



NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 408

COURSE TITLE: POLYMER CHEMISTRY

CHM 408

POLYMER CHEMISTRY

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Course Guide

Introduction

Welcome to this chemistry course. We have packaged this chemistry course in such a way that you will learn chemistry using a technique peculiar to the open learn system. This technique has been adopted by the National Open University of Nigeria in most of the courses offered to students. The language is simple, interesting and specific to the subject, 'Polymer Chemistry'. This course guide tells you briefly about the course, the course materials available, how to work with them and maximize your learning through effective time management. Polymer chemistry is a two-unit degree course for all students offering Bachelor of Science (B.Sc.) Chemistry.

Polymers are no longer regarded as novelties or cheap substitutes for traditional materials such as metals, wood, glass and ceramic. They are now an important class of materials in their own rights. Examples of their use abound everywhere, in the homes, schools, offices and factories. Relationship between structure, property and behaviour of polymer is now better understood. It is therefore possible to 'tailor-make' polymers, that is, to produce polymers of specified molar mass and structure for specific applications.

Today no designer can afford to neglect the opportunities offered by polymers. Low cost and sometimes superior performance of polymers over traditional materials are significant features that cannot be ignored. Indeed polymers have come to stay. The diversity, flexibility, cost and superior performances are certain to assure their future as new uses are discovered.

We wish you success with the course and hope that you will find it both interesting and useful.

What you will learn in this course

In this course, you will learn about polymerization mechanism; stereospecific polymerization; copolymerization; phase system for polymerization; industrially important thermoplastic and thermosetting polymers; polyurethanes; rubber elasticity; mechanical properties of polymers; degradation of polymers; analysis and testing of polymers.

All the units follow the same pattern and so after the first few units, the rest will become easy to follow. Certainly, the interconnection of polymer chemistry with such fields as medicine, geology, engineering (petroleum, electrical, mechanical, and chemical) and so on will be better appreciated in the process of going through this course.

The Course Aims

The broad aim of this course is to help the student to have an introductory and in-depth knowledge of polymerization processes, applications and degradation of polymers. Thus you will have a solid foundation which will enable you go into advanced science course needing a background of polymer chemistry.

The Course Objectives

The objectives of this course are set out below. On completion of the course, you should be able to:

- 1) Discuss the applications of polymer in our everyday living.
- 2) Explain vividly the key concepts involved in each unit of study.
- 3) Use chemical equations where necessary, to explain the addition and step polymerization processes.
- 4) Classify polymer degradation and enumerate the factors that contribute to polymer degradation.

The Course Materials

The main components of the course are: The course guide, objectives, study units, self-assessment exercises, and tutor marked assignments and references/further reading.

Working through this course

Each unit has specific learning objectives along with other relevant learner guide. Try to read these objectives before you study the unit and also go through it after completing the unit to see whether you have internalized the concepts treated in the unit. Go through the self-assessment exercises and ensure that you answer the questions.

At certain points in this course, you would be asked to submit assignments for assessment purposes. Read each unit with full concentration. You must attend the tutorial sessions so that you can avail yourself the opportunity of comparing notes and ideas. Lastly, read recommended textbooks and other relevant materials.

In this course, there are ten (10) study units.

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Unit 1

Polymer Synthesis

1.0 Introduction

The study of polymer chemistry begins with understanding the methods in which these materials are synthesized. Polymer synthesis is a complex procedure and can take place in a variety of ways. Polymers are prepared by the process of joining small molecules (monomers) by covalent bonds. Hence, **polymerization** is a process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains. In chemical

compounds, polymerization occurs via a variety of reaction mechanisms that vary in complexity due to functional groups present in reacting compounds and their inherent steric effects explained by VSEPR Theory. There are many forms of polymerization and different systems exist to categorize them these include, the Addition polymerization also called Chain-growth polymerization and Condensation polymerization sometimes called Step- growth polymerization.

1.1 Objectives

By the end of this unit, you should be able to:

- Define polymerization
- List and discuss the various types of polymerization.
- Explain the characteristics peculiar to each polymerization process/mechanism.
- Describe the roles of initiation, propagation and termination in polymerization process.
- Differentiate between addition and condensation polymerization process.
- Mention the applications of polymers.

1.2 Addition (Chain-growth) Polymerization

Addition polymerization describes the method where monomers are added one by one to an active site on the growing chain. This is characterized by self-addition of molecules to each other, very rapidly through chain reaction. Monomer in this case retains its structural identity when it gets converted to polymer (product has same elemental composition as the monomer). It can be represented with the chemical equation:



Where n is the degree of polymerization.

In addition polymerization, no by product is formed (i.e, no net loss of atom). The bifunctionality is provided by the double bonds present in the monomer. The most common type of addition polymerization involves Free radical chain reaction of molecule that have C=C bond. For olefins (CH₂=CHR), vinyl compounds (CH₂=CHX), allyl compounds (CH₂=CH-CH₂X) and dienes (CH₂=CR-CH=CH₂), addition reaction polymerization involves the opening of the bond with a free radical initiator. Under addition polymerization, another process known as Ionic polymerization (i.e cationic chain growth and anionic chain growth mechanism) can occur. All these polymerization processes follow three principal steps – **Initiation** (birth), **Propagation** (growth), and **Termination** (death). Typical addition polymers are polystyrene, poly(acrylic acid), polyethylene, poly(vinyl chloride), poly acrylonitrile, poly(vinyl fluoride) etc.

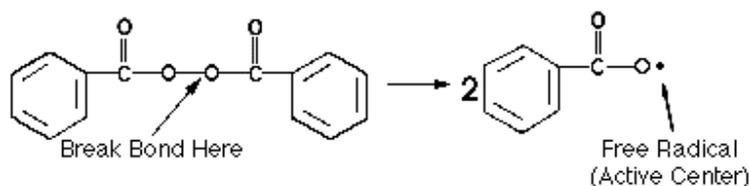
1.3 Free Radical Polymerization

The most common type of addition polymerization is free radical polymerization. A free radical is simply a molecule with an unpaired electron. The tendency for this free radical to gain an additional electron in order to form a pair makes it highly reactive so that it breaks the bond on another molecule by stealing an electron, leaving that molecule with an unpaired electron (which is another free radical).

Free radicals are often created by the division of a molecule (known as an *initiator*) into two fragments along a single bond. Initiators for free radical polymerization include any organic compound with a **labile bond**, such as an azo (-N=N-), disulphide (-S-S-), or peroxide (-O-O-) compound. The labile bond can be broken down either by heat or irradiation such as uv or γ -radiation giving a radical. An example of a free radical initiator



The following diagram shows the formation of a radical from its initiator, in this case benzoyl peroxide.



The stability of a radical refers to the molecule's tendency to react with other compounds. An unstable radical will readily combine with many different molecules. However a stable radical will not easily interact with other chemical substances. The stability of free radicals can vary widely depending on the properties of the molecule. The **active center** is the location of the unpaired electron on the radical because this is where the reaction takes place. In free radical polymerization, the radical attacks one monomer, and the electron migrates to another part of the molecule. This newly formed radical attacks another monomer and the process is repeated. Thus the active center moves down the chain as the polymerization occurs until it is terminated.

1.3.1 Mechanism of Free radical Polymerization

The formation of a polymer by this process is an example of a chain reaction. Once a chain reaction gets started, it is able to keep itself going. The three steps of this reaction to focus on are Initiation, Propagation and Termination.

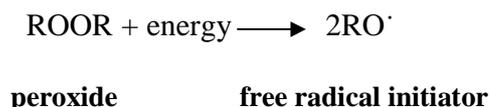
1.3.2 Initiation Reaction

The first step in producing polymers by free radical polymerization is initiation. This step begins when an *initiator* decomposes into free radicals in the presence of monomers. The instability of carbon-carbon double bonds in the monomer makes them susceptible to reaction with the unpaired electrons in the radical. In this reaction, the active center of the radical "grabs" one of the electrons from the double bond of the monomer, leaving an unpaired electron to appear as a

new active center at the end of the chain. Addition can occur at either end of the monomer. Example: Consider the polymerization of ethylene ($\text{CH}_2=\text{CH}_2$) to polyethylene.

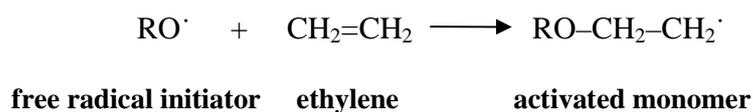
A peroxide molecule breaks up into two reactive free radicals. Light or heat can provide the energy needed for this process- first part of the initiation step:

We can write an equation for this process:



The second part of initiation occurs when the free radical initiator attacks and attaches to a monomer molecule. This forms a new free radical, which is called the activated monomer.

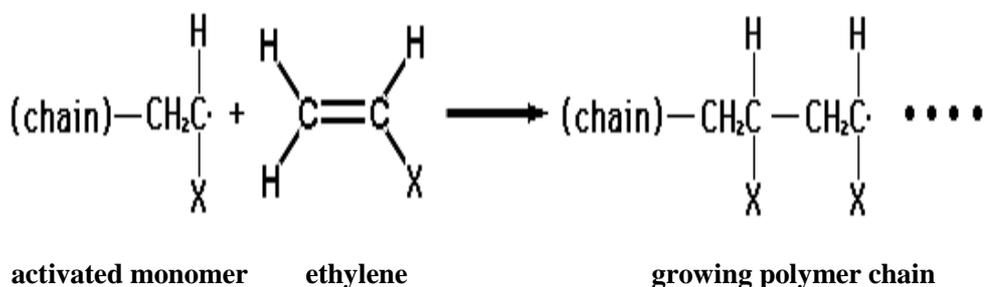
An equation for the reaction is as thus:



One of the two Π - electrons in the ethylene has been used to form a single bond with the $\text{R}-\text{O}\cdot$ radical. The other remains on the second carbon atom, leaving it as a seven-valence electron atom that reacts with another ethylene molecule.

1.3.3 Propagation Reaction

After a synthesis reaction has been initiated, the propagation reaction takes over. In the propagation phase, the newly formed activated monomer attacks and attaches to the double bond of another monomer molecule. The process of electron transfer and consequent motion of the active center down the chain proceeds. In this diagram, (chain) refers to a chain of connected monomers, and X refers to hydrogen atom. Hence the monomer would be ethylene and the polymer polyethylene.

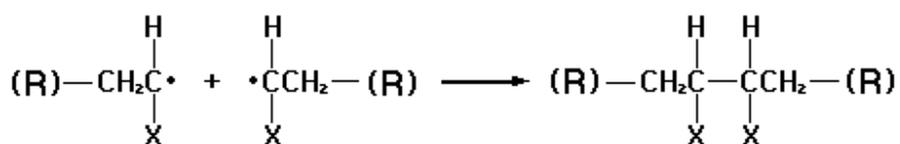


In free radical polymerization, the entire propagation reaction usually takes place within a fraction of a second. Thousands of monomers are added to the chain within this time. The entire process stops when the termination reaction occurs.

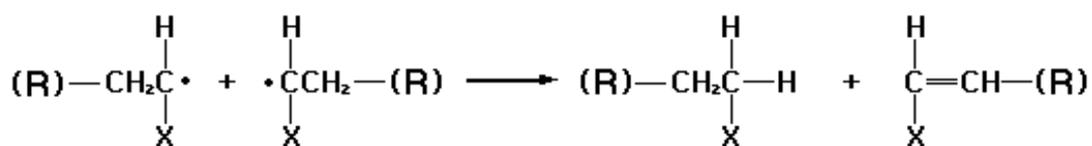
1.3.4 Termination Reaction

This chain reaction cannot go on forever. The reaction must terminate, but how?. In theory, the propagation reaction could continue until the supply of monomers is exhausted. However, this outcome is very unlikely. Most often the growth of a polymer chain is halted by the termination reaction. Termination typically occurs in two ways: **combination** and **disproportionation**.

- **Combination** occurs when the polymer's growth is stopped by radical end groups on two growing chains that join and form a single chain. The following diagram depicts combination, with the symbol **(R)** representing the rest of the chain.



- **Disproportionation** halts the propagation reaction when a free radical strips a hydrogen atom from an active chain. A carbon-carbon double bond takes the place of the missing hydrogen. Termination by disproportionation is shown in the diagram.



Disproportionation can also occur when the radical reacts with an impurity. This is why it is so important that polymerization be carried out under very clean conditions.

Note: Chemists can control the way a polymer does each of these steps by varying the reactants, the reaction times and the reaction condition. The physical properties of a polymer chain depend on the polymer's average length, the amount of branching, and the constituent monomers.

1.4 Ionic Polymerization

Ion initiated polymerization follow the same basic steps as free radical polymerization (initiation, propagation and termination) however, there are some differences. Ionic mechanism of chain polymerization also involves attack on the Π electron pair of the monomer.

Note: In free radical, the unpaired electron of the free radical does the attack but in ionic, the positive or negative ion does the attack.

In ionic polymerization, either a **carbanion (c⁻)** or **carbonium (c⁺)** ionic site can be formed in the initiation process. Radical-initiated polymerizations are generally non-specific but this is not true for ionic initiators, since the formation and stabilization of a carbonium ion or carbanion depends largely on the nature of the group R in the vinyl monomer,



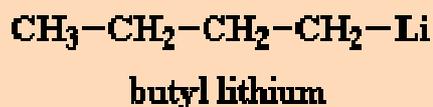
For this reason cationic initiation is usually limited to monomers with electron-donating groups (e.g., alkoxy, alkyl, alkenyl, phenyl) which help to stabilize the delocalization of the positive charge in the Π – orbitals of the double bond. Anionic initiators require electron withdrawing substituents (e.g cyano (–CN), carbonyl –aldehyde, ketone, acids and ester) to promote the formation of a stable carbanion, and when there is a combination of both mesomeric and inductive effects the stability is greatly enhanced. As these ions are associated with a counter-ion the solvent has a profound influence. Therefore chain propagation will depend significantly on the separation of the two ions and this will also control the mode of entry of an adding monomer.

While polar and highly solvating media are obvious choices for ionic polymerizations many cannot be used because they react with and negate the ionic initiators. Ionic-initiated polymerizations are much more complex than radical reactions. When the chain carrier is ionic, the reaction rates are rapid, difficult to reproduce, and yield high molar mass material at low temperatures by mechanisms which are often difficult to define. Initiation of an ionic polymerization can occur in one of four ways involving essentially the loss or gain of an electron e⁻ by the monomer to produce an ion or radical ion.

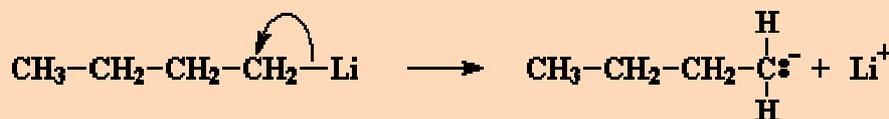
- (a) $\text{M} + \text{I}^+ \longrightarrow \text{MI}^+$ Cationic
- (b) $\text{M} + \text{I}^- \longrightarrow \text{MI}^-$ Anionic
- (c) $\text{M} + \text{e}^- \longrightarrow \cdot\text{M}^-$ Anionic
- (d) $\text{M} - \text{e}^- \longrightarrow \cdot\text{M}^+$ Cationic (charge transfer)

1.4.1 Anionic Polymerization

Anionic polymerization is a form of addition polymerization that involves the polymerization of vinyl monomers with strong electronegative groups. This polymerization is carried out through a carbanion active species. Like all addition polymerizations, it takes place in three steps: chain initiation, chain propagation, and chain termination. The initiator in an anionic polymerization may be any strong nucleophile which include covalent or ionic metal amides, alkoxides, hydroxides, cyanides, phosphines, amines and organometallic compounds (alkyl lithium compounds and Grignard reagents). The most commercially used of these initiators is the alkyl lithium initiator – butyl lithium.



This can split to form a positive lithium cation and a negative butyl anion. We call an anion like this where the negative charge is on a carbon atom a carbanion.



Example 1: Polymerization of acrylonitrile.



Note: The butyl anion is (abbreviated Bu[−])

1.4.2 Chain Initiation

Using butyl lithium as an anionic initiator, it reacts with the end carbon in a molecule of acrylonitrile to give new anion.



activated monomer initiator

During initiation process, the addition of the butyl anion to acrylonitrile produces a carbanion at the head end in association with the positively charged Lithium counterion. The new anion then reacts with an additional molecule of acrylonitrile.

1.4.3 Chain Propagation

Propagation in anionic polymerization results in the complete consumption of monomer. It is very fast and occurs at low temperatures. This is due to the anion not being very stable, the speed of the reaction as well as that heat is released during the reaction.



propagation stage

Anionic polymerization is called **Living polymerization** because when additional monomer is added (even months later) they resume growth and increase in molar mass.

1.4.4 Chain Termination

When carried out under the appropriate conditions, termination reaction do not occur in anionic polymerization. However, termination can occur through unintentional quenching due to trace

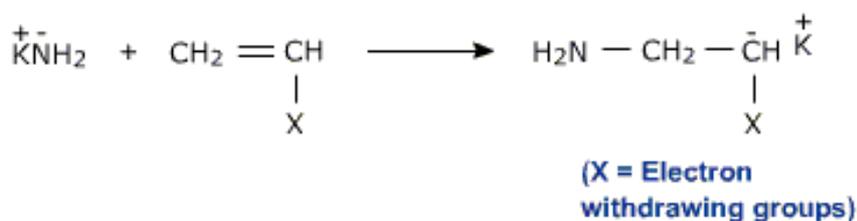
impurities. This includes trace amounts of oxygen, carbon dioxide or water. Intentional termination can occur through the addition of water or alcohol.



termination stage

Termination is achieved here by addition of water to replace the Li^+ with a hydrogen ion.

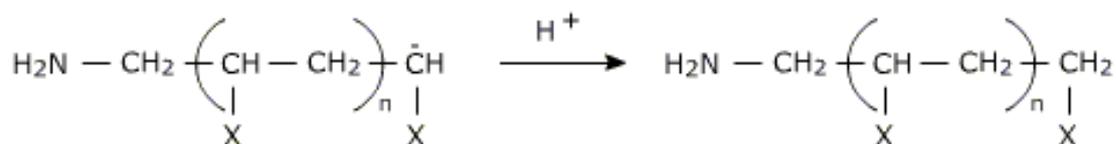
Example 2: Using Potassium amide as an initiator. In the initiation step, the base adds to a double bond to form a carbanion.



In the chain propagation, this carbanion adds to the double bond and the process repeats to form a polymeric carbanion.



The chain reaction can be terminated by addition of an acid.



Examples of polymers that can undergo anionic polymerization are polystyrene, poly acrylonitrile, poly (ethylene oxide), poly (methyl methacrylate).

1.5 Cationic Polymerization

This is a type of chain growth polymerization in which a cationic initiator transfers charge to a monomer which becomes reactive. This reactive monomer goes on to react similarly with other monomers to form a polymer. The types of monomers necessary for cationic polymerization are

limited to olefins with electron-donating substituents and heterocycles. Similar to anionic polymerization reactions, cationic polymerization reactions are very sensitive to the type of solvent used. Specifically, the ability of a solvent to form free ions will dictate the reactivity of the propagating cationic chain. Monomers for cationic polymerization are nucleophilic and form a stable cation upon polymerization.

Cationic polymerization of olefin monomers occurs with olefins that contain electron-donating substituents. These electron-donating groups make the olefin nucleophilic enough to attack electrophilic initiators or growing polymer chains. At the same time, these electron-donating groups attached to the monomer must be able to stabilize the resulting cationic charge for further polymerization.

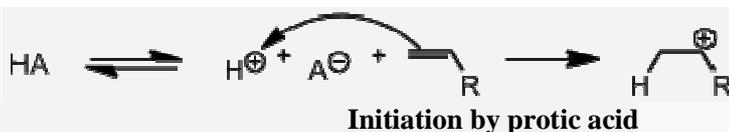
1.5.1 Initiator for Cationic Polymerization

There are a variety of initiators available for cationic polymerization, and some of them require a co-initiator to generate the needed cationic species.

▪ Classical protic acids

Strong protic acids can be used to form a cationic initiating species. High concentrations of the acid are needed in order to produce sufficient quantities of the cationic species.

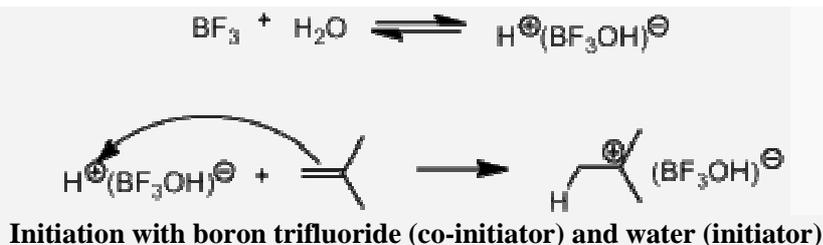
The counterion (A^-) produced must be weakly nucleophilic so as to prevent early termination due to combination with the protonated olefin. Common acids used are phosphoric, sulfuric, fluoro-, and triflic acids. Only low molecular weight polymers are formed with these initiators.



▪ Lewis acids/Friedel-Crafts catalysts

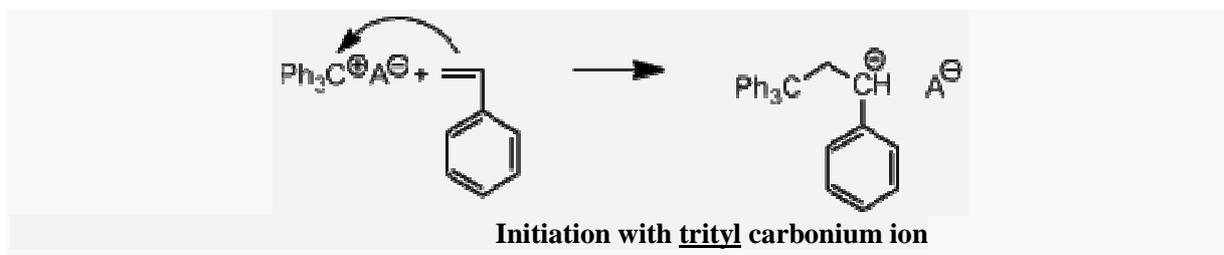
Lewis acids are the most common compounds used for initiation of cationic polymerization. The more popular Lewis acids are $SnCl_4$, $AlCl_3$, BF_3 , and $TiCl_4$. Although these Lewis acids alone are able to induce polymerization, the reaction occurs much faster with a suitable cation source. The cation source can be water, alcohols, or even a carbocation donor such as an ester or an anhydride. In these systems the Lewis acid is referred to as a co-initiator while the cation source is the initiator. Upon reaction of the initiator with the co-initiator, an intermediate complex is formed which then goes on to react with the monomer unit.

The counterion produced by the initiator-coinitiator complex is less nucleophilic than that of the Brønsted acid A^- counterion. Halogens, such as chlorine and bromine, can also initiate cationic polymerization upon addition of the more active Lewis acids.



- **Carbonium ion salts**

Stable carbonium ions are used to initiate chain growth of only the most reactive olefins and are known to give well defined structures. These initiators are most often used in kinetic studies due to the ease of being able to measure the disappearance of the carbonium ion absorbance. Common carbonium ions are trityl and tropylium cations.



1.5.2 Propagation by Ionic chain carriers

Chain growth takes place through the repeated addition of a monomer in a head-to-tail manner to the carbonium ion, with a retention of the ionic character throughout. The propagation mechanism depends on the counter-ion, the solvent, the temperature, and the type of monomer. The solvent and the counterion (the gegen ion) have a significant effect on the rate of propagation. The counterion and the carbonium ion can have different associations, ranging from a covalent bond, tight ion pair (unseparated), solvent-separated ion pair (partially separated), and free ions (completely dissociated).

| | | | |
|-------------------------|------------------------------------|-------------------------------------|---------------------------------------|
| $\sim\sim\sim\text{RX}$ | $\sim\sim\sim\text{R}^+\text{X}^-$ | $\sim\sim\sim\text{R}^+/\text{X}^-$ | $\sim\sim\sim\text{R}^+ + \text{X}^-$ |
| covalent | tight ion pair | solvent-separated ion pair | free ions |

Range of associations between the carbonium ion (R^+) and gegen ion (X^-)

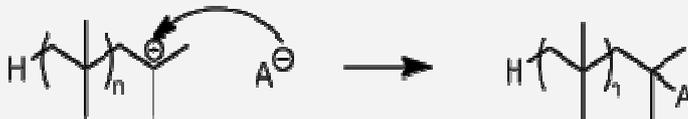
The association is strongest as a covalent bond and weakest when the pair exists as free ions. In cationic polymerization, the ions tend to be in equilibrium between an ion pair (either tight or solvent-separated) and free ions. The more polar the solvent used in the reaction, the better the solvation and separation of the ions. Since free ions are more reactive than ion pairs, the rate of propagation is faster in more polar solvents.

The size of the counterion is also a factor. A smaller counterion, with a higher charge density, will have stronger electrostatic interactions with the carbonium ion than will a larger counterion which has a lower charge density. Further, a smaller counterion is more easily solvated by a polar solvent than a counterion with low charge density. The result is increased propagation rate with increased solvating capability of the solvent. Chain length is also affected by temperature. Low reaction temperatures, in the range of 170–190 K, are preferred for producing longer chains.

1.5.3 Termination

Termination generally occurs via unimolecular rearrangement with the counterion. In this process, an anionic fragment of the counterion combines with the propagating chain end. This

not only inactivates the growing chain, but it also terminates the kinetic chain by reducing the concentration of the initiator-coinitiator complex.



Termination by combination with an anionic fragment from the counterion

1.5.4 Chain transfer

Chain transfer can take place in two ways. One method of chain transfer is hydrogen abstraction from the active chain end to the counterion. In this process, the growing chain is terminated, but the initiator-coinitiator complex is regenerated to initiate more chains.



Chain transfer by hydrogen abstraction to the counterion

The second method involves hydrogen abstraction from the active chain end to the monomer. This terminates the growing chain and also forms a new active carbonium ion-counterion complex which can continue to propagate, thus keeping the kinetic chain intact.

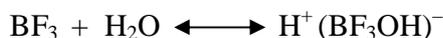


Chain transfer by hydrogen abstraction to the monomer

1.5.5 Example: Polymerization of Styrene

▪ Chain Initiation

Initiation employs a strong Lewis acid which requires or proceeds faster in the presence of a proton donor. The proton donor is referred to as the initiator while the Lewis acid is the co-initiator, since the proton donor ultimately supplies the proton which adds to monomer that initiates polymerization. Here a strong Lewis acid boron trifluoride is used as the co-initiator, while water is the proton source and it is known as the initiator.



Initiator co-initiator complex

The initiator,-co-initiator complex donates a proton to the styrene molecule to give **carbonium ion**.



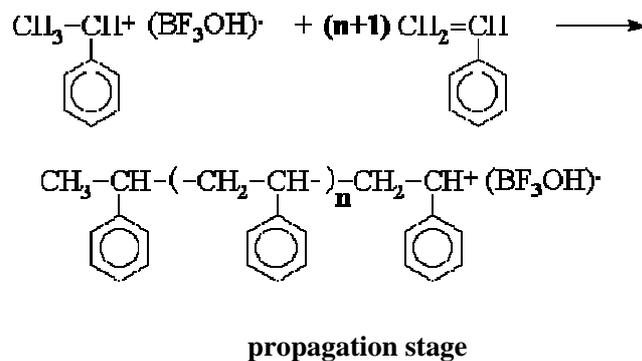
Styrene

activated monomer

Proton addition yields a styrene carbonium ion that forms association with a $\text{BF}_3 \cdot \text{OH}$ counterion.

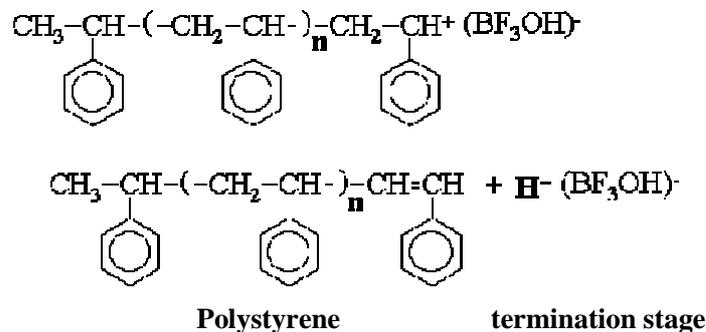
- **Chain Propagation**

Carbonium ion adds to double bond of another styrene molecule.



- **Chain Termination**

Termination by combination of two cationic polymer chains cannot occur instead proton transfer to a monomer, polymer, solvent or counterion will usually occur.



As termination step shows, the original initiating specie is restored at the end of polymerization which can then reinitiate polymerization as an active catalyst. The termination process above is called **ion-pair precipitation** (there is a proton donation and reformation of BF_3 hydrate at the end of polymerization). Examples of polymers formed by cationic polymerization are poly isobutylene, polystyrene, poly (oxymethylene) etc.

1.6 Summary of Characteristics of Addition Polymerization:

- It takes place in three distinct steps - chain initiation, chain propagation, and chain termination.

- ii. Some side reactions may occur, such as: chain transfer to monomer, chain transfer to solvent, and chain transfer to polymer.
- iii. High molecular weight polymer is formed at low conversion.
- iv. No small molecules, such as H₂O, are eliminated in this process.
- v. New monomer adds on the growing polymer chain via the reactive active centre which can be a free radical in radical polymerization, carbocation in cationic polymerization and carbanion in anionic polymerization.

Table 1.1 Some important Addition Polymers, their monomer precursors, properties and uses.

| Name(s) | Formula | Monomer | Properties | Uses |
|---------------------------------------------------------------|-----------------------------------------------------------------|----------------------------------------------------------------------------------|-------------------------------------------------------------------------------|---------------------------------------------|
| Polyethylene low density (LDPE) | $-(\text{CH}_2-\text{CH}_2)_n-$ | ethylene $\text{CH}_2=\text{CH}_2$ | soft, waxy solid | film wrap, plastic bags |
| Polyethylene high density (HDPE) | $-(\text{CH}_2-\text{CH}_2)_n-$ | ethylene $\text{CH}_2=\text{CH}_2$ | rigid, translucent solid | electrical insulation bottles, toys |
| Polypropylene (PP) different grades | $-(\text{CH}_2-\text{CH}(\text{CH}_3))_n-$ | propylene $\text{CH}_2=\text{CHCH}_3$ | <u>atactic</u> : soft, elastic solid <u>isotactic</u> : hard, strong solid | similar to LDPE carpet, upholstery |
| Poly(vinyl chloride) (PVC) | $-(\text{CH}_2-\text{CHCl})_n-$ | vinyl chloride $\text{CH}_2=\text{CHCl}$ | strong rigid solid | pipes, siding, flooring |
| Poly(vinylidene chloride) (Saran A) | $-(\text{CH}_2-\text{CCl}_2)_n-$ | vinylidene chloride $\text{CH}_2=\text{CCl}_2$ | dense, high-melting solid | seat covers, films |
| Polystyrene (PS) | $-(\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5))_n-$ | styrene $\text{CH}_2=\text{CHC}_6\text{H}_5$ | hard, rigid, clear solid soluble in organic solvents | toys, cabinets packaging (foamed) |
| Polyacrylonitrile (PAN, Orlon, Acrilan) | $-(\text{CH}_2-\text{CHCN})_n-$ | acrylonitrile $\text{CH}_2=\text{CHCN}$ | high-melting solid soluble in organic solvents | rugs, blankets clothing |
| Polytetrafluoroethylene (PTFE, Teflon) | $-(\text{CF}_2-\text{CF}_2)_n-$ | tetrafluoroethylene $\text{CF}_2=\text{CF}_2$ | resistant, smooth solid | non-stick surfaces electrical insulation |
| Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas) | $-(\text{CH}_2-\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3)_n-$ | methyl methacrylate $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$ | hard, transparent solid | lighting covers, signs skylights |
| Poly(vinyl acetate) | $-(\text{CH}_2-\text{CHOCOCH}_3)_n-$ | vinyl acetate $\text{CH}_2=\text{CHOCOCH}_3$ | soft, sticky solid | latex paints, |

| | | | | |
|----------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------------------|----------------------|------------------------------------------|
| (PVAc) | – | 3 | | adhesives |
| cis-Polyisoprene natural rubber | $-\text{[CH}_2\text{-CH=C(CH}_3\text{)-CH}_2\text{]}_n-$ | isoprene $\text{CH}_2=\text{CH-}$ $\text{C(CH}_3\text{)=CH}_2$ | soft, sticky solid | requires vulcanization for practical use |
| Polychloroprene (cis + trans) (Neoprene) | $-\text{[CH}_2\text{-CH=CCl-CH}_2\text{]}_n-$ | chloroprene $\text{CH}_2=\text{CH-}$ CCl=CH_2 | tough, rubbery solid | synthetic rubber oil resistant |

1.7 Condensation (Step) Polymerization

This takes place between two bifunctional molecules to produce one larger polyfunctional molecule. The bifunctional molecules (monomers) usually condense with one another, and in so doing repeatedly eliminate a small molecule such as H_2O , NH_3 , HCl , etc., as the reaction proceeds. The reaction continues until almost or all of the reactants are used up. This polymerization takes place by series of steps. The type of end product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react. Monomers with only one reactive group terminate a growing chain, and thus give end products with a lower molecular weight. Linear polymers are created using monomers with two reactive end groups and monomers with more than two end groups give three dimensional polymers which are crosslinked. The monomers that are involved in condensation polymerization are not the same as those in addition polymerization. They have two main characteristics:

- ⇒ Instead of double bonds, these monomers have functional groups (like alcohol, amine, or carboxylic acid groups).
- ⇒ Each monomer has at least two reactive sites, which usually means two functional groups. Some monomers have more than two reactive sites, allowing for branching between chains, as well as increasing the molecular mass of the polymer. During the polymerization process, the monomers tend to form dimers (two linked monomers) and trimers (three linked monomers) first. Then, these very short chains react with each other and with monomers. It is only near the end of polymerization that very long chains are formed. Example of condensation polymers are polyamides, polyacetals, polyesters, polycarbonates and polyurethanes.

1.7.1 Mechanism of Condensation Polymerization

Recall that monomers that are joined by condensation polymerization have two functional groups, hence they have two reactive sites and can form long-chain polymers. Given below are examples of condensation polymerization reactions.

A carboxylic acid and an amine forms an amide linkage



diacid diamine polyamide

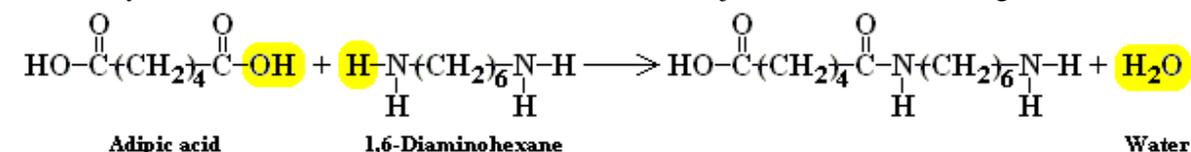
A carboxylic acid and an alcohol forms an ester linkage –



diol diacid polyester

1.7.2 Example 1:

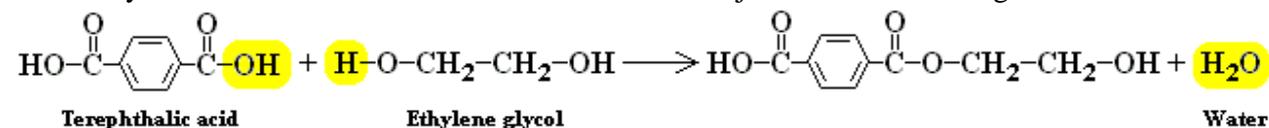
A carboxylic acid monomer and an amine monomer can join in an amide linkage.



As seen above, a water molecule is removed, and an amide linkage is formed. An acid group remains on one end of the chain, which can react with another amine monomer. Similarly, an amine group remains on the other end of the chain, which can react with another acid monomer. Thus, monomers can continue to join by amide linkages to form a long chain. Because of the type of bond that links the monomers, this polymer is called a polyamide. The polymer made from these two six-carbon monomers is known as nylon-6, 6.

1.7.3 Example 2:

A carboxylic acid monomer and an alcohol monomer can join in an ester linkage.



A water molecule is removed as the ester linkage is formed. Notice the acid and the alcohol groups that are still available for bonding. Because the monomers above are all joined by ester linkages, the polymer chain is polyester.

1.7.4 Self-condensation

In condensation polymerization, it is possible sometimes to have two reactive functional groups on the same monomer, in which case, it can lead to a self-polycondensation reaction. An example is the polycondensation of amino enanthic acid to form polyenanthoamide:



1.8 Summary of the Characteristics of Condensation Polymerization

- i. The molecules should have one or two functional groups and the reaction can take place between the same or different functional group.
- ii. They proceed by step-wise reaction between reactive functional groups.
- iii. Hydrogen bonding gives them a crystalline structure with a tensile strength.
- iv. They have a very high melting point.
- v. They are thermosets as once molded, they cannot be remolded.
- vi. They have high T_g and T_m values that makes them rigid as glass and transparent.
- vii. The reaction can take place between two monomers, one monomer and one dimer, or a dimer with an oligomer, or a chain with another chain of polymers.
- viii. The polymers formed still contains both the reactive functional groups at its chain ends (as end groups) and hence, is 'active' and not 'dead', as in chain polymerization.
- ix. They possess mixed properties of both the molecules and functional group.

Table 1.2 Some condensation polymer examples with their components and uses.

| Name | Components | Uses |
|-----------------|-------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------|
| Dacron | para HO ₂ C-C ₆ H ₄ -CO ₂ H HO-CH ₂ CH ₂ -OH | Used in making curtains, dress fabrics, woven sportswear, knitted wear, etc. |
| Nylon 66 | HO ₂ C-(CH ₂) ₄ -CO ₂ H H ₂ N-(CH ₂) ₆ -NH ₂ | Used in making tyres, ropes, carpet fibers, conveyor belts, air bags, etc. |
| Kevlar | para HO ₂ C-C ₆ H ₄ -CO ₂ H para H ₂ N-C ₆ H ₄ -NH ₂ | Used in making jackets, combat helmets, bicycle tyres, loudspeaker cones, woven rope, etc. |
| Nomex | meta HO ₂ C-C ₆ H ₄ -CO ₂ H meta H ₂ N-C ₆ H ₄ -NH ₂ | Used in making nomex hood used by the fire fighters, driving suits, flights suits, thermal blankets, etc. |
| Lexan | (HO-C ₆ H ₄ -) ₂ C(CH ₃) ₂ | Used as kitchen ware, alternative of glass, laparoscopic instruments, electric meters, cellphones, etc. |

| | | |
|--|-------------------------------------------------------------------|--|
| | (Bisphenol A) $X_2C=O$ (X = OCH ₃ or Cl) | |
|--|-------------------------------------------------------------------|--|

1.9 Self-Assessment Exercise

- Explain the following addition polymerization processes using equations where necessary (a) free radical mechanism (b) ionic mechanism.
- Discuss the significance of these steps in addition polymerization (a) initiation (b) propagation (c) termination.
- Define condensation polymerization.
- List five examples of addition and condensation polymers and their uses.
- Distinguish between cationic and anionic chain polymerization.
- Mention the initiators for free radical, cationic and anionic polymerization processes.

1.10 Conclusion

Polymerization is the process of combining many small molecules known as monomers into a covalently bonded chain. Addition polymers or chain-growth polymers which involve the reaction of unsaturated monomers are formed by a straightforward linking together of monomer units, with no loss or gain of material whereas Condensation polymers are any kind of polymers formed through a condensation reaction, releasing small molecules as by-products such as water or methanol.

1.11 Summary

In this unit, you have learnt that:

- Polymerization is the process of linking together of small molecules known as monomers to form a giant molecule called polymer.
- Polymers are synthesized through, addition polymerization process which can take either a free radical pathway or ionic pathway and condensation polymerization process.
- In radical polymerization, the initiator is a radical and the propagating site of reactivity (*) is a carbon radical.
- In cationic polymerization, the initiator is an acid and the propagating site of reactivity (*) is a carbocation.
- In anionic polymerization, the initiator is a nucleophile and the propagating site of reactivity (*) is a carbanion.
- Addition polymers are formed by reaction of unsaturated monomers units with no loss or gain of materials.
- Condensation polymers are formed through condensation reaction releasing small molecules by products such as water.

1.12 Tutor-Marked Assignment

- Define polymerization.
- Briefly explain the characteristics of addition polymerization.
- Differentiate between the condensation polymerization and addition polymerization.

1.13 References/Further Reading

- 1) E.M. Katchy (2000); Principles of Polymer Science; 1st edtn., El'demak publishers Enugu, Nigeria. Pgs 29 – 31 & 65 – 73.
- 2) V. R Gowariker., N. V Visawanathan and Jayader Sreedhar (1986); Polymer Science; 1st edtn, New Age International Ltd; Publishers New Delhi. Pgs 21 – 23, 31 – 38 & 40 – 44.
- 3) Joel R. Fried (2005), Polymer Science & Technology; 2nd edtn., Prentice-Hall, Inc. New Jersey, USA. Pgs 24 – 26 & 29 – 34.
- 4) Anionic Addition Polymerization:
en.wikipedia.org/wiki/anionic_addition_polymerization
- 5) Polymerization: *en.wikipedia.org/wiki/polymerization*

Unit 2

Stereospecific Polymerization

2.0 Introduction

Reactions in which bonds are broken and made at a single asymmetric atom (usually but not necessarily carbon), and which lead largely to a single stereoisomer, are said to be stereospecific. If the configuration is altered in the process, the reaction is said to involve inversion of configuration. If the configuration remains the same, the transformation occurs with retention of configuration. In each polymer molecule, the atoms are bound together by covalent bonds. However, the separate molecules, or segments of the same molecule, are attracted to each other by weak “intermolecular forces”, also termed “secondary” or “Vander Waals” forces. In general, covalent bonds govern the thermal and chemical stability of polymers. On the other hand, secondary forces determine most of the physical properties we associate with specific compounds.

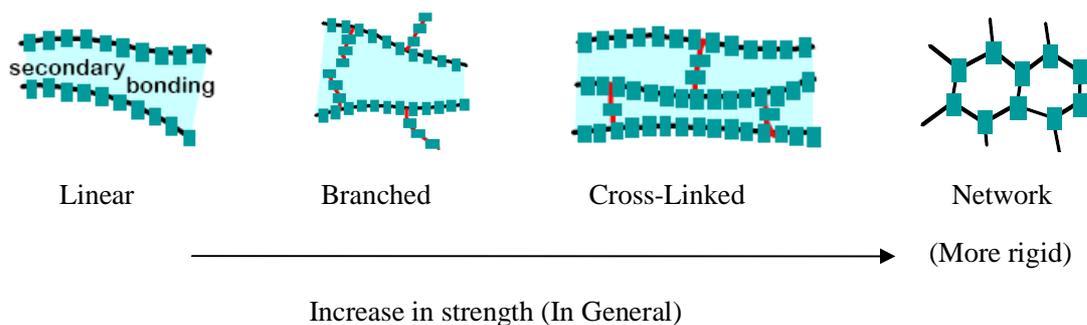
2.1 Objectives

By the end of this unit, you should be able to:

- Define a stereospecific reaction.
- List the types of microstructure a polymer chain can exhibit.
- Explain the different types of polymer isomerism.
- Give examples of linear, branched, cross-linked and networked polymers each.

2.2 Polymer Stereochemistry

The type of monomer(s) constituting a polymer chain and the way they are linked, by and large, determine the properties of the polymer. Thus there may be more than one type of monomer and, or the monomers may be arranged to give a linear, branched, cross-linked or network structure. Examples -



e.g.,

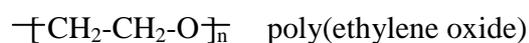
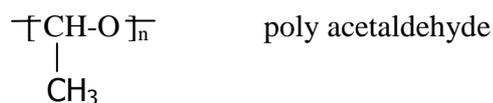
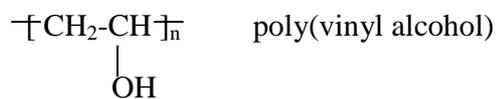
- Linear Polymers: Polyethylene, poly (vinyl chloride) (PVC), polystyrene, polymethyl methacrylate (plexiglass), nylon, fluorocarbons (teflon).
- Branched Polymers: Many elastomers or rubbers.

- Cross-linked Polymers: Thermosetting polymers, many elastomers or rubbers are also cross-linked (vulcanized).
- Network Polymers: Epoxies, phenol-formaldehydes.

These result in differences in the polymer microstructure giving rise to isomerism in polymers. There are four important types of polymer isomerism, namely; Structural (Architectural) isomerism, Configurational isomerism, Orientational isomerism and Geometrical isomerism.

2.3 Structural Isomerism

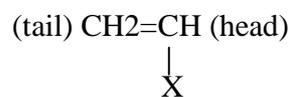
This arises from the fact that atoms or group of atoms are bonded differently in the formation of branches, side chains or network. Polymers derived from isomeric monomers, e.g., poly(vinyl alcohol), poly(ethylene oxide) and poly acetaldehyde have the same chemical composition C_2H_4O but different atomic arrangements with side chains in two of them.



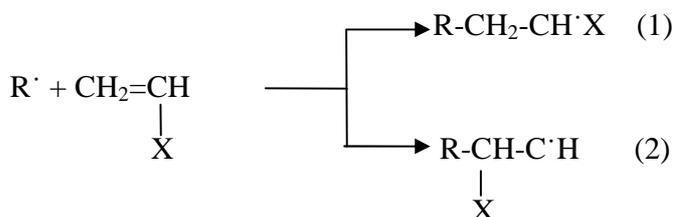
Note: The physical property of the polymers, e.g., The glass transition temperature; T_g for poly(vinyl alcohol) is 350K, T_g for poly acetaldehyde is 243K and T_g of poly (ethylene oxide) is 206K.

2.4 Orientational Isomerism

This results from the different orientations of monomer addition at the active center during vinyl polymerization. Consider a vinyl monomer $CH_2=CHX$ where X is any substituent. One carbon atom of the double bond may be arbitrarily labeled the head and the other the tail of the monomer, that is

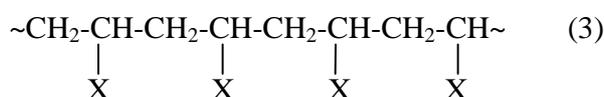


The active center can be formed by two possible reactions-



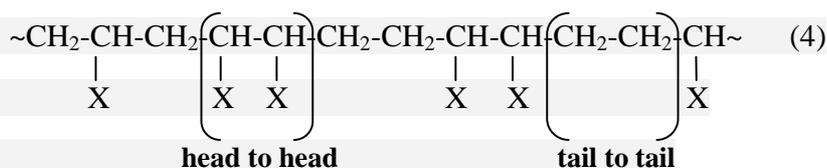
The monomers then add to the active centers leading to the formation of polymer with the following chain structures:

If route (1) is favoured, the arrangement is known as *head to tail* configuration.



head to tail

If route (2) is followed, that is chain containing a portion of *head to head*, *tail to tail* arrangement or a random structure containing both is obtained.

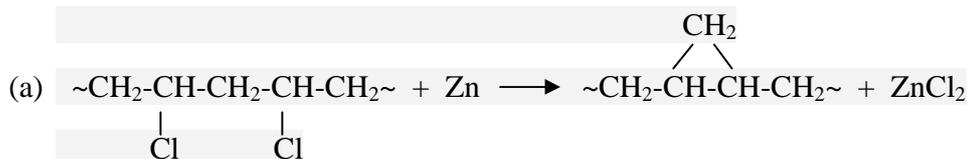


The real mode of addition depends on two factors; the stability of the product and the possible steric hindrance to the approach of $R\cdot$ caused by a large group X in the molecule. The reaction in route (1) is highly favoured, because:

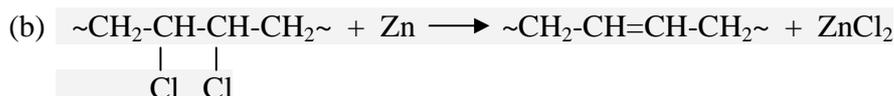
- There is a greater possibility of resonance stabilization of this structure due to interaction between group X and the unpaired electron on the adjacent α - carbon atom.
- The direction of radical attack is least impeded by substituent X.

Therefore the preferred structure is the *head to tail* orientation (3) while the alternative structure (4) may occur occasionally in the chain, especially when termination by combination predominates; the existence of an exclusively head to head orientation is unlikely unless synthesized via special route. It is experimentally proven that structure (3) (head to tail) is predominant in majority of polymers.

The most notable exceptions are poly(vinylidene fluoride) with 4 to 6% and poly(vinyl fluoride) with 25 to 35% head to head links detected by N.M.R studies. The presence of head to tail structures can be demonstrated in different ways e.g., When a dilute solution of poly(vinyl chloride) in dioxane is heated with zinc dust, chlorine is eliminated. This can proceed via two mechanisms:



Head to Tail polymer



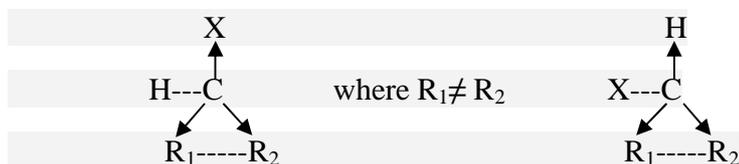
Head to Head polymer

Analysis of chlorine loss via route (a) shows that only 86.4% of the chlorine will react because elimination is a random process, the other 13.6% become isolated during the reaction and will remain in the chain. Elimination by mechanism (b) results in total removal of chlorine.

Poly(vinyl chloride) after treating with zinc dust indicated 84 - 86% chlorine elimination. This suggested that the polymer is almost the *head to tail* orientation.

2.5 Configurational Isomerism

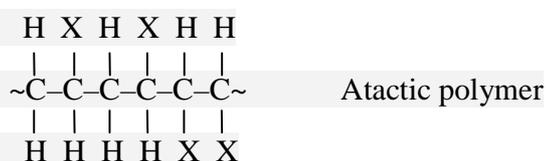
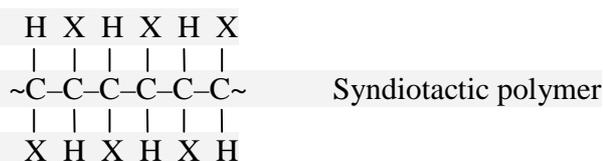
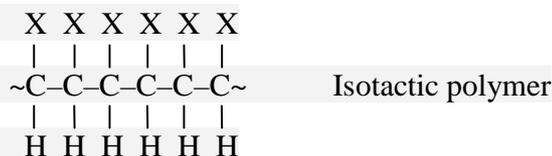
If a tertiary carbon atom in a polymer chain has two different side groups attached to it, the spatial arrangement of bonds in a molecule will be different. The presence of the asymmetric carbon atom (or chiral center) gives rise to configurational isomerism. Thus a group $-\text{CHX}-$ can only have two possible configurations since carbon atom is tetrahedral.



These configurations cannot be interconverted merely by rotation about single bonds, bonds have to be broken and reformed. To distinguish them, they are arbitrarily assigned (d-) or (l-) configurations using the terminology of stereochemistry. **Note** [The term merely refers to whether X is below or above the chain in a planar projection]. It is apparent that the distribution of (d-) and (l-) configurations determine the extent of regularity or order in the polymer. Using the nomenclature of Natta, polymers with highly regular distribution of (d-) or (l-) are known as **Tactic** (or stereoregular) **Polymers** and those with random distribution as **Atactic Polymers**. Two types of tactic structures can occur: Isotactic and Syndiotactic.

In *isotactic polymers*, the asymmetric carbon atom in each repeat unit in the chain has the same configuration. That is, all the X substituents are located on one side, either all above or below the carbon-carbon polymer chain. Polymers in which all the successive asymmetric carbon atoms in the chain have opposite configuration are called *syndiotactic polymers*.

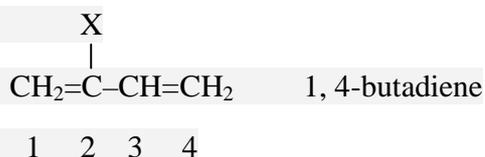
A random arrangement of substituent groups in the chain results in *atactic polymers*. The X substituents are located alternating on opposite side of the plane of the chain. These structures are represented below by Fischer projections :



Fisher Projection of Isotactic, Syndiotactic and Atactic Polymers with repeating unit –CHX–

2.6 Geometrical Isomerism

When diene monomers containing conjugated carbon-carbon double bonds are polymerized, geometrical isomerism arises as a result of different configuration of substituents on the double bonds. The diene may be represented by the general formular -



1, 4 polymerisation, leads to a polymer with double in the chain and so can have either cis- or trans- configuration. In the cis- isomers, the chain parts are on the same side of the double bond while on the trans- isomers, they are on opposite sides.



2.7 Self-Assessment Exercise

- What is stereospecific reaction?

- Discuss in detail polymer isomerism.
- Give at least two examples each of linear, branched, cross-linked and networked polymers.
- Differentiate between tactic and atactic polymers.

2.8 Conclusion

The microstructure of a polymer (sometimes called configuration) relates to the physical arrangement of monomer residues along the backbone of the chain. These are the elements of polymer structure that require the breaking of a covalent bond in order to change. Structure has a strong influence on the other properties of a polymer. Hence, polymer microstructure gives rise to the following isomerisms; structural isomerism, geometrical isomerism, orientational isomerism and configurational isomerism.

2.9 Summary

In this unit, you have learnt that:

- The type of monomers, and the way they are arranged in a polymer chain determines the polymer property.
- In structural isomerism, the polymers have the same chemical composition but different atomic arrangement.
- The different orientations of monomer addition at the active center during vinyl polymerization results in orientational isomerism.
- Polymerization of diene monomers containing conjugated carbon-carbon double bonds gives a geometrical cis- and trans- isomers.
- Tactic polymer is that with highly regular substituent distribution, e.g., isotactic and syndiotactic polymers while polymer with random distribution of substituents is called atactic polymer.

2.10 Tutor-Marked Assignment

- Explain with illustration the following orientation isomerism in the polymer - Head to tail, Head to head, and Tail to tail.
- Write short notes on the following : (a) Structural isomerism (b) Configurational isomerism (c) Geometrical isomerism.

2.11 References/Further Reading

- 1) Lecture 1-01, Introduction to polymeric materials.
- 2) Polymers: <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/polymers.htm>

- 3) E.M. Katchy (2000); Principles of Polymer Science; 1st edtn., El' demak publishers Enugu, Nigeria. Pgs 217 – 228.

Unit 3

Copolymerization

3.0 Introduction

When a polymer is made by linking only one type of small molecule or monomer together, it is called a homopolymer. When two different types of monomers are joined in the same polymer chain, the polymer is called a copolymer.

Copolymerization may be defined as the simultaneous polymerization of two or more monomers to form a polymer containing both or all the monomers. The product is termed a copolymer. There is a definite reaction between the monomers, and the process can be represented as



Simultaneous polymerization of more than two monomers is usually referred to as multicomponent copolymerization with the products termed terpolymer, quadripolymer, etc.

3.1 Objectives

By the end of this unit, you should be able to:

- Give a detailed explanation of copolymerization.
- Mention the benefits of copolymerization
- List and discuss the different types of copolymers.

3.2 Types of copolymers

The synthesis of macromolecules composed of more than one monomeric repeating unit has been explored as a means of controlling the properties of the resulting material. In this respect, it is useful to distinguish several ways in which different monomeric units might be incorporated in a polymeric molecule. Assume that two monomers will be called A and B, examples include:

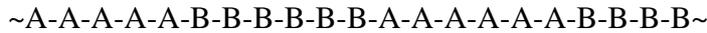
- (a) Random copolymers - Here the monomeric units are distributed randomly, and sometimes unevenly, in the polymer chain:



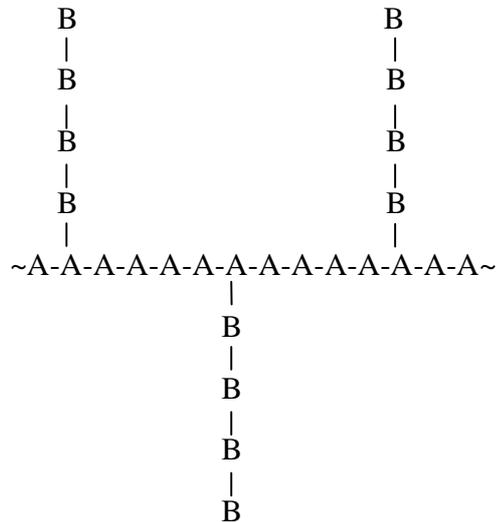
- (b) Alternating copolymers - The monomeric units are distributed in a regular alternating fashion, with nearly equimolar amount of each in the chain:



- (c) Block copolymers - Instead of a mixed distribution of monomeric units, a long sequence or blocks of one monomer is joined to a block of the second monomer:



(d) Graft copolymers - Here the blocks of one monomer are grafted or attached to the backbone of another monomer as branches.



Block and Graft copolymers are of special interest. Their most interesting characteristics is that they exhibit many properties associated with each homopolymer. Thus they show two transition temperatures and if both polymer types are crystalline, two crystalline melting points are observed. Random and alternating copolymers on the other hand, have characteristics somewhere between those of the two homopolymers.

3.3 Benefits of copolymerization

Copolymerization provides a means of exercising control over polymer properties - It improves tensile strength, impact strength (toughness), ductility (elongation of break), flexibility, chemical resistance, permeability to water vapour, gas permeability, surface modification, and ease of processing. Examples -

- Polystyrene is a brittle thermoplastic with poor impact strength, poor solvent resistance and low softening point. However, copolymerization of styrene with acrylonitrile yields a transparent product with better impact strength, increased solvent resistance and higher softening point.
- Copolymerization with butadiene yields elastomers while copolymerization of three monomers, styrene, acrylonitrile and butadiene a product in which all the three properties are simultaneously improved (a true engineering plastic).

3.4 Self-Assessment Exercise

- Define copolymerization

- State the advantages of copolymerization.
- Discuss the types of copolymers.

3.5 Conclusion

Copolymers are made up of two or more types of chemically distinct monomers. It may be composed of two bifunctional units and may alternate to give a well-defined recurring unit or the two different monomers may be joined in a random fashion in which no recurring unit can be defined.

3.6 Summary

In this unit, you have learnt that:

- Copolymerization is the simultaneous polymerization of two or more monomers to form a polymer containing both or all the monomers.
- Different monomeric units might be incorporated in a polymeric molecule resulting in alternating copolymer, random copolymer, block copolymer or graft copolymer.

3.7 Tutor-Marked Assignment

- List any five advantages of copolymerization.
- Write short notes on the following types of copolymers - graft copolymer, alternating copolymer, block copolymer and random copolymer.

3.8 References/Further Reading

- 1) E.M. Katchy (2000); Principles of Polymer Science; 1st edtn., El'demak publishers Enugu, Nigeria. Pgs 150 & 151.
- 2) Lecture 1-01, Introduction to polymeric materials.
- 3) Polymers: <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/polymers.htm>

Unit 4

Polymer Solutions

4.0 Introduction

Polymer solutions are of considerable interest both in theoretical and practical point of view because of the useful information they can furnish. For example, size and shape of polymer molecules can be obtained from polymer solutions.

Recall: Low molecular weight substance readily undergoes dissolution whereas polymers take a considerable time to do so. At low concentration, polymer solutions are highly viscous compared to low molecular weight substance, which are less viscous even at high concentrations.

Small molecular weight substances are held by Vander waal forces or electrostatic forces. As soon as the solvent and the solute are brought together, the solvent molecules surround the solute molecules at the surface, establish a solvent-solute interaction and break the solute-solute attraction. As this happens, the solute molecules which are discrete are isolated from the solid phase and as their sizes are comparable to that of the solvent molecules, they diffuse fast into the solvent phase. Dissolution here is almost instantaneous.

Larger molecular weight substances (Polymer) are giant molecules compared to solvent molecules and are made of hundreds of chain segments. These long molecules are not in the form of extended straight chains, but are in the form of **tightly folded random coils**. Individual molecular coils are also not discrete and separate but are interpenetrating and entangled with one another. There are varying degrees of cohesive and attractive forces between different segments of the same molecular coils as well as neighbouring coils. Forces such as dispersion, induction, dipole-dipole interaction and hydrogen bonding (both intramolecular and intermolecular) hold the molecular coils and their segments together tightly.

4.1 Objectives

By the end of this unit, you should be able to:

- Explain the thermodynamics of polymer solutions.
- Define a good solvent and a poor solvent.
- Discuss how physical properties and chemical structure affect solubility of polymers.
- Describe the process of polymer dissolution.

4.2 Thermodynamics of Polymer Solution

This is the interaction of long chain molecules with liquids. For linear and branched polymers, liquids can usually be found which will dissolve the polymer completely to form a homogenous solution while crosslinked polymers will only swell when in contact with the compatible liquids.

When an amorphous polymer is mixed with a suitable solvent, it disperses in the solvent and behaves as if it is liquid. Solvents for polymers are classed as good or poor solvent.

- a) A good solvent is one which is highly compatible with the polymer; the liquid-polymer interactions expand the polymer coil, from its unperturbed dimensions, in proportion to the extent of these interactions.
- b) A poor solvent is one which the liquid-polymer interactions are fewer and coil expansion of perturbation is restricted.

Note: Thermodynamic principles governing the dissolution of low and molecular weight substances are essentially same. Molar mass of macromolecules can be determined from the thermodynamic properties of polymer solution.

The basic thermodynamic parameters used to describe these system relates to the Gibbs free energy function (G), to the Enthalpy (H) and Entropy (S).

G is defined by the relation

$$G = H - TS \quad \text{----- (1)}$$

Normally the differences of these quantities in two specified states of the system are used, Thus $\Delta G = G_2 - G_1$ or $\Delta H = H_2 - H_1$ etc.

$$\Delta G = \Delta H - T\Delta S \quad \text{----- (2)}$$

For the solution process, the following are defined.

$$\Delta G_m = G_{\text{solution}} - \sum G_{\text{components}} \quad \text{(Free energy of mixing) ----- (3)}$$

$$\Delta H_m = H_{\text{solution}} - \sum H_{\text{components}} \quad \text{(Enthalpy of mixing) ----- (4)}$$

$$\Delta S_m = S_{\text{solution}} - \sum S_{\text{components}} \quad \text{(Entropy of mixing) ----- (5)}$$

A solvent of Gibbs free energy G_{solvent} will dissolve a polymer of Gibbs free energy G_{polymer} . If the Gibbs free energy of mixing ΔG_m is negative, that is $\Delta G_m \leq 0$. In other words, the Gibbs free energy of the solution, $\Delta G_{\text{solution}}$ is less than the solution of the Gibbs free energies of the components before dissolving.

That is,

$$G_{\text{solution}} < G_{\text{solvent}} + G_{\text{polymer}} \quad \text{----- (4)}$$

$$\text{Or } \Delta G_m = G_{\text{solution}} - (G_{\text{solvent}} + G_{\text{polymer}}) \quad \text{----- (5)}$$

From equation (2) then,

$$\Delta G_m = \Delta H_m - T\Delta S < 0$$

For any solution, ΔS_m is positive. If there are no interactions between the solvent and the solute (polymer), then the enthalpy of mixing must be zero, $\Delta H_m = 0$, giving an ideal solution. Hence

$$\Delta G_m = - T\Delta S_m \quad (\text{ideal solution})$$

It is therefore possible to determine ΔG_m if ΔS_m is known. ΔS_m can be calculated using a liquid lattice model. Polymer solutions only approach ideal behaviour at infinite dilution although at theta (Θ) conditions they exhibit pseudo-ideal behaviour. With polymer solutions, $\Delta H_m \neq 0$ because of interactions between the polymer and solvent molecules.

Note: The ideal solution model does not correspond to real solutions.

The sign of the Gibbs free energy change determines if solubility takes place on mixing the components. A negative Gibbs free energy change means that solution process is thermodynamically feasible. This has been stated as

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0$$

T is positive and ΔS_m is thought to be always positive so that the sign of ΔG_m is determined by the sign and magnitude of ΔH_m . If ΔH_m is negative, then ΔG_m will be negative and solution assured. If however ΔH_m is positive, then $\Delta H_m < T\Delta S_m$ for the polymer to be soluble.

In general, $T\Delta S$ is so small for high molar mass polymers that if ΔH_m is positive, then it must be very small if not close to zero for the solution of polymer to be possible. Thus solution depends on the existence of a zero or small values of ΔH_m .

4.3 Phase Equilibrium

In general, polymeric mixtures are far less miscible than mixtures of small molecule materials. This effect results from the fact that the driving force for mixing is usually 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 smaller 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.

Furthermore, the phase behavior of polymer solutions and mixtures is more complex than that of small molecule mixtures. Whereas most small molecule solutions exhibit only an upper critical solution temperature phase transition, at which phase separation occurs with cooling, polymer mixtures commonly exhibit a lower critical solution temperature phase transition, at which phase separation occurs with heating.

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 theta 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. The transition between the states is known as a coil-globule transition.

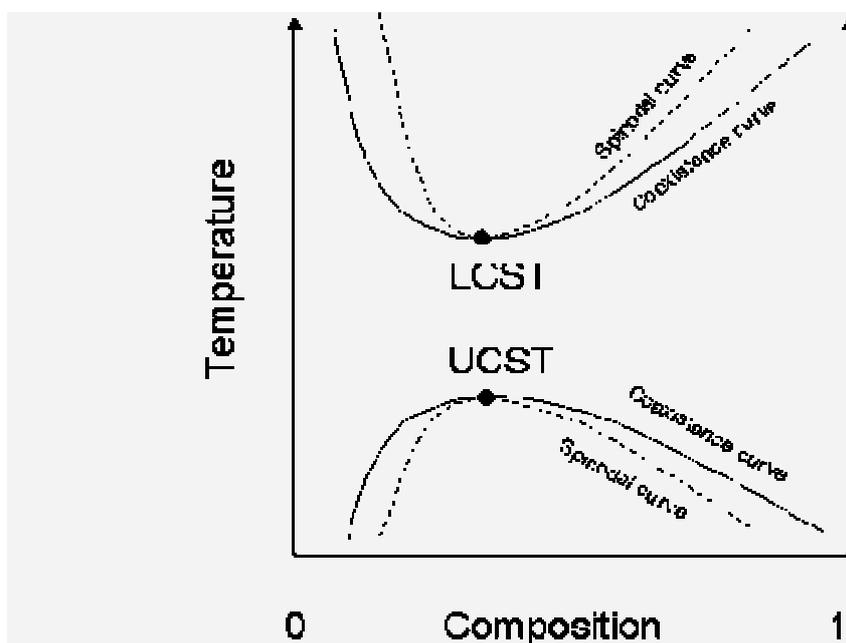


Fig 4.0 Phase diagram of the typical mixing behavior of weakly interacting polymer solutions.

4.4 Polymer Solubility

That not all polymers can be dissolved, and even though when they can, the dissolution process may take up to several days or weeks. It is important that a polymer does not interact with liquid with which it may come in contact during service. Also it is necessary to know what solvents attack what polymers.

The solution process when a polymer is added to a solvent, takes place in two stages:-

- (a) The first stage which is a slow process is called *solvation*. Solvent molecules are absorbed on the surface of the polymer molecules. They then diffuse into the bulk of the polymer resulting in an increase in the average dimension of the polymer molecule, a phenomenon known as *swelling*.

(b) In the second stage the swollen polymer, if in a good solvent gradually disperses to yield a polymer solution. This stage may be speeded up by agitation, though the solution process for polymer is slow.

The dissolution of polymers depends not only on their physical properties, but also on their chemical structures, such as – polarity or non-polarity, molecular weight, branching, crosslinking degree and crystallinity.

- Crosslinking degree - Solubility of a polymer decreases as crosslinking (strong intermolecular forces) increases, since strongly crosslinked polymers will inhibit the interaction between polymer chains and solvent molecules preventing those polymers from being transported into solution.
- Crystallinity (strong hydrogen bonding) - They act like crosslinking in that crystalline polymers are swollen or softened by solvents. Crystalline polymers dissolution can be forced if an appropriate solvent is available, or warming the polymer up to temperature slightly below its crystalline melting point (T_m), e.g., highly crystalline linear polyethylene ($T_m = 135^\circ\text{C}$) can be dissolved in several solvents above 100°C . Nylon 6,6 ($T_m = 265^\circ\text{C}$), a crystalline polymer which is more polar than polyethylene, can be dissolved at room temperature in the presence of solvent with enough ability to interact with its chains.
- Branching - Branched polymer chains generally increases solubility, although the rate at which this solubility occurs, depends on the particular type of branching. Chains containing long branches, cause dense entanglement making difficult the penetration of solvent molecules. Therefore the rate of dissolution in these cases becomes slower. Short branches loosen up the main chain structure thereby allowing solvent molecules to penetrate.
- Molecular weight - The molecular weight of polymer plays an important role in their solubility. In a given solvent at a particular temperature, as molecular weight increases, the solubility of the polymer decreases.
- Polarity or non-polarity - Polar solvents tend to dissolve polar polymers while non-polar solvents dissolve non polar polymers. Therefore polar polymers should be used in non-polar media e.g. poly(vinyl alcohol), poly(acrylic acid), poly(acrylamide) and other polymers containing hydroxyl groups are non-resistant to water but polyethylene, polypropylene, teflon, polystyrene, poly(vinyl chloride) are resistant to water.

Table 4.1 Polymers and their Dissolution Solvents

| Polymer | Solvents | □ Temperature ($^\circ\text{C}$) |
|--------------|----------------------------|------------------------------------|
| Polyethylene | n-Hexane, | 133 |
| | n- Hexanol/Xylene (70:30), | 170 |
| | n- Octane | 210 |

| | | | |
|--------------------------|----------------------------------------------------------------------------------------|---------------------------|----|
| Polypropylene (atactic) | n-Butanol/Carbon tetra-chloride (33:67), n-Butanol/n-Hexane (32:68), Cyclohexane | 25 92 | 25 |
| Polystyrene | Benzene/n-Butanol (58:42), Cyclohexane, Cyclohexanol | 35 34 - 35 79 - 87 | |
| Poly(vinyl acetate) | Ethanol, Ethanol/Methanol (40:60) | 19 25 | |
| Poly(vinyl alcohol) | Ethanol/Water (41.5:58.5), Water | 25 97 | |
| Poly(vinyl chloride) | Cyclohexane, Dimethylformamide | 22 36.5 | |
| Poly acrylamide | Methanol/Water (2:3) | 20 | |
| Poly methyl methacrylate | Acetone, Cyclohexane, Toluene, Dioxane/water | -126 77.6 -65 25 | |

4.5 Self-Assessment Exercise

- Discuss how physical properties and chemical structure affect solubility of polymers.
- Mention at least five polymers and their dissolution solvents.
- Give the thermodynamic equation used for describing a given system defining each term.

4.6 Conclusion

Dissolution of polymers involves a slow process called solvation where solvent molecules are absorbed on the surface of the polymer molecules, and then they diffuse into the bulk of the polymer resulting in an increase in the average dimension of the polymer molecule, a phenomenon **known** as swelling. This swollen polymer, if in a good solvent gradually disperses to yield a polymer solution. At low concentration, polymer solutions are highly viscous compared to low molecular weight substance, which are less viscous even at high concentrations. Polymeric mixtures are far less miscible than mixtures of small

molecule materials. This effect results from the fact that the driving force for mixing is usually entropy, not interaction energy.

4.7 Summary

In this unit, you have learnt that:

- The dissolution process of polymers may take up to several days or weeks.
- Size and shape of polymer molecules can be obtained from polymer solutions.
- Polymers are giant molecules compared to solvent molecules and hence are in the form of tightly folded random coils but not in the form of extended straight chains.
- A good solvent is highly compatible with the polymer; therefore the liquid-polymer interactions expand the polymer coil.
- A poor solvent is one which the liquid-polymer interactions are fewer and coil expansion of perturbation is restricted.
- Each polymer has its dissolution solvent and temperature.

4.8 Tutor-Marked Assignment

- What condition is to be satisfied for a solution process to be thermodynamically feasible.
- Define good solvent and poor solvent.
- Explain in details, how the following affects polymer solubility – polarity, crosslinking, molecular weight and branching.

4.9 References/Further Reading

- 1) Polymer: en.wikipedia.org/wiki/polymer
- 2) E.M. Katchy (2000); Principles of Polymer Science; 1st edtn., El' demak publishers Enugu, Nigeria. Pgs 234 – 249.
- 3) V. R Gowariker., N. V Visawanathan and Jayader Sreedhar (1986); Polymer Science; 1st edtn, New Age International Ltd; Publishers New Delhi. Pgs 332 – 341

Unit 5

Thermoplastic and Thermosetting Polymers

5.0 Introduction

The polymer chains can be free to slide past one another (*thermoplastic*) or they can be connected to each other with crosslinks (*thermoset*). Thermoplastics (including thermoplastic elastomers) can be reformed and recycled. This reflects the fact that above T_g they may be shaped or pressed into molds, spun or cast from melts or dissolved in suitable solvents for later fashioning. On the other hand, Thermosets which also includes cross linked elastomers are not reworkable. They are characterized by a high degree of cross-linking, resist deformation and solution once their final morphology is achieved. Such polymers are usually prepared in molds that yield the desired object because once formed, cannot be reshaped by heating.

5.1 Objectives

By the end of this unit, you should be able to:

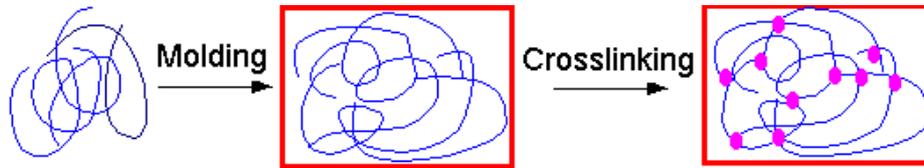
- Explain what thermoplastic and thermosetting polymer is.
- Give examples of industrially important thermoplastic and thermosetting polymers.
- Distinguish between thermoplastic and thermosetting polymers.

5.2 Thermoplastics

Polymers that flow when heated; thus, easily reshaped and recycled. This property is due to presence of long chains with limited or no crosslinks. In a thermoplastic material the very long chain-like molecules are held together by relatively weak Vander Waals forces. When the material is heated the intermolecular forces are weakened so that it becomes soft and flexible and eventually, at high temperatures, it is a viscous melt (it flows). When the material is allowed to cool it solidifies again. E.g., polyethylene (PE), polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), nylon (polyamide), unvulcanized natural rubber (polyisoprene)

5.3 Thermosets

Decompose when heated; thus, cannot be reformed or recycled. Presence of extensive crosslinks between long chains induces decomposition upon heating and renders thermosetting polymers brittle. A thermosetting polymer is produced by a chemical reaction which has two stages. The first stage results in the formation of long chain-like molecules similar to those present in thermoplastics, but still capable of further reaction. The second stage of the reaction (crosslinking of chains) takes place during moulding, usually under the application of heat and pressure. During the second stage, the long molecular chains have been interlinked by strong covalent bonds so that the material cannot be softened again by the application of heat. If excess heat is applied to these materials they will char and degrade.



[Materials by Design, Dept. of Mat. Sci. Eng., Cornell Univ., <http://www.mse.cornell.edu/courses/engri111/>]

e.g., epoxy, unsaturated polyesters, phenol-formaldehyde resins, vulcanized rubber.

Table 5.1 Characteristics of Thermoplastic and Thermosetting Polymers

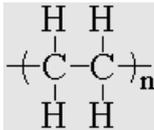
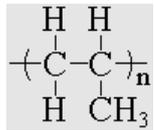
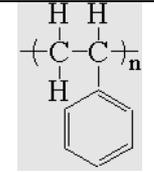
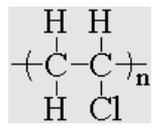
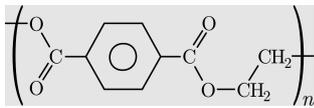
| Thermoplastics | Thermosets |
|---------------------------------------------|--------------------------------------------------------------------------------------|
| Good elasticity but depends on the type | Very poor elasticity |
| Easily reshaped on heating | Highly intractable crosslink i.e cannot be remoulded |
| Weak attractive forces between chains | Stronger attractive forces between chains |
| They are soluble in organic solvents | Not soluble in organic compounds |
| Super abrasion and dimensional stability | Better flexural and input resistance |
| They are flexible and not rigid | They are not flexible but rigid because of network structure formed by cross-linking |
| Softens without chemical change when heated | Undergoes irreversible change which causes it to harden or set |

5.4 Industrially important thermoplastic and thermosetting polymers

A number of thermoplastics with very good mechanical, electrical, thermal and chemical characteristics are usually referred to as engineering plastics. They are polycarbonates, polyacetals, polyamides, polyethylene, polystyrene, polypropylene, poly(vinyl chloride) and polytetrafluoroethylene. It does not mean that only these are useful within the engineering context. Thus there are epoxides, formaldehyde-based resins (i.e., phenol-formaldehyde, urea-formaldehyde, melamine-formaldehyde) and unsaturated polyesters (reinforced as appropriate). There are five major areas of application for polymers, namely, plastics, elastomers, fibers, surface finishes, protective coatings and adhesives.

The same polymer may be used in two or more applications. For example, nylon, a well known textile fiber is also used as a plastic molding material and as a film. Similarly epoxides are used in paints and adhesives as well as composites. The main factors determining the application of a given polymer is its mechanical behavior. If this can be appropriately altered by physical and chemical means then the polymer can be used in more than one application.

Table 5.2 Industrially Important Thermoplastics Polymers

| Polymer | Chemical Notation | Application |
|--------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Polyethylene (PE) |  $\left(\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right)_n$ | <p>HDPE* (High Density Polyethylene): milk and juice containers, grocery bags, toys, pipe, liquid detergent bottles, drums, sheet/film, ...etc</p> <p>LDPE* (Low Density Polyethylene): bread bags, frozen food bags, grocery bags, flexible tubing, squeeze bottles, toys, houseware, coatings, packaging films, ...etc</p> |
| Polypropylene (PP) |  $\left(\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{CH}_3 \end{array} \right)_n$ | carpet fibers, ropes, liquid containers, (cups/buckets/tanks), pipes, bicycle racks, automobile and appliance parts, oil funnels, furniture, film packaging, landscape borders, ...etc |
| Polystyrene (PS) |  $\left(\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{C}_6\text{H}_5 \end{array} \right)_n$ | packaging foams, egg cartons, lighting panels, rulers, houseware, coffee cups, knives, spoons and forks, cafeteria trays, meat trays, fast-food sandwich containers, ...etc |
| Poly(vinyl chloride) (PVC) |  $\left(\begin{array}{cc} \text{H} & \text{H} \\ & \\ -\text{C} & -\text{C}- \\ & \\ \text{H} & \text{Cl} \end{array} \right)_n$ | shampoo bottles, hoses, pipes, valves, electrical wire insulation, flooring, playground equipment toys, raincoats, film and sheet |
| Poly(ethylene terephthalate) (PET or PETE) |  $\left(\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2 \right)_n$ | bottles, beverage and food packaging, synthetic fibers, dishwashing liquid containers, laser toner cartridges, picnic tables, hiking boots, lumber, mailbox posts, fencing, furniture, ...etc |

* HDPE (High Density Polyethylene): Linear structure, better mechanical properties but more difficult to process than LDPE.

LDPE (Low Density Polyethylene): Branched structure, easier to process than HDPE.

Table 5.3 Industrially Important Thermosetting Polymers

| Polymer | Property | Application |
|-------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Epoxides | High chemical and corrosive resistance, outstanding adhesive properties, low shrinkage upon cure, and good electrical properties. | Protective coatings, composite matrices, and adhesives. |
| Polyester resins | High impact resistance, low crosslink density. | Construction and marine applications, adhesives |
| Formaldehyde resins (phenoplast and aminoplast) | Good chemical, electrical, temperature and moisture resistance. | Lacquers and varnishes, molding compounds, (e.g., wall panels and table tops), decorative plastic dinnerware. Reinforcing fillers and electrical fittings. |

5.5 Self-Assessment Exercise

- Define thermoplastic and thermosetting polymers.
- Mention at least five applications each of thermoplastic and thermosetting polymers.

5.6 Conclusion

Thermoplastic softens when heated, and hardens when cooled. Hence thermoplastics can be remoulded many times while Thermosets once formed do not soften on heating below their decomposition temperatures. They undergo irreversible chemical change which causes them to harden and set, a process called curing or crosslinking.

5.7 Summary

In this unit, you have learnt that:

- Mechanical properties of a polymer determine its application.
- Weak Vander Waals forces hold thermoplastic polymer chain together so that when the material it is heated, the intermolecular forces are weakened and becomes soft and flexible.
- Decomposition upon heating on thermosetting polymers is as a result of extensive crosslinks between the long chains.

- Application of polymers includes - plastics, elastomers, fibers, surface finishes, protective coatings and adhesives.

5.8 Tutor-Marked Assignment

- Distinguish between thermoplastic and thermosetting polymers.
- Explain in detail, thermoplastic and thermosetting polymers.

5.9 References/Further Reading

- 1) Lecture 1-01, Introduction to polymeric materials.
- 2) Polymers: <http://www2.chemistry.msu.edu/faculty/reusch/VirtTxtJml/polymers.htm>
- 3) E.M. Katchy (2000); Principles of Polymer Science; 1st edtn., El' demak publishers Enugu, Nigeria. Pgs 16 – 20.
- 4) Joel R. Fried (2005), Polymer Science & Technology; 2nd edtn., Prentice-Hall, Inc. New Jersey, USA. Pgs 354 – 385.

Unit 6

Mechanical Properties of Polymer

6.0 Introduction

The mechanical properties of a polymer involve its behavior under stress. These properties tell a polymer scientist or engineer many of the things he or she needs to know when considering how a polymer can be used.

- **How strong is the polymer?** How much can you stretch it before it breaks?
- **How stiff is it?** How much does it bend when you push on it?
- **Is it brittle?** Does it break easily if you hit it hard?
- **Is it hard or soft?**
- **Does it hold up well under repeated stress?**

The mechanical properties of polymers are one of the features that distinguish them from small molecules.

6.1 Objectives

By the end of this unit, you should be able to:

- Discuss the various kinds of strength exhibited by polymers.
- Explain the mechanical properties of polymers.
- Enumerate the factors that affect mechanical properties of a polymer.

6.2 Mechanical Properties of Polymers

Mechanical properties refer to those properties or characteristics of a material which determine its response to an applied stress or strain. The stress may be applied in increments, in flexure, tension or shear. Or it may be applied very abruptly or in cyclic (alternating) manner. Mechanical properties are manifested in the ability of the material to resist failure and/or its deformational behaviour. Polymers being viscoelastic materials, their mechanical properties in contrast to other materials, depend on time factor, temperature, structure, nature and previous history. Time factor means elapsed time under load, rate of loading, rate of deformation etc. Structure means molar mass, branching, crosslinking and crystallinity. Nature means types of additives, defects, blending and orientation. Previous history covers method of fabrication and sample preparation.

Other factors based on the nature and structures of the polymer which also affect the mechanical properties are:

Effects of Additives - Additives are normally incorporated into polymers for one reason or another. Some, such as water and monomer, may be unavoidably present. These additives may have significant effect on the mechanical properties and this must be taken account especially in design consideration. In general, solid additives such as fillers and reinforcing agents, improve the impact strength, flexural strength, tensile strength and heat distortion temperature of polymers. Plasticizers have a considerable effect on the mechanical properties of polymers. Addition of plasticizer lowers the glass transition temperature. Modulus and yield stress drop with increasing plasticizer content.

Effect of Blending and Copolymerization - The need for polymers having specific or improved properties is sometimes met not by synthesizing new polymers but by copolymerizing two or more monomers or by blending homopolymers, copolymer and terpolymers of different structures. Thus, when vinyl acetate or acrylonitrile is copolymerized with increasing amounts of vinyl chloride, the glass transition temperature rises from 303K for poly(vinyl acetate) or drops from about 380K for polyacrylonitrile to about 353K for poly(vinyl chloride). The copolymers become increasingly softer and tougher at room temperature but the softening point is lowered.

Effect of Molar Mass - The large molar mass of polymers is responsible for most of their useful properties. Nevertheless, too large a molar mass can make a polymer difficult to process and fabricate. It follows then that a balance has to be found between easy processability and maximum physical properties. Molar mass has little effect on yield stress and modulus. Increasing molar mass improves the rupture properties and impact resistance of a polymer. As the molar mass increases, more tie molecule hold the crystallite together, there is more flexibility and hence greater toughness.

The mechanical properties of polymers are usually described using the following terms; elasticity, plasticity, strength, toughness, ductility, brittleness and hardness.

- Elasticity - This refers to the ability of material to recover to its initial shape and dimensions when the applied stress is removed.
- Hardness refers to the ability of a material to surface deformation, indentation or abrasion.
- Dimensional stability - Is the ability of a polymer to withstand progressive removal of material from its surface as a result of mechanical action of rubbing, scrapping or corrosive nature; E.g. eraser and chalk have low scratch and abrasion resistance.
- Plasticity - A material is said to exhibit plasticity if on releasing the applied stress it retains a permanent deformation.
- Brittleness - A brittle material shatters suddenly without noticeable plastic deformation preceding failure.
- Ductility - A ductile material undergoes large irrecoverable deformation before rupture.
- Strength refers to the ability of a material to withstand a gradually applied stress without rupture. There is more than one kind of strength. The kind of strength a polymer has depends on how well the polymer holds up to whatever you are trying to do to it. For example;

- 1) Tensile strength is the stress needed to break a sample. It is an important property for polymers that are going to be stretched.
- 2) Compressive strength of a polymeric material refers to the ability of a material to resist crushing when a squeezing force is applied to it. An example of material with high compressive strength is foam material.
- 3) Impact strength measures the ability of a material to resist sharp blows or shock. E.g. Glass has zero impact strength.

Here are some kinds of strength, starting with tensile strength. Each one depends on what you are trying to do with the sample.

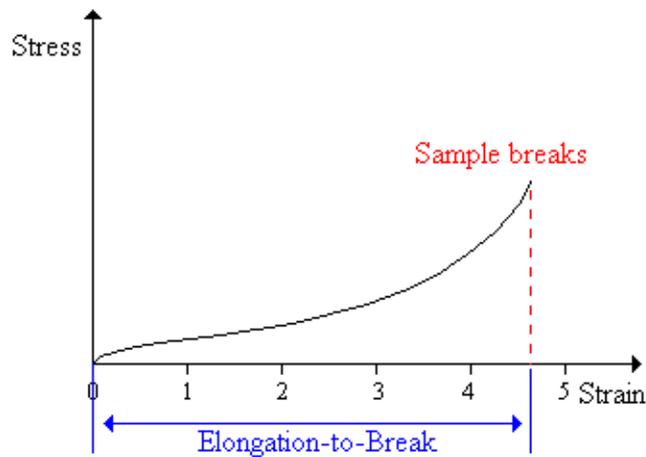
Table 6.1 Different kinds of Strength exhibited by polymers

| Action on polymer | Strength |
|-------------------------------------------------------------|-----------------|
| Try to pull it Impact -- | Tensile |
| Try to bend (or flex) it -- | Flexural |
| Try to twist it -- | Torsional |
| Try to compress it -- | compressional |
| Try to hit it sharply and suddenly -- (as with a hammer) | Impact |

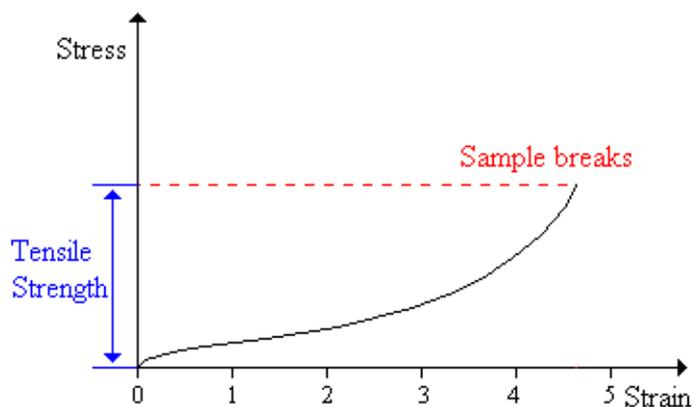
6.3 Stress - Strain Properties

The mechanical behaviour of a polymer can be assessed by its stress - strain properties. Some of the terms used in describing the response of material to stress - strain include:

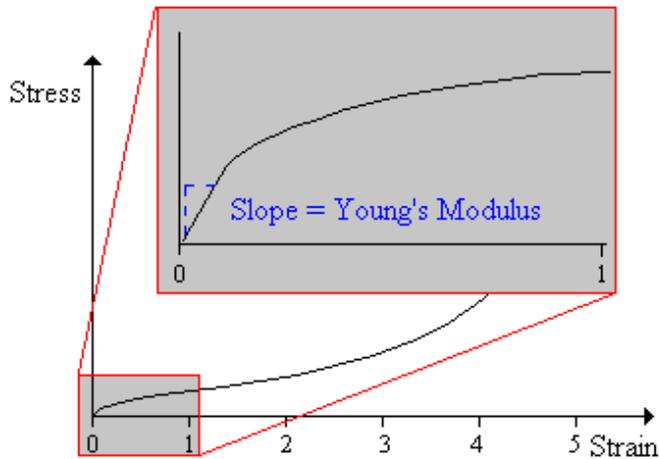
- 1) Ultimate elongation: is the extent of elongation at the point of failure. The elongation-to-break is the strain on a sample when it breaks. This usually is expressed as a percent. Fibers have a low elongation-to-break and elastomers have a high elongation-to-break.



- 2) Tensile strength: the stress required to rupture the object. This is the most important indicator of strength of a polymer and it is the force used to stretch a sample, divided by the cross-sectional area. Tensile strength is expressed in Pascals or psi (pounds per square inch). 1 MPa = 145 psi



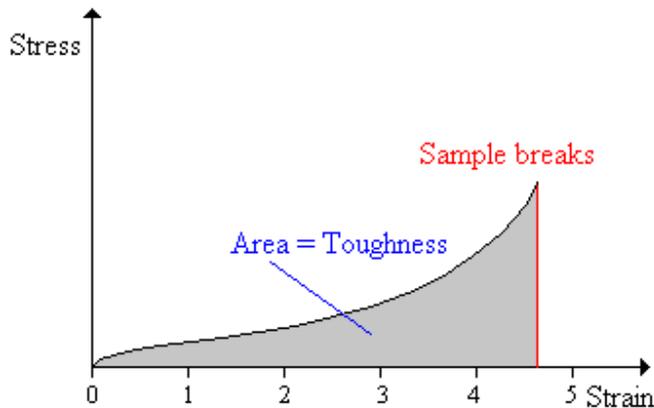
- 3) Young modulus: the resistance to deformation. This is given by the ratio of initial stress to initial strain. It also is called the modulus of elasticity or the tensile modulus. Young's modulus is the slope of stress-strain curve. Stress-strain curves are often not straight-line plots, indicating that the modulus is changing with the amount of strain. In this case the initial slope usually is used as the modulus, as is illustrated in the diagram below. Rigid materials, such as metals, have a high Young's modulus. In general, fibers have high Young's modulus values, elastomers have low values, and plastics lie somewhere in between.



- 4) Toughness: The toughness of a material is the area under a stress-strain curve. The stress is proportional to the tensile force on the material and the strain is proportional to its length. The area under the curve then is proportional to the integral of the force over the distance the polymer stretches before breaking.

$$\text{Area} \propto \int F(L) dL$$

This integral is the work (energy) required to break the sample. The toughness is a measure of the energy a sample can absorb before it breaks.



There is a difference between toughness and strength, as is illustrated in the three plots at the below. A material that is strong but not tough is said to be brittle.



Brittle substances are strong, but cannot deform very much. Polystyrene (PS) is brittle, for example. High impact polystyrene (HIPS), a blend of polystyrene and polybutadiene (a rubbery polymer above its glass transition temperature) is said to be rubber-toughened.

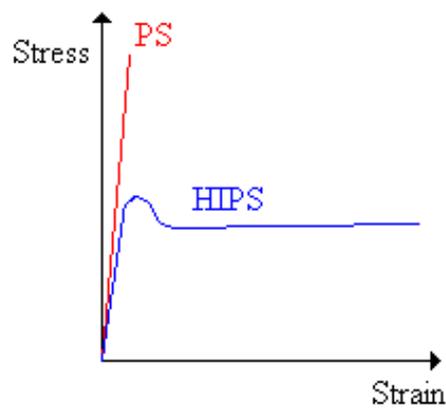


Table 6.2 Typical Materials - Mechanical Properties

| Material | Tensile Strength (MPa) | % Elongation-to-Break | Young's Modulus (GPa) |
|-----------------------|------------------------|-----------------------|-----------------------|
| Stainless Steel Balls | 2,000 | Very small | 200 |
| Cellophane Film | 50 – 120 | 10 - 50 | 3 |
| Nitrile Rubber Sheet | 20 – 30 | 250 - 500 | Very low |
| Fiberglass Yarn | 1400 – 2000 | 3 - 4 | 72 |
| Nylon | 50 | 150 | 2 |

6.4 Self-Assessment Exercise

- Write short notes on the following stress-strain properties; ultimate elongation, toughness, tensile strength, young's modulus.
- State and explain the factors that affect the mechanical properties of polymer.

6.5 Conclusion

Polymers are commonly used in many engineering applications. This is attributed mainly to their unique properties especially their high strength and large recoverable deformation, corrosion and abrasion resistance, low friction, and ease of fabrication. Their general level of tensile strength and moduli fall below those of metals and ceramics but their specific strength and stiffness are comparable with those of traditional materials; E.g., aluminum, brass and steel.

6.6 Summary

In this unit, you have learnt that:

- The property of a polymer tells a polymer scientist or engineers how a polymer can be processed.
- Polymeric materials possess unique properties like high strength and large recoverable deformation, corrosion and abrasion resistance.
- The strength of the polymer depends on how much you can stretch it before it breaks.
- Compressive strength of a polymeric material refers to the ability of a material to resist crushing when a squeezing force is applied to it.
- The following factors can affect mechanical properties of a polymer; time factor, structure, nature and temperature.

6.7 Tutor-Marked Assignment

- Define mechanical property of a polymer.
- What does the following mechanical properties of polymer mean; compressive strength, impact strength, elasticity, hardness, plasticity and dimensional stability.

6.8 Reference and Further Reading

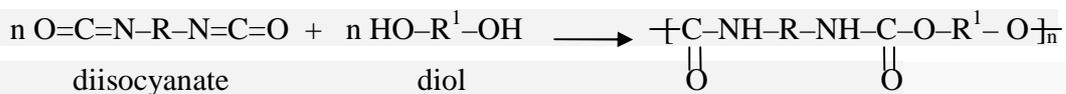
- 1) E.M. Katchy (2000); Principles of Polymer Science; 1st edtn., El'demak publishers Enugu, Nigeria. Pgs 401 – 424.
- 2) Mechanical Properties:
<http://faculty.uscupstate.edu/llever/polymerresources/mainmenu.htm>
- 3) J.O Ogbuagu and I.Ogburubi (2001); Polymer Chemistry- Practice and Industrial Application; 1st edtn., Optimum publishers Awka, Anambra State, Pgs 35 – 37.

Unit 7

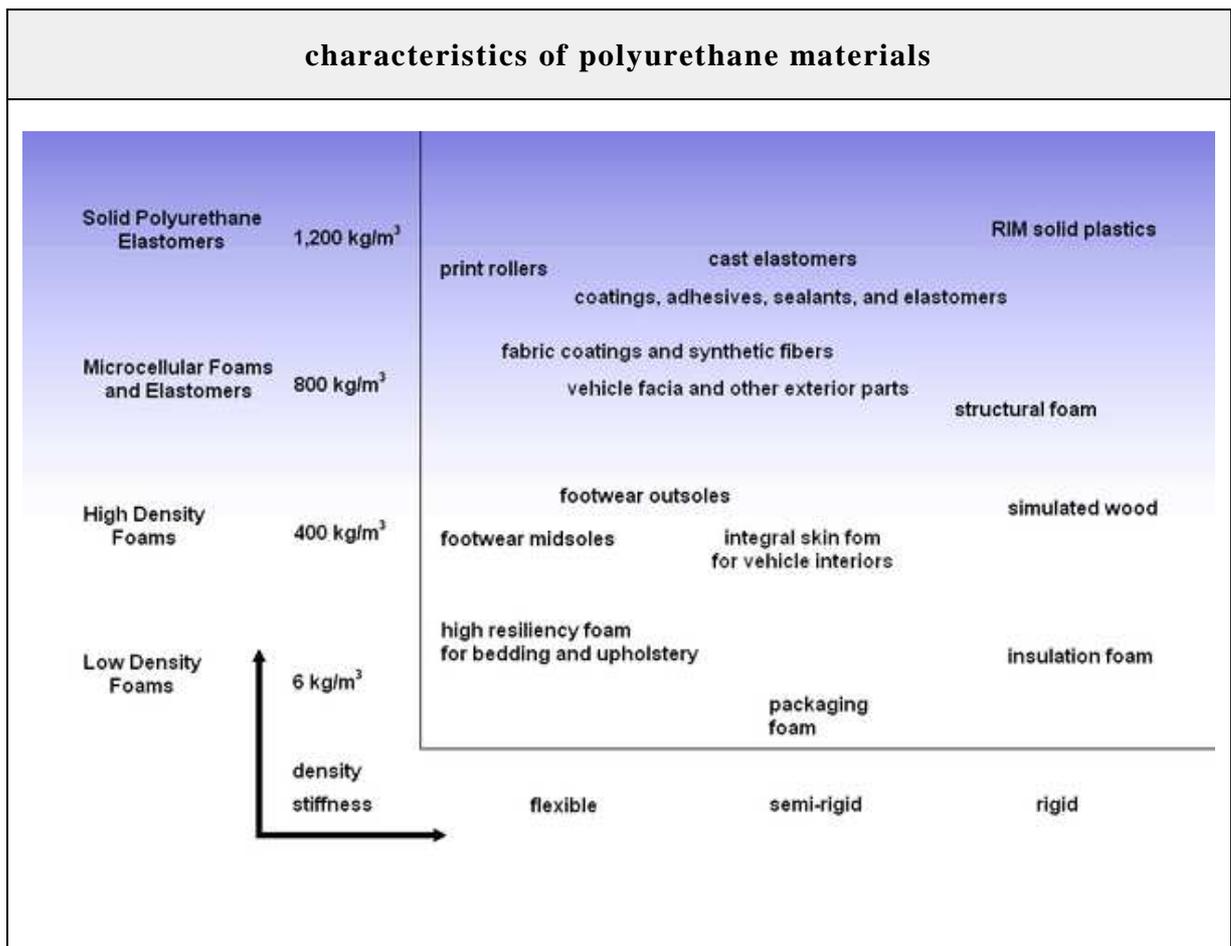
Polyurethanes

7.0 Introduction

Polyurethane (PUR and PU) is any polymer composed of a chain of organic units joined by carbamate (urethane) links. Polyurethane polymers are formed through step-growth polymerization, by reacting a monomer (with at least two isocyanate functional groups) with another monomer (with at least two hydroxyl or alcohol groups) in the presence of a catalyst.



Route to the synthesis of polyurethane from diisocyanates



7.1 Objectives

By the end of this unit, you should be able to:

- Discuss the properties of polyurethane.
- Enumerate the benefits of polyurethane
- Explain how polyurethane is synthesized.

7.2 Properties of Polyurethane

Polyurethane is a unique material that offers the elasticity of rubber combined with the toughness and durability of metal. These polymers have high strength, good resistance to gas, oil, and aromatic hydrocarbons, high abrasion resistance, and excellent resistance to oxygen and ozone, but are susceptible to microbial attack. Because urethane is available in a very broad hardness range (eraser-soft to bowling-ball-hard), it allows the engineer to replace rubber, plastic and metal with the ultimate in abrasion resistance and physical properties.

7.3 Advantages of Polyurethane

Abrasion resistant - Parts made of polyurethane will often outwear other materials by a margin of 5 to 50/one when severe abrasion is a factor. It has been proven to be vastly superior to rubber plastics and metal in many applications.

Tear resistant – Tear strength ranges between 500-100 lbs./linear inch, which is far superior to rubbers. As a result, urethane is often used as drive belts, diaphragms, roll covers, cutting pads, gaskets and chute liners.

Oil and solvent resistant - Polyurethane has excellent resistance to oils, solvents, fats, greases and gasoline.

Excellent noise abatement properties - The hard urethanes are now being used as gears in products where engineers desire sound reduction. The soft urethanes are used to replace rubbers for improved sound/vibration dampening.

Load bearing capacity - Polyurethane has a higher load-bearing capacity than any conventional rubber. Because of this characteristic, it is an ideal material for load wheels, heavy duty couplings, metal-forming pads, shock pads, expansion joints and machine mounts.

Weather resistant - Polyurethane has outstanding resistance to oxygen, ozone, sunlight and general weather conditions.

Flex-Life - Most formulations offer extremely high flex-life and can be expected to outlast other elastomer materials where this feature is an important requirement. Dust boots, bellows, diaphragms, belts, couplings and similar products are made from urethane for this reason.

Electrical properties - Polyurethane have excellent electrical insulating properties and are used successfully in many moulded wire and cable harness assemblies.

Heat and cold resistant - Continuous use above 225°F is not recommended nor is urethane recommended in hot water over 175°F. At low temperatures, polyurethane will remain flexible down to -90°F. Gradual stiffening will occur at 0°F, but will not become pronounced until much lower temperatures are obtained.

7.4 Applications of Polymers

In metal forming pads, belts, wear strips, bumpers, gears, bellows, machinery mounts, cutting surfaces, sound-dampening pads, chute and hopper liners, prototype machined parts, gaskets, seals, rollers, roller covers, sandblast curtains, diaphragms.

The table below shows how polyurethanes are used (US data from 2004)

Table 7.1 Usage per application of polymer

| Application | Usage (millions of pounds) | Percentage of total |
|----------------------------|----------------------------|---------------------|
| Building & Construction | 1,459 | 26.8% |
| Transportation | 1,298 | 23.8% |
| Furniture & Bedding | 1,127 | 20.7% |
| Appliances | 278 | 5.1% |
| Packaging | 251 | 4.6% |
| Textiles, Fibers & Apparel | 181 | 3.3% |
| Machinery & Foundry | 178 | 3.3% |
| Electronics | 75 | 1.4% |
| Footwear | 39 | 0.7% |
| Other uses | 558 | 10.2% |
| Total | 5,444 | 100.0% |

7.5 Self-Assessment Exercise

- List ten applications of polyurethane.
- With equations show how polyurethane can be synthesized.

7.6 Conclusion

Polyurethanes have replaced metals in sleeve bearings, wear plates, sprockets, rollers and various other parts, with benefits such as weight reduction, noise abatement and wear improvements being realized. They have better abrasion and tear resistance than rubbers, while offering higher load bearing capacity. Compared to plastics, polyurethanes offer superior impact resistance, while offering excellent wear properties and elastic memory.

7.7 Summary

In this unit, you have learnt that:

- Polyurethane can exist as solid polyurethane elastomers, micro cellular foam and elastomers, high density foams, and low density foams.
- Polyurethane can be prepared by the step-growth polymerization of diisocyanates with dihydroxyl (diol) compounds.
- The hard urethanes are now being used as gears in products where engineers desire sound dampening.
- Polyurethanes have excellent electrical insulating properties and are used successfully in many moulded wire and cable harness assemblies.

7.8 Tutor-Marked Assignment

- Discuss the properties that makes polyurethane a unique polymer.
- Mention the uses of solid polyurethane elastomers.

7.9 References/Further Reading

- 1) POLYURETHANE: www.sdplastic.com/polyuret.html
- 2) Polyurethane: en.wikipedia.org/wiki/polyurethane
- 3) List of polyurethanes: <http://en.wikipedia.org/wiki/file.purgrid.png>

Unit 8

Rubber Elasticity

8.0 Introduction

Natural rubber, also called China rubber or caoutchouc, is an elastomer (an elastic hydrocarbon polymer) that was originally derived from latex, a milky colloid produced by some plants. The purified form of natural rubber is the chemical polyisoprene, which can also be produced synthetically. Natural rubber is used extensively in many applications and products, as is synthetic rubber. It is normally very stretchy and flexible and extremely waterproof.

Rubber Elasticity is defined as ability of rubber to exhibit very large deformability with complete recoverability. Rubber elasticity can be quantitatively compared to the behaviour of a metallic spring. When we apply some force to a spring, it elongates by virtue of its uncoiling and when we release the force, the spring regains its original shape owing to recoiling. A similar thing happens in the case of rubber band also. The chain molecules undergo uncoiling and recoiling on the application and release of a small force. In order to undergo coiling and recoiling, the molecular chains in the rubber band should comprise flexible segments capable of attaining free rotation.

In the unstrained state, they should tend to take up the more probable randomly coiled conformation such that the entropy factor is the highest at its normal state. When strained, the chains should be able to get extended and be brought to more ordered conformations. An ordered arrangement of the chain molecules gives rise to partial crystallinity and also a decrease in the entropy factor. It is then the entropy factor that favours recoiling on release of the force. Hence, rubber exhibits unique physical and chemical properties. Its stress-strain behavior exhibits the Mullins effect, the Payne effect, and is often modeled as hyperelastic. Rubber strain crystallizes. Owing to the presence of a double bond in each repeat unit, natural rubber is sensitive to ozone cracking.

8.1 Objectives

By the end of this unit, you should be able to:

- Give a detailed explanation on rubber elasticity.
- Mention some characteristics and application of rubber.
- Distinguish between the elastic behaviour of rubber and metallic spring.

8.2 Natural rubber

Latex is a natural polymer of isoprene (most often cis-1,4-polyisoprene) – with a molecular weight of 100,000 to 1,000,000. Typically, a small percentage (up to 5% of dry mass) of other materials, such as proteins, fatty acids, resins and inorganic materials (salts) are found in natural

rubber. Polyisoprene is also created synthetically, producing what is sometimes referred to as "synthetic natural rubber".

Some natural rubber sources called gutta-percha are composed of trans-1, 4-polyisoprene, a structural isomer which has similar, but not identical, properties.

Natural rubber is an elastomer and a thermoplastic. However, it should be noted that once the rubber is vulcanized, it will turn into a thermoset. Most rubber in everyday use is vulcanized to a point where it shares properties of both; i.e., if it is heated and cooled, it is degraded but not destroyed.

8.3 Elasticity of Rubber

In most elastic materials, such as metals used in springs, the elastic behaviour is caused by bond distortions. When force is applied, bond lengths deviate from the (minimum energy) equilibrium and strain energy is stored electrostatically. Rubber is often assumed to behave in the same way, but it turns out this is a poor description. Rubber is a curious material because, unlike metals, strain energy is stored thermally. When rubber is stretched, the "loose pieces of rope" are taut and thus no longer able to oscillate. Their kinetic energy is given off as excess heat. Therefore, the entropy decreases when going from the relaxed to the stretched state, and it increases during relaxation. This change in entropy can also be explained by the fact that a tight section of chain can fold in fewer ways (W) than a loose section of chain, at a given temperature (note: entropy is defined as $S=k*\ln(W)$). Relaxation of a stretched rubber band is thus driven by an increase in entropy, and the force experienced is not electrostatic, rather it is a result of the thermal energy of the material being converted to kinetic energy.

8.4 Thermodynamics of Rubber Elasticity

The first and second law of thermodynamics applied to a reversible, equilibrium process provides the relationship between internal energy (U), entropy (S), and work (W) as

$$dU = TdS - dW \quad (8.1)$$

For deformation of a rubber band, the work is a combination of pressure-volume expansion and the work due to the (tensile) force (f) applied to the rubber band, given as

$$dW = pdV - fd\ell \quad (8.2)$$

Where the convention is that work done by the system (i.e., pressure-volume work) is positive and the work done on the system (i.e., force-displacement work) is negative. Enthalpy is related to the internal energy as

$$dH = dU + pdV. \quad (8.3)$$

Substituting eqtns. 8.1 and 8.2 (in the form $pdV = dW + fd\ell$) into eqtn. 8.3 gives

$$dH = TdS + fd\ell. \quad (8.4)$$

At constant temperature and pressure, rearrangement of eqtn. 8.4 in terms of force and taking the (partial) derivative with respect to length at constant temperature and pressure gives

$$\left(\frac{\partial H}{\partial \ell} \right)_{T, p} = f \quad (8.5)$$

$$f = \left. \frac{\delta H}{\delta \ell} \right|_{T,p} - T \left. \frac{\delta S}{\delta \ell} \right|_{T,p} \quad (8.5)$$

Equation 8.5 shows that elastic force has both an enthalpic and entropic component ($f = f_e + f_s$).

In order to obtain an expression for the temperature dependence of force, we make use of the relation

$$\left. \left(\frac{\delta S}{\delta \ell} \right) \right|_{T,p} = - \left. \left(\frac{\delta f}{\delta T} \right) \right|_{p, \ell} \quad (8.6)$$

Substituting eqtn 8.6 into eqtn 8.5 gives

$$f = \left. \left(\frac{\delta H}{\delta \ell} \right) \right|_{T,p} + \left. \left(\frac{\delta f}{\delta T} \right) \right|_{p, \ell} \quad (8.7)$$

8.5 Main uses of Natural Rubber

Because of its elasticity, resilience and toughness, natural rubber (NR) is the basic constituent of many products used in the transportation, industrial, consumer, hygienic and medical sectors. Compared to vulcanized rubber, uncured rubber has relatively few uses. It is used for cements, for adhesive, insulating, and friction tapes; and for crepe rubber used in insulating blankets and footwear. Vulcanized rubber, on the other hand, has numerous applications. Resistance to abrasion makes softer kinds of rubber valuable for the treads of vehicle tyres and conveyor belts, and makes hard rubber valuable for pump housings and piping used in the handling of abrasive sludge.

The flexibility of rubber is often used in hose, tires, and rollers for a wide variety of devices ranging from domestic clothes wringers to printing presses; its elasticity makes it suitable for various kinds of shock absorbers and for specialized machinery mountings designed to reduce vibration. Being relatively impermeable to gases, rubber is useful in the manufacture of articles such as air hoses, balloons, balls, and cushions. The resistance of rubber to water and to the action of most fluid chemicals has led to its use in rainwear, diving gear, and chemical and medicinal tubing, and as a lining for storage tanks, processing equipment, and railroad tank cars. Because of their electrical resistance, soft rubber goods are used as insulation and for protective gloves, shoes, and blankets; hard rubber is used for articles such as telephone housings, parts for radio sets, meters, and other electrical instruments. Also rubber is found useful in the medical and health sector (notably, condoms, catheters and surgical gloves) as well as seismic materials (for instance, over 500 and 2,500 buildings are respectively fitted with seismic rubber bearings in China and Japan). The coefficient of friction of rubber, which is high on dry surfaces and low on wet surfaces, leads to the use of rubber both for power-transmission belting and for water-lubricated bearings in deep-well pumps.

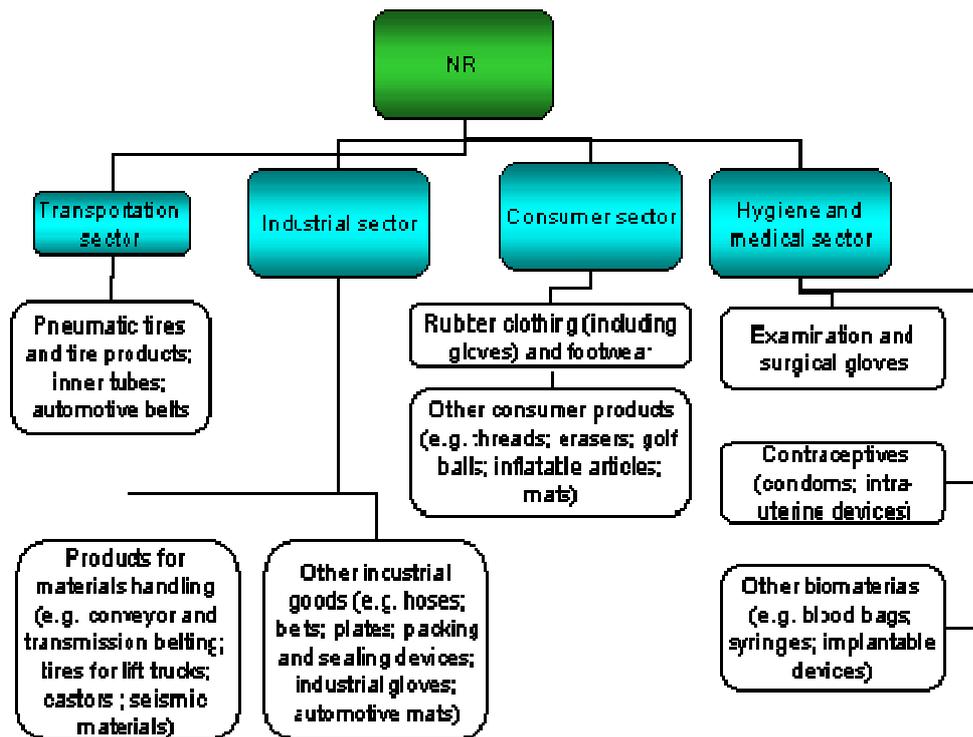


Fig 8.1 Natural Rubber major end uses

8.6 Self-Assessment Exercise

- How does stretching of rubber affect entropy?
- Define rubber elasticity.

8.7 Conclusion

It has been established that rubber elasticity can only be exhibited by such polymeric system consisting of long flexible coils with very weak interchain cohesion and interconnected here and there through crosslinks to form a three dimensional network. Thus the properties of an elastomeric material can be summarized by a simple term, 'rubber elasticity', which represents a combination of softness, stretchability, resilience and toughness.

8.8 Summary

- Natural rubber is an elastomer and a thermoplastic but will turn into a thermoset once it is vulcanized.
- Rubber exhibits very large deformability with complete recoverability.
- Natural rubber is sensitive to ozone cracking because of the presence of a double bond in its repeat unit.

8.9 Tutor-Marked Assignment

- Discuss the thermodynamics of rubber elasticity.
- Mention the uses of rubber.

8.10 References/Further Reading

- 1) Natural rubber: *en.wikipedia.org/wiki/natural_rubber*
- 2) V. R Gowariker., N. V Visawanathan and Jayader Sreedhar (1986); Polymer Science; 1st edtn, New Age International Ltd; Publishers New Delhi. Pgs 429 – 430
- 3) Joel R. Fried (2005), Polymer Science & Technology; 2nd edtn., Prentice-Hall, Inc. New Jersey, USA. Pgs 249 – 250
- 4) Uses of rubber: *www.heustononline.com/uses.htm*

Unit 9

Testing and Analysis of Polymers

9.0 Introduction

Several methods can be used to identify and analyze polymers whence their composition, both quantitative and qualitative, chain configuration and microstructure are characterized. These methods range from simple tests that may require minimum equipment to highly sophisticated, expensive and complex instrumental techniques such as gas-liquid chromatography, x-ray scattering, gel permeation chromatography, thermal analysis, and spectroscopy.

Polymers usually contain a number of additives such as antioxidants, crosslinking agents, fillers, lubricants, plasticisers, stabilisers, etc., which modify their behaviour. They may interfere with the identification of the polymer in which case it may be necessary to remove them by solvent separation techniques. Thus plasticized poly(vinyl chloride) may not be self-extinguishing and natural rubber containing antimony sulphide may be self-extinguishing. Colour, transparency and density are not characteristic of a polymer as they could be drastically altered by the incorporation of suitable additives.

9.1 Objectives

By the end of this unit, you should be able to:

- Identify a polymer using simple tests.
- List and discuss the instrumental techniques for polymer analysis.

9.2 Simple Identification Tests

Many polymers can be rapidly identified by simple tests without resorting to complex instrumental techniques or detailed chemical analysis. In order to accomplish this, knowledge of mechanical properties and processing methods of polymers in addition to familiarity with the results of such tests is extremely useful.

9.2.1 Direct Observation

The first step is to find out if the polymer is a thermoplastic, thermoset or rubber. This can be inferred by examining the appearance, 'feel', odour and rigidity of the sample. The sample may be a raw polymer intended for subsequent compounding and or processing. Examples are smoked sheet, crepe rubber, polyethylene granules and poly(vinyl chloride) granules. It may be a compounded stock intended for further processing. For example, novolak, dough moulding compound (DMC), PVC paste etc. it may be a finished article such as PVC bottle, tyre and garden hose. The nature of the article excludes certain polymers. Thus car tyres can only be moulded from rubber.

Fabrication method can also provide information for useful deduction so that features such as sprue marks, flash, weld lines, etc., should be sought for on the finished article. Generally thermoplastics are extruded, injection moulded and calendered; thermosets are compression moulded and cast; while rubbers are extruded, compression moulded and calendered. Some polymers such as polysulphides and natural rubber smoked sheet have pronounced odours.

Others have a feel peculiar to them. Thus polyethylene and polytetrafluoroethylene have a waxy feel. Rubber can be bent or stretched to maximum without fracture. Flexible thermoplastic are not so highly extensible and have no elastic 'snap back'. Rigid thermoplastic on being bent too far will first crack and then break. A notable exception is uncompounded polystyrene which is extremely brittle and fragile. Thermosets are very rigid and quite often, attempts to break them result in a sharp fracture with the freshly created surfaces rough.

9.2.2 Immersion in Water

This gives an indication of whether the specific gravity of the polymer sample is greater or less than unity by observing if a small pieces floats in water or not. If the specific gravity is less than unity then some of the more dense polymers are eliminated from the probe.

9.2.3 Beilstein Test

This test detects halogens. It involves bringing a sample on a hot copper wire to colourless bunsen flame. A green flame confirms the presence of a halogen.

9.2.4 Melting and Combustion

Heating a small piece of the sample near a bunsen flame and without decomposition will indicate fusibility, Thermoplasticity, fiber-forming properties or presence of crosslinking. The sample may soften appreciably thus indicating it is a thermoplastic or unvulcanized rubber. The heating may have little or no effect on the sample hence it is thermoset or vulcanized rubber. The sample may soften initially and then harden on continued heating thus indicating it is an uncured compounded polymer which crosslinks as the heating progresses. On placing the sample in the flame the following observations are made:

- i. Does the material burn and if yes how easily?
- ii. What is the odour of the fumes and are they acid, alkaline or neutral?
- iii. Does the sample continue to burn after removal from the flame?
- iv. What are the nature and colour of any flame?
- v. What is the nature of any residue?

9.2.5 Lassaigne Test

This test detects halogens, nitrogen, phosphorus or sulphur. From the results an indication of the possible nature of the polymer sample is obtained following classification of polymers according to elements present.

9.3 Complex/Sophisticated Instrumental Techniques

The simple tests on polymers aids in the identification of the polymers (i.e., if the polymer is a rubber or plastic). For the final analysis and characterization, complex instrumental techniques are used to determine the properties of polymers. Some of these techniques include spectroscopy (NMR, Raman, IR, FTIR, etc.), chromatography (gel permeation and gas-liquid), x-ray diffraction, differential scanning calorimetry, thermogravimetric analysis; etc.

9.3.1 Infra-Red (IR) Spectroscopy

IR spectroscopy is widely used in polymer science for structural characterization, determination of crystallinity, and examination of decomposition products to establish the mechanism of degradation. For example, the extent of branching in polyethylene can be estimated from the measurement of the relative absorbance of the methylene and methyl groups. The degree of tacticity in poly(methyl methacrylate), polypropylene and polystyrene can be ascertained from the ratios of characteristic absorbance bands related to tacticity. Thus, for poly(methyl methacrylate) a methyl deformation at 1380cm^{-1} ($7.25\mu\text{m}$) is not affected by microstructure hence the syndiotacticity is the ratio of absorbance at 1064cm^{-1} ($9.40\mu\text{m}$) to that at 1380cm^{-1} ($7.25\mu\text{m}$). The band at 1064cm^{-1} ($9.40\mu\text{m}$) is present in atactic and syndiotactic polymers and not in the isotactic polymer.

9.3.2 Fourier Transform Infra-Red (FTIR)

Modern laboratories now use the Fourier transform infrared (FTIR) spectrometer where the monochromator is replaced by an interferometer. FTIR is used for identification of polymer or plastic; bonding groups; pharmaceutical materials, including pill coatings and timed-release agents; organic contaminants, and for adhesive bond failure investigation.

9.3.3 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR is an important tool in the study of microstructure of polymers. It utilizes the property of some atomic nuclei to possess magnetic moments which interact with applied magnetic field. It is a useful tool for identification of polymers and for quantitative work.

9.3.4 X-ray Diffraction (XRD)

The X-ray region lies between the γ - ray and ultra violet portion of the electromagnetic spectrum, the wavelength being of the order of 10^{-8}cm . The special usefulness of X-ray diffraction in the study of solid substances lies in its ability to distinguish ordered from disordered states. Besides using X-ray diffraction to detect order in polymers, it can be used to determine the degree of crystallinity, crystallite size, preferred orientation of the crystallites, phase composition in crystalline polymers and the chain repeat distance for a drawn fibre. Also it is found useful in the investigation of adhesive bonding failures due to surface segregation of plasticizer or inorganic fill particles such as talc; or due to mold release agent or other contaminant; or due to stress in coating caused by internal layer contamination; or due to adhesive or primer degradation.

9.3.5 Gas-Liquid Chromatography (GLC)

Chromatography is the process of separating mixtures using a stationary phase and a moving phase. In gas-liquid chromatography the solutes are partition between a moving inert gas phase and an involatile liquid which is firmly absorbed on to a fixed solid. GLC finds applications in analysis of additives, detection of impurities in monomers, characterization of polymers and copolymers by degradation. The technique may also be used on a preparative scale to separate volatile substances which may then be analyzed by other methods such as infrared and spectroscopy. It is therefore an elegant technique for separation, identification and quantification.

9.3.6 Gel Permeation Chromatography

Gel permeation chromatography is used to determine the number average molecular weight, weight average molecular weight, and polydispersity of a polymer.

9.3.7 Thermal Analysis

Various property changes with temperature occurring in a substance may be investigated by dynamic mechanical thermal analysis (DMTA); thermogravimetric analysis (TGA); differential scanning calorimetry (DSC) or differential thermal analysis (DTA) and thermomechanical analysis (TMA).

Most substances undergoing physical and chemical changes such as evaporation and decomposition, involve change in heat content - heat absorption (endothermic) or heat liberation (exothermic). These changes in heat content may be detected as differences in temperature between the material and its environment.

- Differential scanning calorimetry or Differential thermal analysis may be used to measure specific heats and any thermal transitions (glass transition, melting, softening, crystallisation, degradation, etc). They are used to study the synthesis, processing, thermal and mechanical histories of polymers, gelation, and rate of cure of polymers such as elastomers, epoxy resins and unsaturated polyester resins.
- Thermogravimetric analysis monitors the weight change of the sample against temperature or time. Thermogravimetry is a useful technique to study the polymerization and composition of filled polymers. Its primary use has been for measuring oxidation and degradation rates, investigating thermal stability and evaluation of antidegradants. Detailed analyses of TG curves also allow us to know a bit of the phase segregation in polymers. Rheological properties are also commonly used to help 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.
- Thermomechanical analysis measures the mechanical response of a polymer into a sample as the temperature is changed. The technique may be used to detect softening and melting and to measure coefficient of expansion and their anisotropy.
- Dynamic mechanical thermal analysis measures the dynamic storage modulus, dynamic loss modulus and damping factor of a material under oscillatory load as a function of temperature or time at various frequencies. It is a useful tool in the study of polymer blends and composites, and curing processing thermosets.

9.4 Self-Assessment Exercise

- What do you understand by testing and analysis of polymer and why is it necessary?

- Discuss any six instrumental techniques used for identification and characterization of polymers.

9.5 Conclusion

The identification and characterization of a polymer requires several parameters which need to be specified. This is because a polymer actually consists of a statistical distribution of chains of varying lengths, and each chain consists of monomer residues which affect its properties.

9.6 Summary

In this unit, you have learnt that:

- A variety of laboratory techniques are used to determine the properties of polymers these can go from simple identification tests to more complex techniques.
- Simple identification tests for polymer include; direct observation, lassaigne test, immersion in water, beilstein test, melting and combustion.
- Complex and sophisticated analysis for polymer are; spectroscopy (NMR, IR, & FTIR), chromatography (gas-liquid and gel permeation), x-ray diffraction, thermal analysis (TGA, TMA, DSC, & DMTA).
- In processing of polymers, thermoplastics are extruded, injection moulded and calendered; thermosets are compression moulded and cast; while rubbers are extruded, compression moulded and calendered.
- Additives used in polymer processing can modify their behaviour and as well interferes during characterization.

9.7 Tutor-Marked Assignment

- Enumerate the simple identification tests for polymer.
- List three physical properties of a polymer that can be identified using the following test methods: (a) Differential scanning calorimetry (b) Infrared or FTIR (c) Thermomechanical analysis.

9.8 References/Further Reading

- 1) E.M. Katchy (2000); Principles of Polymer Science; 1st edtn., El'demak publishers Enugu, Nigeria. Pgs 316 – 331.
- 2) Anderson material evaluation: www.andersonmaterials.com/plastic.html
- 3) Polymer: en.wikipedia.org/wiki/polymer

Unit 10

Polymer Degradation

10.0 Introduction

Polymer degradation involves all the actions which when happened on a polymer will reduce the quality of the polymer, practically, the ageing of rubber, the deterioration of meat, the rotting and burning of wood are examples of degradation of polymers, which have constantly challenged man's control over environment. Chemically, degradation is a reaction involving rupture of chemical bonds in the main chain of the macromolecules. Depending on the type of chemical bond (covalent or ionic) three mechanisms of polymer degradation are possible, namely; radical, ionic and iono-radical. Deterioration in the physical property of a polymer due to exposure to sun and rain is known as weathering.

10.1 Objectives

By the end of this unit, you should be able to:

- Define polymer degradation.
- List the factors that contribute to polymer degradation.
- Classify polymer degradation.

10.2 Polymer Degradation

Polymer degradation is a change in the properties - tensile strength, colour, shape, etc., of a polymer or polymer-based product under the influence of one or more environmental factors such as heat, light or chemicals such as acids, alkalis and some salts. These changes are usually undesirable, such as cracking and chemical disintegration of products or, more rarely, desirable, as in biodegradation, or deliberately lowering the molecular weight of a polymer for recycling. The changes in properties are often termed "aging". In a finished product such a change is to be prevented or delayed. Degradation can be useful for recycling/reusing the polymer waste to prevent or reduce environmental pollution. Degradation can also be induced deliberately to assist structure determination.

Polymeric molecules are very large (on the molecular scale), and their unique and useful properties are mainly a result of their size. Any loss in chain length lowers tensile strength and is a primary cause of premature cracking.

Today there are primarily seven commodity polymers in use: polyethylene, polypropylene, polyvinyl chloride, polyethylene terephthalate or PET, polystyrene, polycarbonate, and poly(methyl methacrylate) (Plexiglass). These make up nearly 98% of all polymers and plastics encountered in daily life. Each of these polymers has its own characteristic modes of degradation and resistances to heat, light and chemicals. Polyethylene, polypropylene, and poly(methyl methacrylate) are sensitive to oxidation and UV radiation, while PVC may discolour at high temperatures due to loss of hydrogen chloride gas, and become very brittle. PET is sensitive to hydrolysis and attack by strong acids, while polycarbonate depolymerizes rapidly when exposed to strong alkalis.

Degradation therefore, can be classified into physical, chemical and biological depending on the agent causing the bond rupture in the chain. Physical degradation falls into thermal (heat), mechanical, photolytic (light), ionizing - radiation and fire (flame) degradation. Chemical degradation occurs under the action of various chemical agents. The most important types of chemical degradation are oxidative, hydrolysis, acidolysis, and alcoholysis. Biological degradation is caused by enzymes produced by animals which attack the molecules and degrade them.

10.3 Ionizing-Radiation Degradation

Many polymers are susceptible to degradation and cross linking upon exposure to high energy ionization radiation such as X-rays, gamma rays, and electromagnetic waves with the energy of visible light to give lower molecular weight molecules. Sometimes, these effects can be used to an advantage. Some polymers like polystyrene and polysulfone are very radiation resistant, but others like polypropylene will readily degrade upon irradiation. The primary event in radiation damage is the ejection of a high - energy electron.



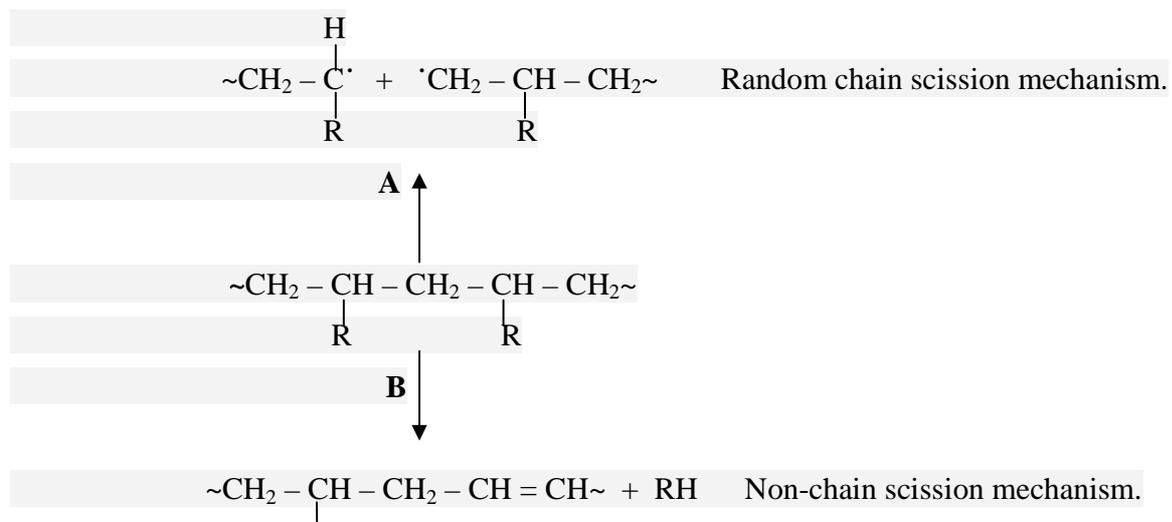
10.4 Photolytic Degradation

This is the type of degradation that occurs under the action of light. The degree of photochemical degradation depends on the wavelength of the ultraviolet light (quantum energy), the intensity of radiation, the conditions of the experiment and the structure of the polymer.

10.5 Thermal Degradation

Thermal degradation is the various chemical and physical changes that occurs when polymers are heated. In general vinyl polymers are particularly susceptible to thermal degradation, which can occur either in chain scission, (route A) involving the breakage of the backbone bonds to yield free radical segments or by non-chain scission, (route B) involving the elimination of a small molecule from a substituent group and subsequent double bond formation.

Example: For a vinyl polymer, we have these routes-



10.6 Hydrolytic Degradation

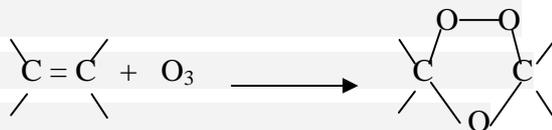
Step-growth polymers like polyesters, polyamides and polycarbonates can be degraded mainly by hydrolysis to give lower molecular weight molecules. The hydrolysis takes place in the presence of water containing an acid or a base as catalyst. Polyamide is sensitive to degradation by acids and polyamide mouldings will crack when attacked by strong acids. For example, the fracture surface of a fuel connector showed the progressive growth of the crack from acid attack to the final cusp of polymer. The problem is known as stress corrosion cracking, and in this case was caused by hydrolysis of the polymer.

10.7 Oxidative Degradation

This is degradation by atmospheric oxygen and other oxidants. The resistance of a polymer to oxidizing agent depends on its structure and primarily on the presence of readily oxidizable groups and bonds in the macromolecule. That is, oxidizable carbon-carbon molecular compounds and unsaturated hydrocarbons, e.g., natural and butadiene rubbers. Light and heating intensify oxidative degradation. The presence of double bonds in the main chains is more active during oxidative degradation than double bonds in side chain vinyl groups.

Ozone is a vigorous oxidizing agent. In the light, ozone degrades natural rubber strongly. Carbon-carbon saturated polymer compounds (polyethylene, polystyrene) are more resistant to oxidation. Polymers exposed to ozone are found to crack on stretching.

Example of ozone oxidation:



Ozonoide

10.8 Galvanic action

Polymer degradation by galvanic action was first described in the technical literature in 1990.

This was the discovery that "plastics can corrode", i.e. polymer degradation may occur through galvanic action similar to that of metals under certain conditions. Normally, when two dissimilar metals such as copper (Cu) and iron (Fe) are put into contact and then immersed in salt water, the iron will undergo corrosion, or rust. This is called a galvanic circuit where the copper is the noble metal and the iron is the active metal, i.e., the copper is the cathode or positive (+) electrode and the iron is the anode, or negative (-) electrode. A battery is formed. It follows that plastics are made stronger by impregnating them with thin carbon fibers only a few micrometers in diameter known as carbon fiber reinforced polymers (CFRP). This is to produce materials that are high strength and resistant to high temperatures. The carbon fibers act as a noble metal similar to gold (Au) or platinum (Pt). When put into contact with a more active metal, for example with aluminum (Al) in salt water the aluminum corrodes.

However in early 1990, it was reported that imide-linked resins in CFRP composites degrade when bare composite is coupled with an active metal in salt water environments. This is because

corrosion not only occurs at the aluminum anode, but also at the carbon fiber cathode in the form of a very strong base with a pH of about 13. This strong base reacts with the polymer chain structure degrading the polymer. Polymers affected include bismaleimides (BMI), condensation polyimides, triazines, and blends thereof. Degradation occurs in the form of dissolved resin and loose fibers. The hydroxyl ions generated at the graphite cathode attack the O-C-N bond in the polyimide structure. Standard corrosion protection procedures were found to prevent polymer degradation under most condition.

Table 10.1 Effect of Environmental Agents on Polymers

| Agent | Susceptible polymers | Examples |
|-----------------------------|-----------------------------------------------------------------|----------------------------------------------------------------|
| Biodegradation | Short-chain polymers, nitrogen-containing polymers, polyesters. | Polyurethanes, Polyether-polyurethane |
| Ionizing radiation | Aliphatic polymers having quaternary carbon atoms | Poly(methyl methacrylate) Polyisobutylene, Polypropylene |
| Moisture | Heterochain polymers | Polyester, Polyamide, Poluyurethane |
| Organic liquids and vapours | Amorphous polymers | Polystyrene, Poly(methyl methacrylate) |
| Ozone | Unsaturated elastomers | Polyisoprene, Polybutadiene |
| Sunlight | Photosensitive polymer | Polyacetals, Polycarbonate |

10.9 Self-Assessment Exercise

- What is weathering?
- Mention the factors that influence polymer degradation.
- Polymer Degradation: *en.wikipedia.org/wiki/polymer_degradation*

10.10 Conclusion

A plastic bucket left for long time in the sun and rain loses its lustre and strength. This deterioration in properties is due to a phenomenon called ‘polymer degradation,’ which is characterized by uncontrolled change in the molecular weight or constitution of the polymer. Conventionally, the term ‘degradation’ is taken to mean a reduction in the molecular weight of polymer.

10.11 Summary

In this unit, you must have learnt that:

- Polymer degradation involves all the actions which when happened on a polymer will reduce the quality of the polymer.
- Chemically, degradation is a reaction involving rupture of chemical bonds in the main chain of the macromolecules.
- Degradation is influence by one or more of these environmental factors - heat, light or chemicals such as acids, alkalis and some salts.
- Biological degradation is caused by enzymes produced by animals which attack the molecules and degrade them.

10.12 Tutor-Marked Assignment

- Define polymer degradation.
- How can it be classified?
- Write a shorts note on the following: oxidative degradation, thermal degradation, photolytic degradation, and hydrolytic degradation.
- Give one polymer that is degradable by the following degradation agents: ozone, bio-organism, oxygen, water, sunlight, burning.

10.13 References/Further Reading

- 1) Polymer Degradation: *en.wikipedia.org/wiki/polymer_degradation*
- 2) V. R Gowariker., N. V Visawanathan and Jayader Sreedhar (1986); Polymer Science; 1st edtn, New Age International Ltd; Publishers New Delhi. Pgs 263 – 290.
- 3) Joel R. Fried (2005), Polymer Science & Technology; 2nd edtn., Prentice-Hall, Inc. New Jersey, USA. Pgs 263 – 274.