applications of liquid crystal phases.
- how to relate different orders and alignments of liquid crystal molecules.
- about nematic, smectic, cholesteric liquid crystals.

6.0 Tutor-Marked Assignment (TMA)

1. State differences between nematic, smectic, cholesteric liquid crystals, and sketch to illustrate each.
2. Explain the phenomenon 'liquid crystal', and its applications.

7.0 References/Further Readings

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Module 5: Structures and Properties of Polymers;

Unit 1: Crystallinity and Amorphous Properties of Polymers

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- 2.0 Objectives
- 3.0 Main Contents
 - 3.1 General information on arrangements of molecules
 - 3.2 Extended and random forms of Polymers
 - 3.3 Structural effects on properties of Polymers
 - 3.4 Practical issues on Properties of Polymers
 - 3.5 Configuration
 - 3.6 Techniques of studying and varying the properties of polymers
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
- 7.0 References/ Further Readings

1.0 Introduction

Structures of polymers that are notably big influence widely its solution properties. Their functions depend on this. Factors like crystallinity, entropy, enthalpy and intermolecular forces [van der Waals, dipole-dipole attractions and H-bonding] will be considered.

2.0 Objectives

At the end of this unit you should

- be able to describe each of crystallinity and amorphous properties of polymers
- be aware that dipole-dipole attractions, van der Waals forces and H-bonding gives the polymer strong intermolecular forces, which is a determinant of properties of polymers
- understand that entropy is negatively affected and enthalpy is positively affected by crystallinity of a polymer
- know that degree of crystallinity of a polymer is the extent to which it is composed of crystallites
- know practical issues on properties of polymers and techniques of studying them

3.0 Main Content

In characterization of a polymer several parameters are specified to statistically estimate distribution of chains of varying lengths, each chain consisting of monomer residues which affect its properties.

Synthetic polymer may be described as crystalline if it contains regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, usually arising from intramolecular folding and/or stacking of adjacent chains.

3.1 The very regular and symmetrical arrangement of molecules in non-ionic solids like most polymers gives it its crystalline nature. The geometric pattern is repeated over and over. For long molecules like polymers to fit into this pattern, since it cannot be looped then it will be patterned in a zig-zag form; which constitute unfavourable entropy for the polymer. Likewise regularity and close fitting of molecules in the crystal form gives the polymer strong intermolecular forces due to dipole-dipole attractions, van der Waals forces and H-bonding supporting its favourable enthalpy, which is its heat energy. The opposite effects of enthalpy and entropy in a specific polymer are the main determinant of what the polymer will be used for. There could be its extended or random forms.

3.2 Extended and random forms of polymers

Few synthetic polymers are entirely crystalline most polymers do not fully exist in crystalline form. Some parts of the molecules in the polymer chain become entangled as amorphous, while some are crystalline. Regions of the polymer where the chains are highly ordered within it are referred to as **crystallites**. Areas between the crystallites are amorphous and non-crystalline leaving the chains randomly arranged. That is the solid polymer will have some part of it crystalline called crystallites, and other parts embedded as amorphous materials. Since synthetic polymers do consist of crystalline and amorphous regions, the more the crystalline, the better the orderings, which makes the polymer harder and more resistant to heat. We estimate the degree of crystallinity of a polymer as the extent to which it is composed of crystallites. The degree of crystallinity may be expressed in terms of a weight fraction or volume fraction of crystalline material.

3.3 Structural effects on properties of polymers

Crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer, which is not usually so. Polymers with microcrystalline regions are

generally tougher, more flexible and more impact-resistant than totally amorphous polymers. Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. Thus for many polymers, reduced crystallinity may also be associated with increased transparency.

3.4 Practical issues on properties of polymers

The basic property of a polymer is the identity of its constituent monomer(s). A second set of properties, known as microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material. Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents.

Identification of the monomer residues (repeat units) from which a polymer is built is the first thing. The chemical properties depend on the functional groups in the monomers. Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer. Polymers that contain only a single type of repeat unit are known as homopolymers, while polymers containing a mixture of two repeat units are known as copolymers. E.g. polystyrene is composed only of styrene monomer residues, and is therefore classified as a homopolymer, whereas polymerization of ethylene vinyl acetate gives a copolymer.

3.5 Configuration is the micro-structure of a polymer. Branching points are important in polymers. An important microstructural feature determining polymer properties is the polymer architecture. The simplest polymer architecture is a linear chain: a single backbone with no branches [no cross-links among chains]. A related unbranching architecture is a ring polymer. A branched polymer molecule is composed of a main chain with one or more substituent side chains or branches. There are types of branched polymers. The special types of branched polymers include star polymers, comb polymers, brush polymers, ladders, and dendrimers. Branching of polymer chains affects the ability of chains to slide past one another by altering intermolecular forces, in turn affecting bulk physical polymer properties. Long chain branches may increase polymer strength, toughness, and the glass transition temperature due to an increase in the number of entanglements per chain. The effect of such long-chain branches on the size of the polymer in solution is characterized by the 'branching index'. Random length and atactic short chains, on the other hand, may reduce polymer strength due to disruption of organization and may likewise reduce the crystallinity of the polymer. For example polyethylene, High-density polyethylene [HDPE] has a very low degree of branching, is quite stiff, and is used in applications such as milk jugs. Low-density polyethylene [LDPE], on the other hand, has significant numbers of both long and short branches, it is quite flexible, and is used in applications such as plastic films.

Structures have strong influence on the other properties of a polymer. For example, two samples of natural rubber may exhibit different durability, even though their molecules comprise the same monomers.

3.6 Techniques involved in studying and varying properties of polymers

Varieties of laboratory techniques are used to determine the properties of polymers. Examples include neutron and X-ray scattering, of wide and small angles, for determining crystalline structure of polymers; gel permeation chromatography for knowing the average molecular weight; FTIR, raman and NMR for composition determination; structural determination by pyrolysis; further characterizations of polymer and polymerization reactions by ACOMP [Automatic Continuous Online Monitoring of Polymerization Reactions]; melting point and glass transition temperatures as thermal properties can be determined by differential scanning calorimetry and dynamic mechanical analysis; thermogravimetry evaluates thermal stability of the polymer; TG curves allow us to know a bit of the phase segregation in polymers; Rheological properties determine molecular architecture, molecular weight, molecular weight distribution and branching, as well as to understand how the polymer will process, through measurements of the polymer in the melt phase;

4.0 Conclusion

Structures influence properties of a polymer. Effects of factors like crystallinity, entropy, enthalpy and intermolecular forces [van der Waals, dipole-dipole attractions and H-bonding] were considered.

5.0 Summary

In this unit we have learnt

- about Crystallinity and amorphous properties of polymers
- that dipole-dipole attractions, van der Waals forces and H-bonding gives the polymer strong intermolecular forces, which is a determinant of properties of polymers
- that entropy is negatively affected and enthalpy is positively affected by Crystallinity of a polymer
- that degree of Crystallinity of a polymer is the extent to which it is composed of crystallites
- practical issues on properties of polymers and techniques of studying them

6.0 Tutor-Marked Assignment (TMA)

1. What is a crystallite?

2. Which effect(s) does crystallinity have on (i) entropy? (ii) enthalpy?

7.0 References/Further Readings

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Unit 2: Types and Effects of Linkages on Nature of Polymers

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- 3.2 Cross-linkings
- 3.3 Bakelite
- 3.4 Implications of Cross-linkings
- 3.5 Configuration
- 3.6 Physical Properties and Arrangements
- 3.7 Ziegler-Natta catalysts
- 3.8 Mechanism of Ziegler-Natta
- 3.9 More Properties of Polymers
- 4.0 Conclusion
- 5.0 Summary
- 6.0 Tutor Marked Assignment (TMA)
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1.0 Introduction

Bonds between chains of polymer are called cross-links. They cause rigidity in polymers. Same types of configurations exist for all monosubstituted ethylenes like propene. Their coordination polymerizations are aided by Ziegler-Natta catalysts which are complexes of transition metal halides with organometallic compounds.

Following discoveries by Karl Ziegler of Max Planck Institute for Coal Research and Giulio Natta of Polytechnic Institute of Milan in 1953 [They jointly got the nobel prize in 1963], ionic polymerization that gives better quality products, started to have more importance than the earlier known free-radical type, with variable properties.

2.0 Objectives

At the end of this unit you should be able to

- know the basic groupings of polymer [homopolymers, copolymers, terpolymers, linear, alternating, statistical, block, grafted]
- describe cross-linkings and its effects, also give examples of cross-linked polymers
- apply earlier knowledge on processes of polymerization (module 3) on practical issues of polymer formations
- explain basic configuration in simple polymers
- describe coordination polymerization
- know what Ziegler-Natta catalysts are and their chemistry
- explain each of the following properties of polymers: Mechanical, Tensile strength, Young's modulus, Transport, Melting point, Boiling point, Glass transition temperature and Miscibility

3.0 Main Content

Stereochemically controlled coordination polymerization gives three basic configurations: isotactic, syndiotactic and atactic polymers. Formation of cross-linkings between chains of polymers is responsible for its rigidity.

3.1 Types of linkages in the polymer

Linear, Alternating, Copolymer and Terpolymer are basic polymers formed due to different linkages of monomers in the polymer. The arrangements of monomers in the polymers are also important [see module 1].

Linear polymers have the simplest structures, they are formed from a type of monomer that has a single functional group. They are referred to as **homopolymers**.-A-A-A-A- etc. An example is natural rubber [poly isoprene], polythene and polypropene.

If a polymer is made of two types of monomers, it is called a **Copolymer**. There could be different types of copolymers based on the arrangements of the two monomers:

- i. **Linear alternating** possess regularly alternating monomers. This copolymer has frequent and regular alternation between the two monomers thus
A-B-A-B-A-B-A-B- etc
- ii. **Statistical copolymers** have the two monomers randomly distributed depending on each monomer's reactivity. They are alternatively called 'random copolymer'. **A-A-B-A-B-B-B-A-A-A-B-B-**
They have monomer residues arranged according to a known statistical rule. A statistical copolymer in which the probability of finding a particular type of monomer residue at a particular point in the chain is independent of the types of surrounding monomers may be referred to as a **truly random copolymer**
- iii. Polymers in **Blocks** have sequence in the copolymer with substantial blocks of each monomer type **-A-A-A-A-B-B-B-B-B-A-A-A-A-B-B-B-B-** etc.

Block copolymers have two or more homopolymer subunits linked by covalent bonds. Polymers with two or three blocks of two distinct chemical species (e.g., A and B) are called **di-block copolymers** and **tri-block copolymers**, respectively. Polymers with three blocks, each of a different chemical species (e.g., A, B, and C) are termed **tri-block terpolymers**.

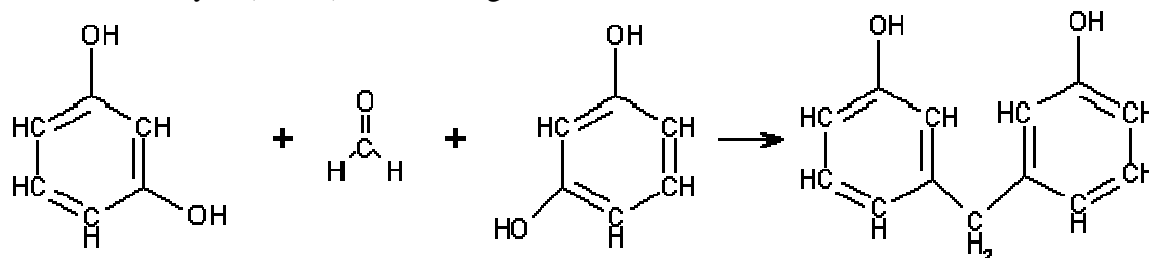
- iv. **Grafted copolymer** have blocks of the monomers grafted on backbone of the others like branches [Module 1]. They contain side chains that have a different composition or configuration than the main chain.
- v. Polymers formed from not less than three different monomers include **terpolymers**. [see **tri-block terpolymers** above].

Activity A: 1. what are Periodic copolymers?

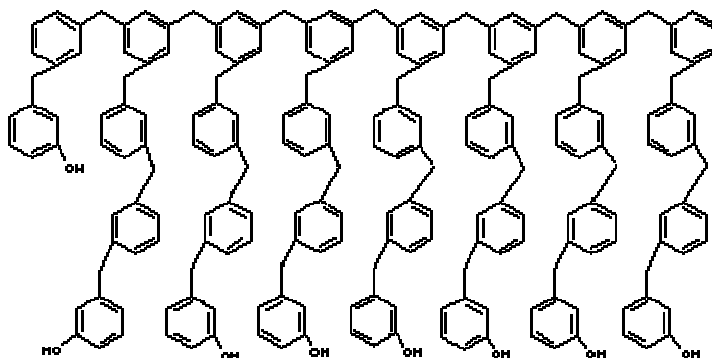
3.2 Cross-linkings

Formation of chemical bonds between the chains of a polymer is called cross-linking. They are networked polymer chains. Polymer molecule with a high degree of crosslinking is referred to as a polymer network. It increases stiffness in polymers. Cross-linkings impose constrain on the relative movement of the chains in the polymer, rendering the material harder and less flexible. Rigidity of a polymer depends on the number of cross-links, the more the cross-links, the harder the polymer. We have considered vulcanization of natural rubber using sulphur as cross-links where the above effect is observed [Module 1, Unit 2]. Absence of cross-links among molecular chains of thermoplastics gives it its flexible properties, and can be remolded. Introduction of cross-links when thermosettings are heated is responsible for their holding to the shapes permanently. Isoprene units in natural rubber [polyisoprene] have double bonds which have the chain extensions on the same side of the double bond- 'cis polyisoprene' making it too flexible and very reactive, so its not very useful. But on addition of sulphur in vulcanization it becomes hardened, stable and less susceptible to oxidation. The sulphur form cross-links at the double bonds. Amount of sulphur added determines rigidity of the rubber.

3.3 Let us see cross-linking in **Bakelite**: Bakelite is a commercially important polymer which is frequently used when a strong, brittle polymer is needed. Shown below is the first step in the formation of the Bakelite. Here, two molecules of resorcinol are heated with formaldehyde (H_2CO) and a strong; covalent bond is formed between them.



When the mixture is heated for a longer time, many more bonds between the molecules are formed. These bonds result in the formation of a polymeric structure with considerable cross-linking. This structure is very difficult to deform because of these bonds and, as a result, is hard and brittle. A small fragment of such a Bakelite polymer molecule is shown below.



3.4 Implications of cross-linking in polymers

In networked polymers sufficiently high crosslink concentrations may lead to the formation of an infinite network, also known as **a gel**, in which networks of chains are of unlimited extent — essentially all chains have linked into one molecule.

The physical properties of a polymer are strongly dependent on the size or length of the polymer chain. For example, as chain length is increased, melting and boiling temperatures increase quickly. Resistance of impact also tends to increase with chain length, likewise the viscosity, or resistance to flow, of the polymer in its melt state. Chain length is related to melt viscosity roughly as $1:10^{3.2}$, so that a tenfold increase in polymer chain length results in a viscosity increase of over 1000 times. Increasing chain length furthermore tends to decrease chain mobility, increase strength and toughness, and increase the **glass transition temperature (T_g)**. This is a result of the increase in chain interactions such as Van der Waals attractions and entanglements that come with increased chain length. These interactions tend to fix the individual chains more strongly in position and resist deformations and matrix breakup, both at higher stresses and higher temperatures.

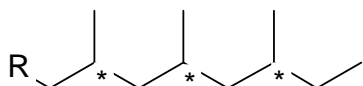
A common means of expressing the length of a chain is the degree of polymerization, which quantifies the number of monomers incorporated into the chain. As with other molecules, a polymer's size may also be expressed in terms of its molecular weight. Since synthetic polymerization techniques typically yield a polymer product including a range of molecular weights, the weight is often expressed statistically to describe the distribution of chain lengths present in the same. The ratio of these two values is the **polydispersity index**, commonly used to express the "width" of the molecular weight distribution. Another measurement is the **contour length**, which can be understood as the length of the chain backbone in its fully extended state. The flexibility of an unbranched chain polymer is characterized by its persistence length.

Activity B: Describe each of 1. glass transition temperature (T_g).

2. polydispersity index 3. contour length 4. van der Waal's forces in polymers

3.5 Configuration

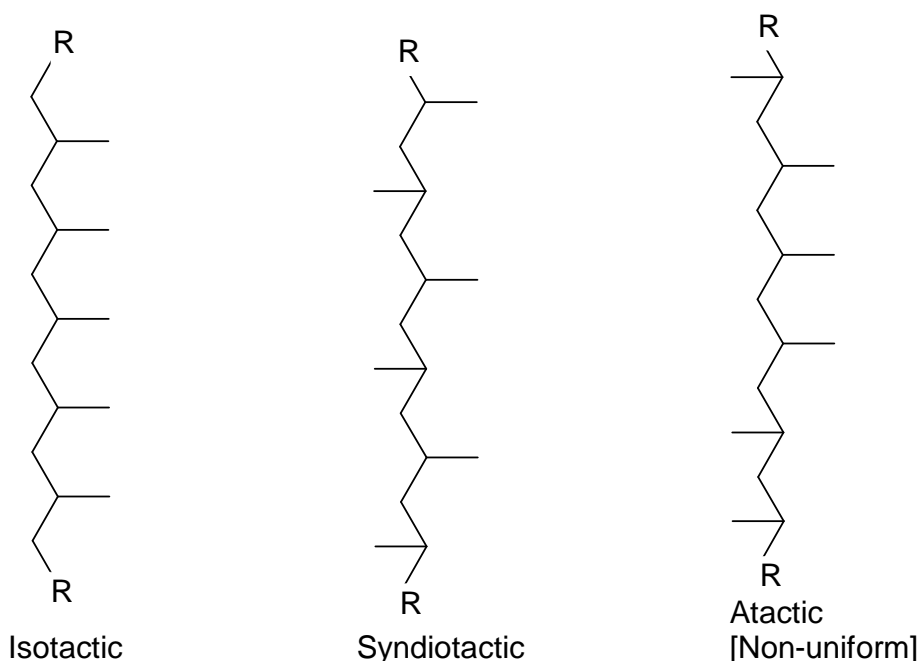
In the polymerization of propene [$\text{CH}_3\text{-CH}=\text{CH}_2$] to give the chain



*carbon are chiral[asymmetric]

There can exist three configurations based on the arrangement and positions of the branched methyls: isotactic, syndiotactic and atactic. This is also called 'tacticity'. It describes the relative stereochemistry of chiral centers in neighboring structural units within a macromolecule. The three types are isotactic with all substituents on the same side; atactic with random placement of substituents; and syndiotactic with alternating placement of substituents.

In isotactic [in Greek implies: 'same order'] polymer every methyl is on one side of the fully extended chain. Regular alternations of the substituent methyl group on both sides exist in syndiotactic which in Greek implies 'alternating'. There is random orientation of the methyl substituents in atactic, making it non-uniform.



3.6 The physical properties of the polymers strongly depend on these arrangements. Regular packing and uniformity of isotactic and syndiotactic polymers may be used in predicting they will likely have high degree of Crystallinity and may be solids. Atactic configuration is more disordered and may not be well packed, hence the polymer may be less rigid and softer. The mechanism by which they are made determines the configuration the polymer will have. Usually branched atactic polymers are formed by radical polymerizations. Polymers with the most stereo-regularity are produced by anionic polymerizations. Percentage of chains with isotactic and syndiotactic configurations increases as temperature of polymerization decreases with decrease in polarity of solvent. Polymers with isotactic and syndiotactic configurations, are harder and stronger than the atactic ones. Also they have better mechanical properties than tactic.

3.7 K. Ziegler and G. Natta in 1953, worked with trialkyl aluminium-titanium chloride [$R_3Al-TiCl_4$]. They posed that some metallic catalysts which will allow stereo-specific reactions do give syndiotactics or isotactics. Structure of a polymer can be controlled if the end of the growing chain and incoming monomer is coordinated with $R_3Al-TiCl_4$ as initiator. Generally these initiators which are complexes of transition metal halides with organometallic compounds are now called **Ziegler-Natta catalysts**. The type of Ziegler-Natta catalyst will determine which of syndiotactic or isotactic polymers will be formed. The Ziegler-Natta catalyst produce more quality products, as well as gives linear molecules and permits stereochemically controlled reactions, than earlier obtained by free-radical polymerizations. Today the Ziegler-Natta processes are very important in syntheses of stronger, stiffer polymers with greater resistance to heat and cracking. High-density polyethylene [HDPE] is an example that utilizes this process.

3.8 Mechanism of the Ziegler-Natta process for substituted ethylenes is explained thus: The monomer give a π -complex with titanium at the open site of coordination, which can accept electrons. The coordinated alkene is inserted between titanium and growing polymer, hence extending polymer chain. A new coordination site is also created. The process is repeated over and over.

At the coordination site a growing carbanion is usually associated with a metallic cation. This ion-pair is important in polymerization reactions. Bonding between the reactive site and the metal is appreciably covalent and it grows, hence called coordination polymerization. The organic chain that is growing is not fully an anion, but has anion-like character. There is nucleophilic addition of double bond in the monomer to the carbanion-like growing organic group of organometallic material as nucleophile. The transition metal also complexes with the π -electrons on the monomer, hence holding it as the reaction site.



3.9 More properties of polymers

i. **Mechanical** Properties refers to the bulk properties of a polymer which are those most often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale.

ii. **Tensile strength** of a material quantifies how much stress the material will endure before failing. This is very important in applications that rely upon a polymer's physical strength or durability. For example, a rubber band with a higher tensile strength will hold a greater weight before snapping. In general tensile strength increases with polymer chain length and cross-linking of polymer chains.

iii. **Young's modulus** of elasticity quantifies the elasticity of the polymer. It is defined, for small strains, as the ratio of rate of change of stress to strain. Like tensile strength, this is highly relevant in polymer applications involving the physical properties of polymers, such as rubber bands. The modulus is strongly dependent on temperature.

iv. **Transport** properties such as diffusivity relate to how rapidly molecules move through the polymer matrix. These are very important in many applications of polymers for films and membranes.

v. **Melting point** when applied to polymers, suggests not a solid-liquid phase transition but a transition from a crystalline or semi-crystalline phase to a solid amorphous phase. Though abbreviated as simply T_m , the property in question is more properly called the crystalline melting temperature. Among synthetic polymers, crystalline melting is only discussed with regards to thermoplastics, as thermosetting polymers will decompose at high temperatures rather than melt.

vi. **Boiling point** of a polymeric material is strongly dependent on chain length. High polymers with a large degree of polymerization do not exhibit a boiling point because they decompose before reaching theoretical boiling temperatures. For shorter oligomers, a boiling transition may be observed and will generally increase rapidly as chain length is increased.

vii. **Glass transition temperature** is a parameter of particular interest in synthetic polymer manufacturing. It describes the temperature at which amorphous polymers undergo a second-order phase transition from a rubber-like, viscous amorphous solid, or from a crystalline solid (depending on the degree of crystallization) to a brittle, glassy amorphous solid. The glass transition temperature may be engineered by altering the degree of branching or cross-linking in the polymer or by the addition of plasticizers.

viii. Generally in **mixing behavior**, polymeric mixtures are far less miscible than mixtures of smaller materials. This effect results from the fact that the driving force for mixing is usually the entropy, not interaction energy. In other words, miscible materials usually form a solution not because their interaction with each other is more favorable than their self-interaction, but because of an increase in entropy and hence free energy associated with increasing the amount of volume available to each component. This increase in entropy scales with the number of particles (or moles) being mixed. Since polymeric molecules are much larger and hence generally have much higher specific volumes than small molecules, the number of molecules involved in a polymeric mixture is far less than the number in a small molecule mixture of equal volume. The energetics of mixing, on the other hand, is comparable on a per volume basis for polymeric and small molecule mixtures. This tends to increase the free energy of mixing for polymer solutions and thus make solvation less favorable. Thus, concentrated solutions of polymers are far rarer than those of small molecules.

In dilute solution, the properties of the polymer are characterized by the interaction between the solvent and the polymer. In a good solvent, the polymer appears swollen and occupies a large volume. In this scenario, intermolecular forces between the solvent and monomer subunits dominate over intramolecular interactions. In a bad solvent or poor solvent, intramolecular forces dominate and the chain contracts. In the solvent, or the state of the polymer solution where the value of the second virial coefficient becomes 0, the intermolecular polymer-solvent repulsion balances exactly the intramolecular monomer-monomer attraction. Under the theta condition (also called the Flory condition), the polymer behaves like an ideal random coil.

ix. Inclusion of plasticizers tends to lower T_g and increase polymer flexibility. Plasticizers are generally small molecules that are chemically similar to the polymer and **create gaps** between polymer chains for greater mobility and reduced inter-chain interactions. A good example of the action of plasticizers is related to polyvinylchlorides or PVCs. A PVC, or unplasticized polyvinylchloride, is used for things such as pipes. A pipe has no plasticizers in it, because it needs to remain strong and heat-resistant.

Plasticized PVC is used for clothing for a flexible quality. Plasticizers are also put in some types of cling film to make the polymer more flexible.

x. Chemical properties are due to attractive forces between polymer chains which play a large part in determining a polymer's properties. Because polymer chains are so long, these inter-chain forces are amplified far beyond the attractions between conventional molecules. Different side groups on the polymer can lend the polymer to **ionic bonding** or **hydrogen bonding** between its own chains. These stronger forces typically result in higher tensile strength and higher crystalline melting points.

The intermolecular forces in polymers can be affected by dipoles in the monomer units. Polymers with amide or carbonyl groups can form H-bonds between adjacent chains; the partially positively charged hydrogen atoms in N-H groups of one chain are strongly attracted to the partially negatively charged oxygen atoms in C=O groups on another. These strong hydrogen bonds, for example, result in the **high tensile strength** and **melting point** of polymers containing urethane or urea linkages. Polyesters have **dipole-dipole bonding** between the oxygen atoms in C=O groups and the hydrogen atoms in H-C groups. Dipole bonding is not as strong as hydrogen bonding, so polyester's melting point and strength are lower than Kevlar's (Twaron), but polyesters have greater flexibility. Ethene, however, has no permanent dipole. The attractive forces between polyethylene chains arise from weak **van der Waals** forces. Molecules can be thought of as being surrounded by a cloud of negative electrons. As two polymer chains approach, their electron clouds repel one another. This has the effect of lowering the electron density on one side of a polymer chain, creating a slight positive dipole on this side. This charge is enough to attract the second polymer chain. Van der Waals forces are quite weak, however, so polyethene can have a lower melting temperature compared to other polymers.

4.0 Conclusion

Linkages are very important in determining properties of polymers.

5.0 Summary

In this unit we have learnt

- about the basic groupings of polymer [homopolymers, copolymers, terpolymers, linear, alternating, statistical, block, grafted]
- description of cross-linking and its effects, also given examples of cross-linked polymers
- to apply earlier knowledge on processes of polymerization (Module 3) on practical issues of polymer formations
- basic configuration in simple polymers
- how to describe coordination polymerization
- what Ziegler-Natta catalysts are and their chemistry
- to explain each of the following properties of polymers: Mechanical, Tensile strength, Young's modulus, Transport, Melting point, Boiling point, Glass transition temperature and Miscibility

6.0 Tutor-Marked Assignment (TMA)

1. What are Ziegler-Natta catalyst?

2. Describe crosslinking. What is the difference between the bonds formed in cross-linking and those formed in polymer synthesis?
3. Describe network chain and formation of gel.
4. Discuss 'tacticity' in polymers.
5. Discuss briefly the following properties of polymers: Mechanical, Tensile strength, Young's modulus, Transport, Melting point, Boiling point, Glass transition temperature and Miscibility.

7.0 References/Further Readings

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Module 6: Fiber Forming Polymers, Biodegradation and Recycling of Polymers.

Unit 1: Polymers as Fibers

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- 1.0 Introduction
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- 5.0 Summary
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1.0 Introduction

Fibers occur naturally, which can be modified and they can be synthesized. Their additions to other polymers impact the threadlike properties on them. van der Waals forces, hydrogen-bonding, and cross-links are the most important intermolecular forces that influence formation of fibers.

2.0 Objectives

At the end of this unit you should

- differentiate between Elastomers and real fibers
- be able to give examples of natural and synthetic fibers
- be able to describe intermolecular forces in fibers

3.0 Main Content

They are threadlike, spun, woven, long and thin materials. Naturally occurring fibers include cotton, wool and silk. They lie stretched out along side each other permanently

with great tensile strength [can be pulled in the direction of the chain], since fibers are linear. They impart strength when they are added to plastics. Strength of the chemical bonds in the chains determines strength of the fiber polymer. Strong intermolecular attractions exist between chains, this disallow it from slipping and returning to random loops and coils, and gives it high degree of molecular orientation [not necessarily crystalline]. Enthalpy prevails over entropy in fiber polymers.

Van der Waal forces are strong enough to maintain alignments as seen in stereo regular chains of isotactic polypropylenes fitting together.

3.1 Intermolecular forces in fibers

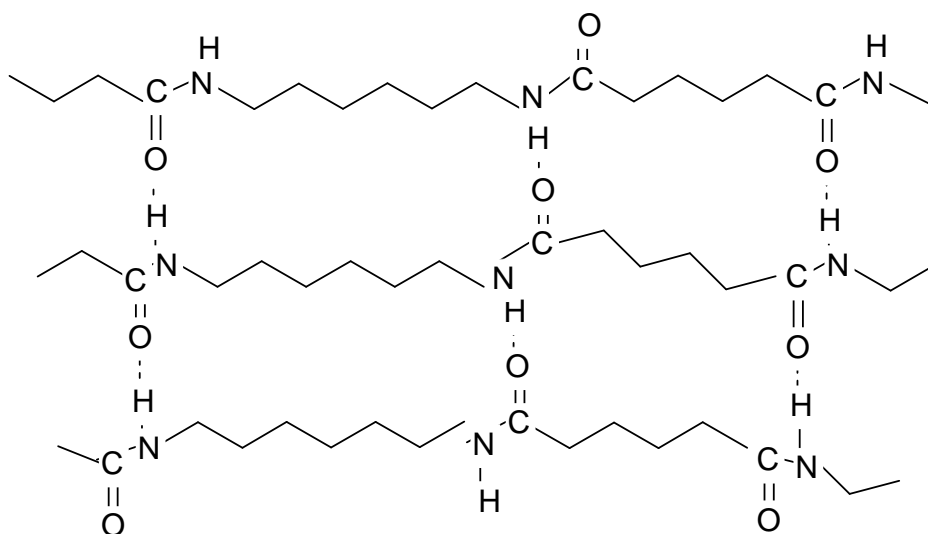
The important intermolecular forces in fibers are van der Waals forces, hydrogen-bonding, and cross-links. They make fibers to be easily pulled (with tensile strength). Hence they can be woven and spun, to impart strength on materials. When drawn the polymeric material in fibers are stretched, fiber molecules are lined-up permanently. This tendency is supported by the strong intermolecular attractions and is responsible for enthalpy overcoming entropy, unlike in Elastomers. Their details have been examined in Module 5, unit 2.

3.2 Elastomer has elastic properties and is similar to fibers. Basic differences are thus: Elastomers have high degree of elasticity and can be deformed while it still retains its original shape. Its molecules are lined up as in fibers, but on stretching to deformity, chains of Elastomers do not remain extended and aligned but return to their original random conformations favored by entropy. They do not remain aligned because the intermolecular forces necessary to hold them this way are weaker than in fibers. Generally Elastomers do not have highly polar groups/ sites for H-bonding. Also extended chains donot fit together enough for van der Waal forces to do the job.

3.3 More examples of Natural and synthetic fibers

Natural fibers include wool, cotton and silk. Examples of synthetic polymers include polyamides [nylons], polyesters [Dacron, terylene, vycron], polyacrylonitriles [orlon, acrilan], polyurethanes [spandex, vycra] and isotactic propylenes. Their structures have been earlier seen. Rayon one of the first useful fibers synthesized in 1865 is an example of fibers that are long silk-like shining strands. They were improved on by Louis Chardonnet and introduced to Paris in France in 1891. The word 'rayon' is from ability of the fiber to shine. Another example of synthetic fiber is vinyon, a copolymer of chloroethylene and ethenyl ethanoate. It has great strength but of limited uses because of its low softening temperature of 65⁰C.

Linear and branched polymers do have materials utilized as fibers. This include the polyalkenes[polyethylenes, PVCs, polystyrenes]. On heating the polymer softens, that is why they are called thermoplastics because they can be moulded or extruded. In polyesters and polyacrylonitriles, their polar carbonyl and cyano groups lead to powerful dipole-dipole attractions. In nylon and polyurethanes, molecular chains are held to each other by hydrogen-bonds, as shown between three chains cross-linked below:



Hydrogen bonding in crystallite of nylon 66

4.0 Conclusion

Fibers can be naturally occurring and they can be synthesized. They can be added to polymers to impact fiber like properties. Elastomers are similar to fibers but have different behaviors.

5.0 Summary

In this unit we have learnt

- Elastomers and real fibers are different, though similar in some respects
- examples of natural and synthetic fibers
- about intermolecular forces in fibers

6.0 Tutor-Marked Assignment (TMA)

1. Give examples of natural and synthetic polymers
2. Highlight the main differences between Elastomers and fibers.
3. Discuss the influence of named intermolecular forces on fibers.

7.0 References/Further Readings

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Unit 2: Biodegradation and Recycling of Polymers

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- 1.0 Introduction
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 - 3.4 Oxidation
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- 5.0 Summary
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- 7.0 References/ Further Readings

1.0 Introduction

We live in an age of polymers. Most products we use daily are polymers, and would be missed if they are eliminated. Disposal of some polymers have been great environmental concerns. Degradations including biodegradations and recycling have made polymers to be more useful to us, as well as prevent them getting extinct. These methods pave way for developments of better polymer materials. Degradations can be caused by artificial factors like heat, temperature changes, effects of catalysts, and so on; or can be natural as in biodegradations, which are usually desirable changes of breaking polymers into smaller fragments caused by enzyme-catalyzed reactions. These are usually hydrolytic reactions.

2.0 Objectives

At the end of this unit you should

- understand processes of biodegradation and recycling
- see degradations as basically leading to depolymerizations to its constituent monomers, and usually by hydrolysis
- know the implications of biodegradations and recycling
- mention importances of biodegradations and recycling
- be able to give practical examples of biodegradations and recycling

3.0 Main Content

Degradations including biodegradations, and recycling have made polymers to be more useful to us, as well as prevent them getting extinct. These methods pave way for developments of better polymer materials.

3.1 Biodegradations in polymers

Use of enzyme-catalyzed reactions to break polymers into smaller segments is said to be biodegradation. Enzymes from micro-organisms are utilized. Carbon-carbon bonds in chain-growth polymers are strong and not easily biodegradable. For them to be degraded a choice is to introduce breakable bonds which are weak links into them that will

participate in the enzyme-catalyzed reactions. e.g. hydrolysable ester groups. It can now be susceptible to biodegradations.

Degradation of polymers is a change in its properties like tensile strength, colour, shape, and so on. It can be as the influence of one or more environmental factors, such as heat, light, chemical, galvanic action. It is due to the hydrolysis of the bonds connecting the polymer chain, which in turn leads to a decrease in the molecular mass of the polymer. These changes may be undesirable, such as changes during use, or desirable, as in biodegradations or to deliberately lower the molecular mass of a polymer. Such changes occur primarily because of the effect of these factors on the chemical composition of the polymer. Ozone cracking and UV degradation are specific failure modes for certain polymers.

It has been found that polymer degradation can occur through galvanic actions. In 1990, Michael Faudree discovered that imide-linked resins in CFRP (carbon fiber reinforced polymers) composites get degraded when bare composite is coupled with an active metal in saline, i.e. salt water environments. This phenomenon, that polymers can undergo galvanic corrosion like metals do has been referred to as the “Faudree Effect”. Standard corrosion protection procedures were found to prevent polymer degradation under most conditions.

The degradation of polymers to form smaller molecules may proceed by random scission or specific scission. The degradation of polyethylene occurs by random scission—a random breakage of the linkages (bonds) that hold the atoms of the polymer together. When heated above 450 °C it degrades to form a mixture of hydrocarbons. Other polymers—like polyalphanethylstyrene—undergo specific chain scission with breakage occurring only at the ends. They literally unzip or depolymerize to become the constituent monomer.

3.2 Recycling

Degradation process can be useful if we understand the structure of a polymer or recycling/ re-use of the polymer waste to prevent or **reduce environmental pollution**. Polylactic acid and polyglycolic acid for example, are two polymers that are useful for their ability to degrade under aqueous conditions. A copolymer of these polymers is used for biomedical applications, such as **hydrolysable stitches** that degrade over time after they are applied to a wound. These materials can also be used for plastics that will degrade over time after they are used and will therefore not remain as litter.

The sorting of polymer waste for recycling purposes may be facilitated by the use of the **Resin identification codes** [see Module 2, unit 1, section 3.3, p.21], developed by the ‘Society of the Plastics Industry’ to identify the type of plastic, and recycle accordingly so as to obtain the desired products.

3.3 Chlorine attack acetal resin plumbing joints.

In a finished product, such a change is to be prevented or delayed. Failure of safety critical polymer components can cause serious accidents, such as fire in the case of cracked and degraded polymer fuel lines. Chlorine-induced cracking of acetal resin plumbing joints and polybutylene pipes has caused many serious floods in domestic properties, especially in the USA in the 1990s. Traces of chlorine in the water supply attacked vulnerable polymers in the plastic plumbing, a problem which occurs faster if

any of the parts have been poorly extruded or injection moulded. Attack of the acetal joint occurred because of faulty moulding leading to cracking along the threads of the fitting, which are serious stress concentrations.

3.4 Ozone cracking in natural rubber tubing

Polymer oxidation has caused accidents involving medical devices. One of the oldest known failure modes is ozone cracking caused by chain scission when ozone gas attacks susceptible elastomers such as natural rubber and nitrile rubber. They possess double bonds in their repeating units which are cleaved during ozonolysis. Cracks in fuel lines can penetrate the bore of the tube and cause fuel leakage. If cracking occurs in the engine compartment, electric sparks can ignite the gasoline and can cause a serious fire.

Fuel lines can also be attacked by another form of degradation: hydrolysis. Nylon 6,6 is susceptible to acid hydrolysis, which in an accident, a fractured fuel line led to a spillage of diesel into the road. If diesel fuel leaks onto the road, accidents to following cars can be caused by the slippery nature of the deposit, which is like black ice.

4.0 Conclusion

Degradations and recycling are means of developing better polymers, as well as making them to be more environmental friendly.

5.0 Summary

In this unit we have learnt

- processes of biodegradation and recycling
- that degradation is basically leading to depolymerizations to constituent monomers, and usually occurs by hydrolysis
- the implications of biodegradations and recycling
- importance of biodegradations and recycling
- practical examples of biodegradations and recycling

6.0 Tutor-Marked Assignment (TMA)

1. What are the common problems of solid waste disposal and recycling of polymers.
2. Give examples of polymers that could be more readily recycled?
3. In what applications would a thermo set polymer be most desirable?
4. Which polymer type would you choose for:
 - a. Microwave dish
 - b. A plastic bag
 - c. Toothbrush handle
 - d. Child's toy (doll or game)
 - e. Dinnerware

7.0 References/Further Readings

- T.L. Brown; H.E. LeMayJr; B.E. Bursten; C.J. Murphy and P. Woodward. (2009): Chemistry the Central Science. 11th Edition. Pearson Education International. P.499-514.
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ANSWERS TO SHORT-STRUCTURED TMA QUESTIONS

Module 1, unit 2:

1. Name some natural polymers. Ans=[Cellulose, proteins, rubber, starch]
2. Name some synthetic polymers. Ans=[Nylon, orlon, rayon, dacron, etc.]

Module 1, unit 3:

1. Will cross-links be possible in polyalkanes? Give reasons for your answers.
Ans = Absence of allylic positions that is reactive, since double bonds are absent. Moreover they are saturated, reluctant to addition reactions, hence cannot form cross-linkings.

Module 2, unit 1

3. What are the major raw material requirements for the manufacturing of cement?
Answer: Clay, limestone and gypsum[CaSO₄.2H₂O]

Module 3, unit 1

3. State the differences between the two basic methods of polymerization.
Answer: Synthetic polymer methods are generally divided into two categories, addition chain-growth polymerization and condensation step-growth polymerization. The essential difference between the two is that in chain growth polymerization, monomers are added to the chain one at a time only, whereas in step-growth polymerization chains of monomers may combine with one another directly. Other differences: need for unsaturation [vinyl group] in chain's monomer; minimum number of functional groups in monomers of each. Etc.

Module 3, unit 2

4. How many molecules of monomers are in the following polymer?
G—CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ CX₂ G
Ans= eight [8].

Module 3, unit 3

1. Justify the influence of initiators on the properties of a polymer.
Ans = No it does not usually have effect 'cos its not in significant amount, compared to the very large molecular weight of the polymer.

Module 3, unit 4

2. Write an equation for the formation of the condensation polymer formed between toluene-2,6-diisocyanate and ethylene glycol.
[A polymer formed from two different monomers that are joined together with the elimination of a small molecule].

Module 4, unit 1

4. What determines the rate of solubilization of a solute?
Ans= solubility product and the surface area of the material

Module 5, unit 2

2. Describe crosslinking. What is the difference between the bonds formed in cross-linking and those formed in polymer synthesis?

Answer: [A process that makes a polymer more rigid and resistant to heat. The cross-links in slime are hydrogen bonds. In the case of butadiene, the vulcanization process with sulfur cross-links the polybutadiene chains with covalent bonds; [Check suggestions about vulcanization].

Module 6, unit 1

3. Discuss the influence of named intermolecular forces on fibers.

Answer: [hydrogen-bonding, van der Waals forces, and cross-links are the main intermolecular forces which influence the nature of fibers.(see details on each in module 5, unit 2, sections 3.4 & 3.9; and p.63-64)].