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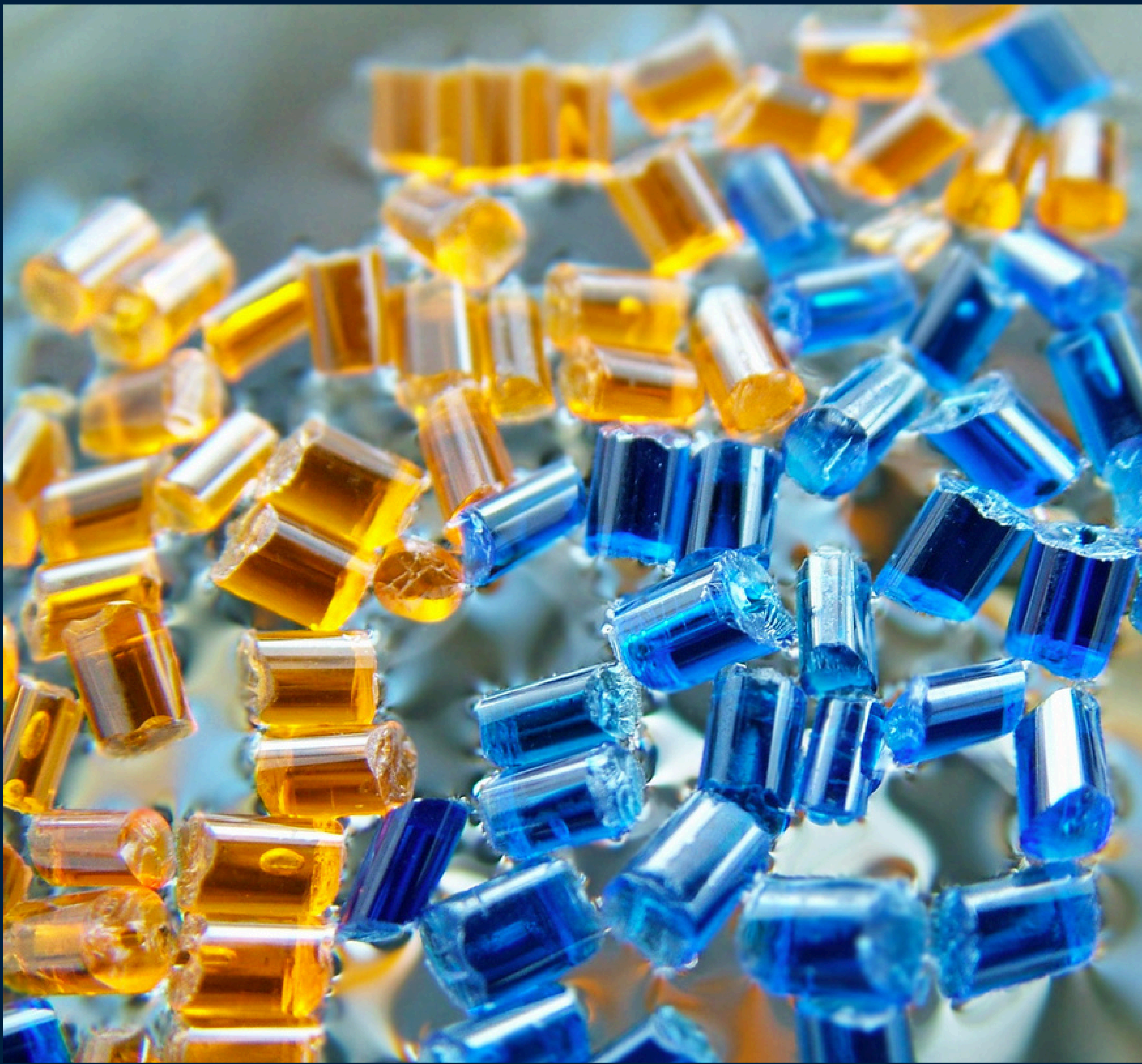

PETROCHEMICAL POLYMER: INTRODUCTION

Polymers are an essential part of everyday materials and industries due to their versatility.

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PREFACE

The petrochemical polymer industry has become a cornerstone of modern civilization, touching nearly every aspect of our daily lives. From packaging to construction, electronics to textiles, and medicine to automotive parts, polymers derived from petrochemicals play an integral role in shaping the materials that define our world. This e-book, Petrochemical Polymers: Introduction, aims to provide readers with a foundational understanding of the key concepts that drive this industry.

The content of this e-book is designed to guide students, researchers, and industry newcomers through the essential topics that define the study of petrochemical polymers. Beginning with a broad overview of polymers and plastics, readers will gain insight into the origins, characteristics, and significance of these materials in various applications. From there, we delve into plastic classification, exploring the various types of plastics and their unique properties. This is followed by an examination of polymer structure, revealing how different molecular architectures influence the material properties that are crucial in selecting the right polymer for each application.

Understanding the formation of polymers is also a vital part of this text. We cover the polymerization process, explaining the mechanisms and techniques that allow monomers to bond into long, durable polymer chains. This section also includes a step-by-step guide to calculating the degree of polymerization—a critical factor in determining the properties and potential uses of a polymer.

This e-book is designed to be accessible to those new to the field while providing a solid technical grounding that will be valuable for more advanced study. Each chapter builds on the last, reinforcing concepts and equipping readers with the knowledge needed to understand both the science and the practical applications of petrochemical polymers.

We hope that this introduction will inspire further exploration and foster a greater appreciation of the pivotal role petrochemical polymers play in advancing technology, innovation, and sustainability.

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Polymers' adaptability allows them to be used in virtually every aspect of modern life, from consumer goods to advanced technologies.

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The structure of a polymer is crucial to its properties and behavior.

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process through which monomers, reactive molecules combine to form a polymer, a large macromolecule with repeating structural units.

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Calculating various aspects of polymers often involves determining molecular weight and degree of polymerization,

1 Introduction

Introduction

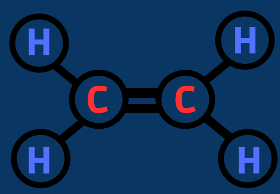
01 | MONOMER

A MONOMER is the single unit or the molecule which is repeated in the polymer chain. It is the basic unit which makes up the polymer. The repeat sub unit in the polymer chain is called a mer.

Key Point:

- **Monomers are the repeating units in a polymer.**
- **They usually have reactive groups that allow them to form bonds with other monomers.**
- **The chemical composition and structure of monomers determine the properties of the resulting polymer.**

The word POLYMER comes from the Greek words “poly” =“many”, and “meros” meaning “parts” or “repeating units”



For example, ethylene (C_2H_4) is the monomer for polyethylene, a common plastic. Multiple ethylene molecules join together in a chain to form the polymer.

02 | POLYMER

A polymer is a large molecule composed of repeating structural units called monomers, which are bonded together. These monomers are small, simple molecules, and when they chemically bond, they form long chains or networks, creating the polymer. Polymers can be either natural or synthetic and are used in a wide range of applications.

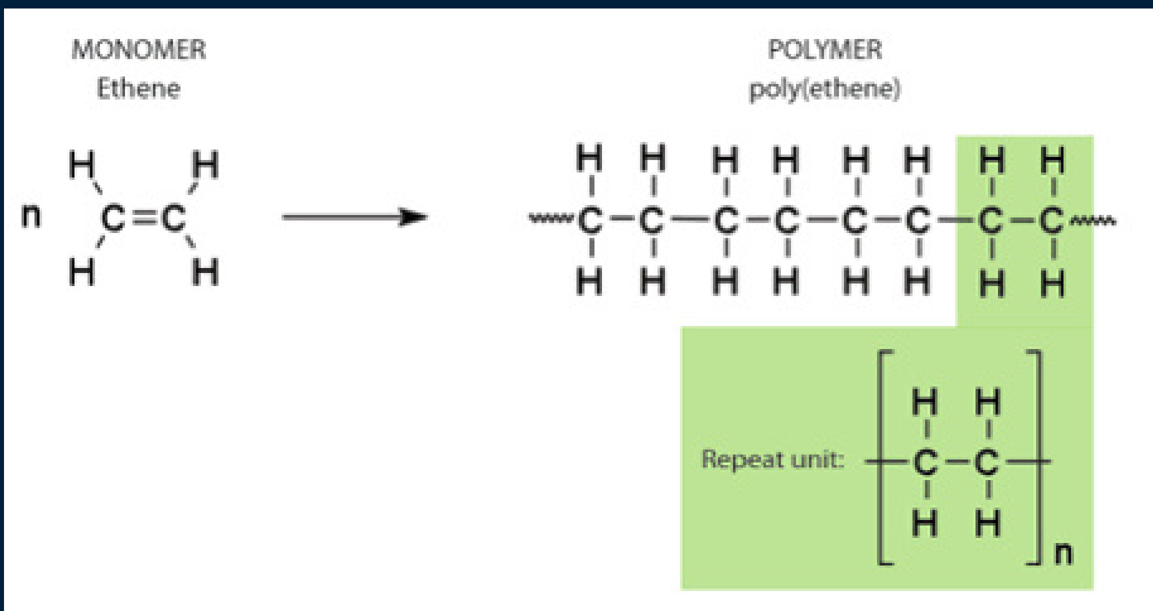
•Polymers are macromolecules formed by repeated linkage of large number of small molecules called monomers
•Most polymers are based on carbon and are therefore considered organic chemicals

03 | POLYMERIZATION

Polymerization is the chemical process in which small molecules called monomers combine to form a larger molecule, known as a polymer. This chemical process in which large numbers of monomers combine together by covalent bonds to form a polymer with or without the elimination of simple molecules like water, HCl, etc.

Key Characteristics:

- Polymerization typically requires an initiator or catalyst to begin the reaction.
- It can occur through different mechanisms, but all result in the linking of monomers into a larger, more complex polymer.



> Polymerization is the fundamental process that underlies the creation of many materials like plastics, fibers, and resins.

04 | PLASTIC

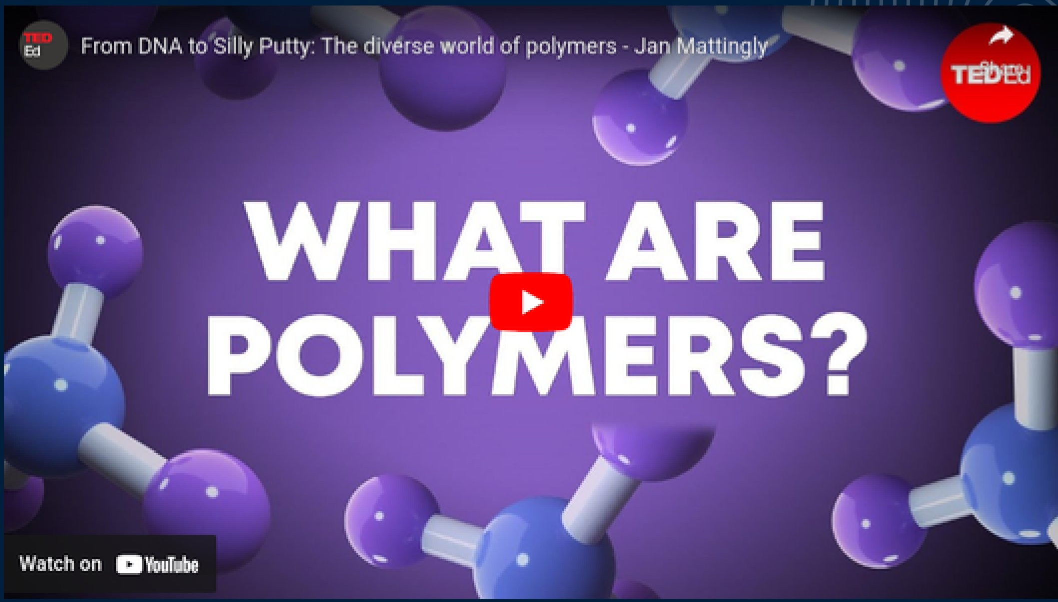
Plastic is a synthetic material made from polymers that can be molded, shaped, or formed into a wide variety of products when soft, and then set into a rigid or flexible form. Plastics are typically derived from petrochemicals such as oil and natural gas, although some are made from renewable materials like corn or sugarcane.

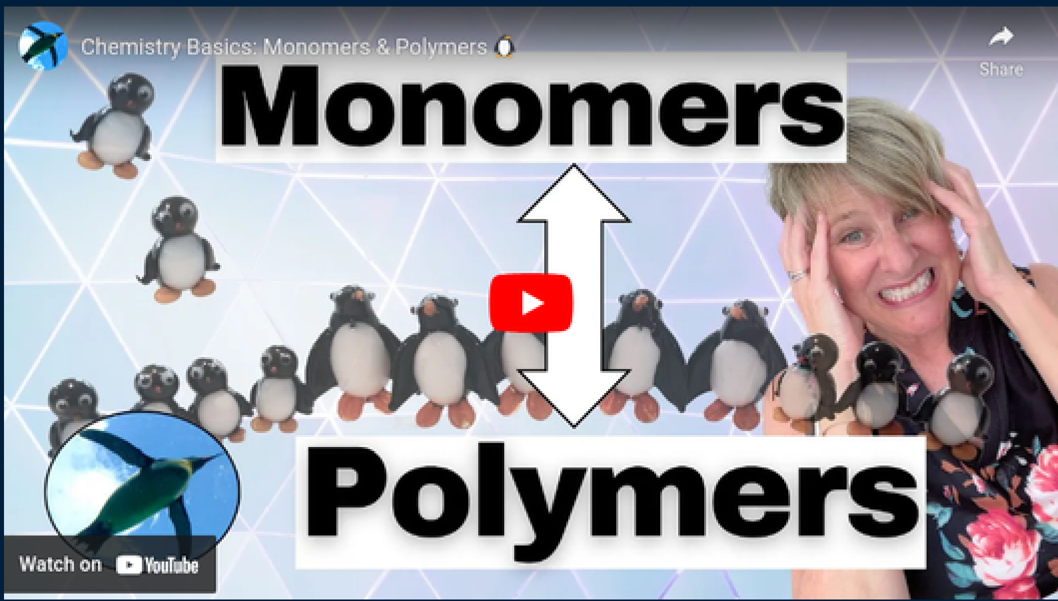
5

•Plastics in general are referred as polymers because they are made up of polymers.
•Plastic is widely used in different forms like bottles, bags, boxes, fibers, films etc.
•The term plastics is defined as a mixture (of a polymer with additives) that can be transformed by flowing or moulding in liquid or molten state.

> PLASTIC word is derived from two Greek words 'plastikos' and 'plastos' which means 'fit for moulding' and 'moulded

OVERVIEW OF POLYMER



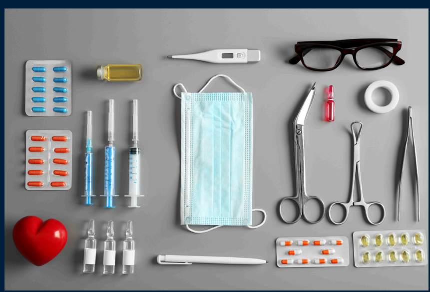


Application of Polymer

Polymers have a wide range of applications across various industries due to their versatility, durability, and adaptability. Here are some key applications of polymers:

PACKAGING

MEDICAL

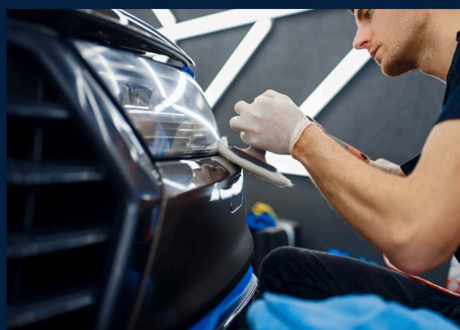


RECREATIONAL

TEXTILES

HOUSEWARES

TRANSPORTATION



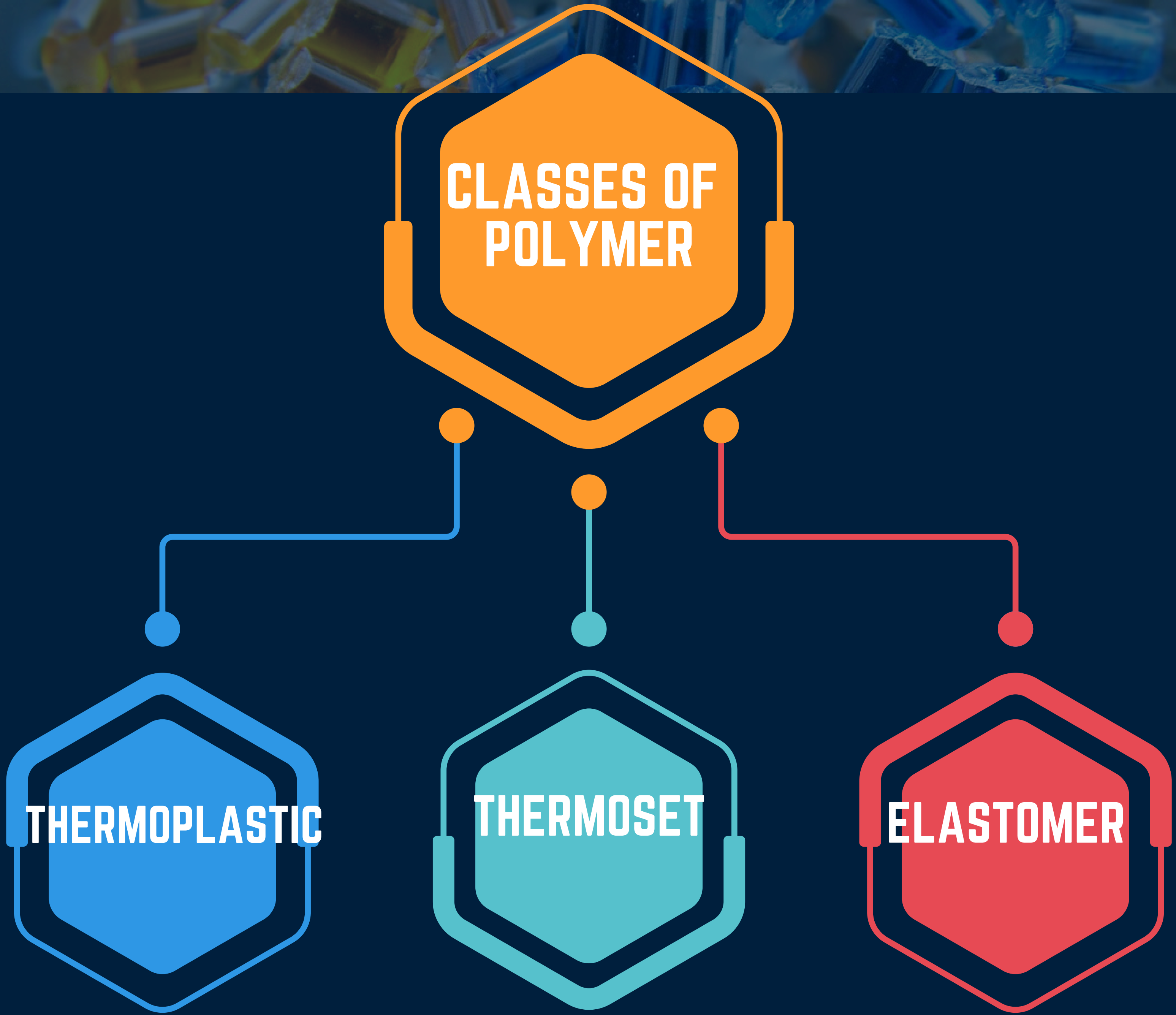
Exercise

Please answer ALL the question below:

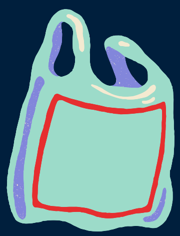
1. Explain the terms of monomer and polymer
2. Draw polymerization of polyethylene
3. Define plastics
4. State the usage of polymer in daily life
5. Identity type of polymer

2 Plastic Classification

Plastic Classification



Plastic Classification



THERMOPLASTIC

A polymer that can be melted and moulded into a shape that is retained when it is cooled

THERMOSET

A polymer that can be moulded when it is first prepared but, once it is cooled, (sometime called “curing”) hardens irreversibly and cannot be re-melted

ELASTOMER

RUBBER – LIKE SOLIDS
WITH **ELASTIC PROPERTIES**

THE POLYMER CHAINS ARE HELD TOGETHER BY THE **WEAKEST INTERMOLECULAR FORCES**

THESE WEAK BINDING FORCES PERMIT THE POLYMER TO BE **STRETCHED**

‘**CROSSLINKS**’ ARE INTRODUCED IN BETWEEN THE CHAINS, - HELP THE POLYMER TO **RETRACT** TO ITS ORIGINAL POSITION AFTER THE FORCE IS RELEASED

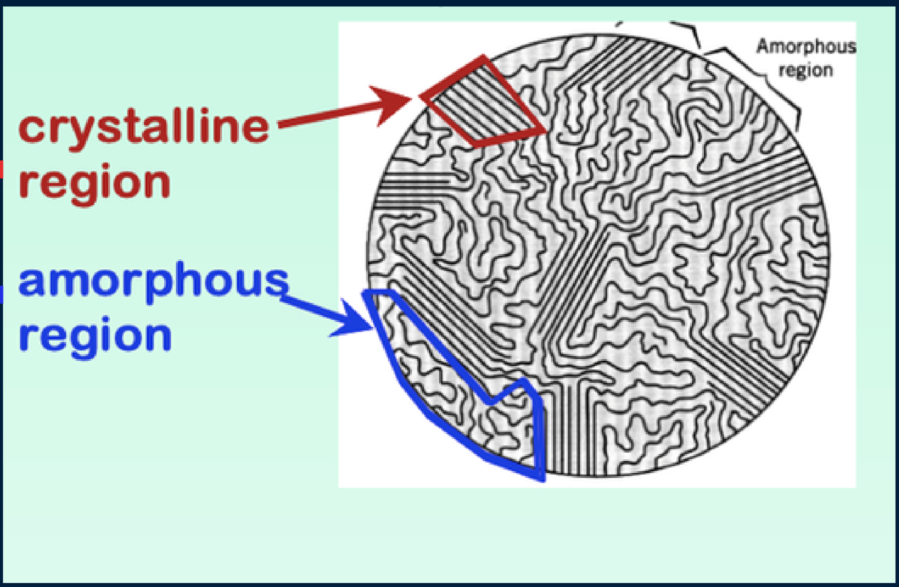
3

Structure of Polymer

Structure of Polymer

AMORPHOUS & CRYSTALLINE

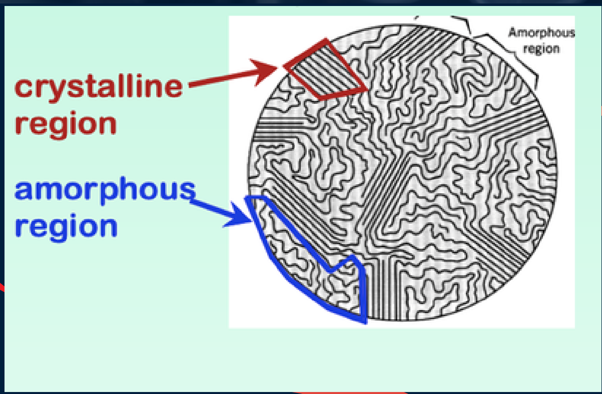
- THE POLYMER CHAINS ARE IN RANDOM ARRANGEMENT
- AMORPHOUS REGIONS PROVIDE **FLEXIBILITY** TO THE POLYMERIC MATERIAL.



CRYSTALLITE

- AN ORDERLY ARRANGEMENT OF MOLECULES. PROVIDE **STRENGTH** AND **HARDNESS**
- THE HIGHER THE CRYSTALLINITY, THE HARDER, STIFFER, AND LESS FLEXIBLE POLYMER
- DENSITY (CRYSTALLINE POLYMER) > DENSITY (AMORPHOS POLYMER)

Structure of Polymer



POLYMERS ARE SEMI-CRYSTALLINE MATERIALS

POLYMER HAVE BOTH AMORPHOUS AND CRYSTALLINE REGIONS.

POLYMERS HAVE REGIONS OF CRYSTALLINITY, CALLED CRYSTALLITES, EMBEDDED IN AMORPHOUS REGIONS

> Crystallites provide strength and hardness and the amorphous regions provide flexibility to the polymeric material

Structure of Polymer

HOMOPOLYMER & COPOLYMERS

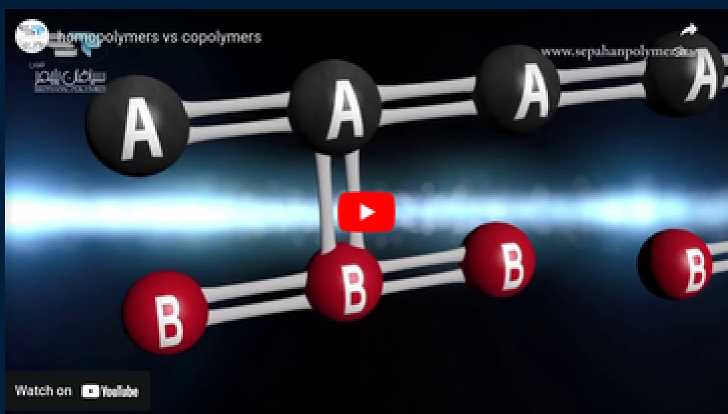
HOMOPOLYMER

THE POLYMERS CONSIST OF MONOMER OF IDENTICAL CHEMICAL STRUCTURE THEN THEY ARE CALLED HOMOPOLYMERS

COPOLYMER

MOLECULES WHICH ARE BUILT UP OF AT LEAST TWO DIFFERENT KINDS OF MONOMER ARE KNOWN AS CO-POLYMERS

TYPES OF COPOLYMERS



> Polymers can be homopolymer or copolymer when the number of monomers are one and two respectively

Structure of Polymer

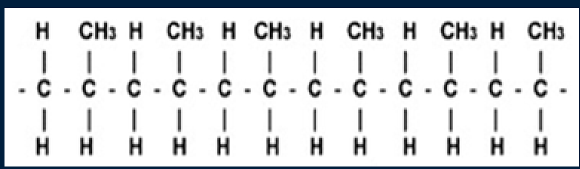
TACTICITY (STEREOISOMERISM)

THE ORIENTATION OF MONOMERIC UNITS OR FUNCTIONAL GROUPS IN A POLYMER MOLECULE CAN TAKE PLACE IN AN ORDERLY OR DISORDERLY MANNER WITH RESPECT TO THE MAIN CHAIN

ISOTACTIC POLYMER

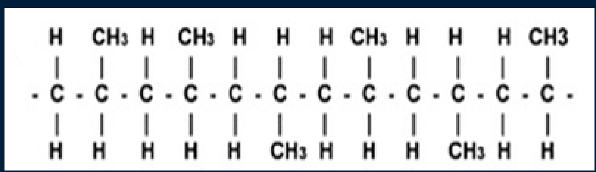
THE GROUPS ATTACHED TO THE CARBON ARE ARRANGED ON THE SAME SIDE OF THE MAIN CHAIN

HAS EXCELLENT MECHANICAL PROPERTIES



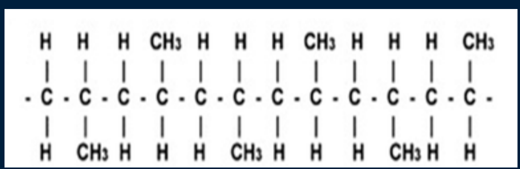
ATACTIC POLYMER

THE GROUPS ATTACHED TOP THE CARBON CHAIN ARE ARRANGED RANDOMLY



SYNDIOTACTIC POLYMER

GROUPS ATTACHED TO THE CARBON CHAIN ARE ARRANGED IN AN ALTERNATING SIDE OF THE MAIN CHAIN



> The difference in configuration (tacticity) do affect their physical properties.

Exercise

Please answer ALL the question below:

1. Explain the terms of homopolymer and copolymer
2. Draw all the tacticity of polypropylene
3. Define thermoplastics
4. State the usage of polymer in daily life
5. Identify classes of polymer

4 Polymerization

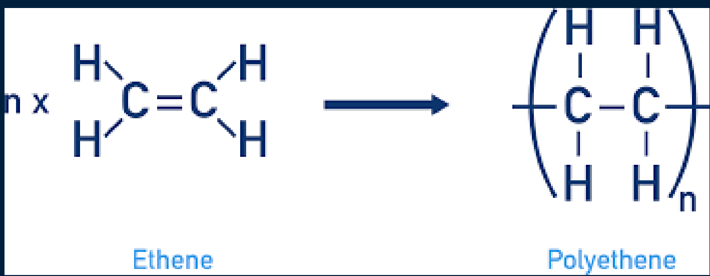
Polymerization

01 | DEFINITION

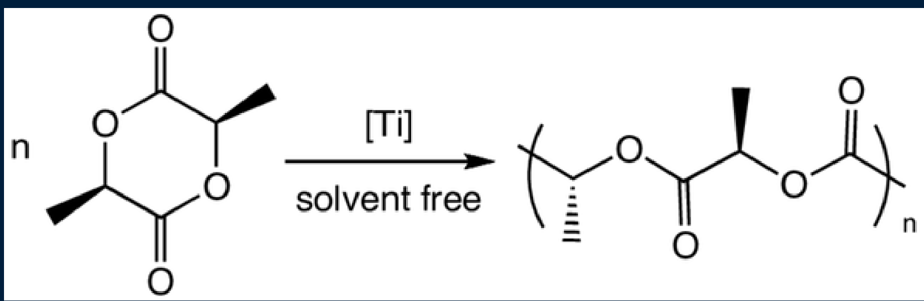
Polymerization is the process by which simple (monomer) molecules join together to form very large (polymer) molecules.

Three different way for polymerization :

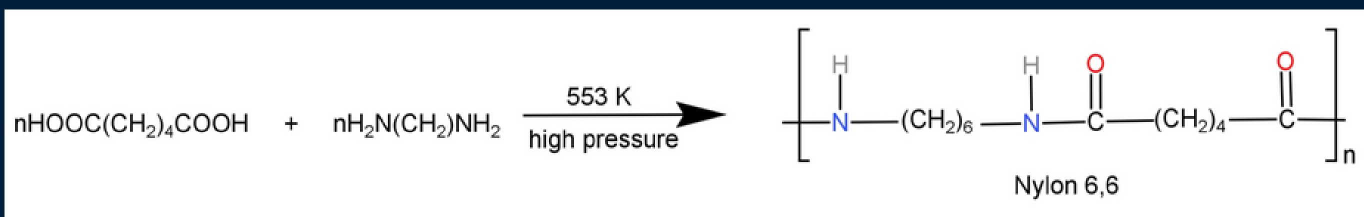
- **by opening a double bond**



- **by opening a ring**



- **by using molecules having two functional groups**



02 | TYPE OF POLYMERIZATION

Types of Polymerization

Addition Polymerization

MONOMERS WITH DOUBLE BONDS ARE JOINED TOGETHER BY COVALENT BONDS TO FORM A LARGE MOLECULE (POLYMER) WITHOUT THE LOST OF A SMALL MOLECULE

THE CARBON-CARBON DOUBLE BOND IN EACH MONOMER IS BROKEN OPEN AND REPLACED BY A CARBON-CARBON SINGLE BOND.

Condensation Polymerization

FORMED BY REPEATED CONDENSATION REACTION BETWEEN TWO DIFFERENT BI-FUNCTIONAL OR TRI-FUNCTIONAL MONOMERIC UNITS

THE ELIMINATION OF SMALL MOLECULES SUCH AS WATER, ALCOHOL, HYDROGEN CHLORIDE, ETC. TAKE PLACE

EXAMPLES: TERYLENE (DACRON), NYLON 6, 6, NYLON 6

> Polymerization is the fundamental process that underlies the creation of many materials like plastics, fibers, and resins. ”

03 | ADDITION POLYMERIZATION

1.0 INITIATION

INVOLVES THE FORMATION OF A FREE-RADICAL FROM A RADICAL INITIATOR SUCH AS BENZOYL PEROXIDES, HYDROGEN PEROXIDE

2.0 PROPAGATION

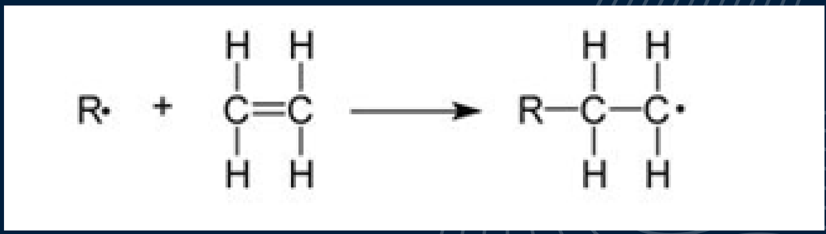
NEW FREE RADICAL NOW ADDS TO ANOTHER MOLECULE OF MONOMER TO FORM ANOTHER NEW FREE RADICAL UNTIL A LARGE FREE RADICAL IS FORMED

3.0 TERMINATION

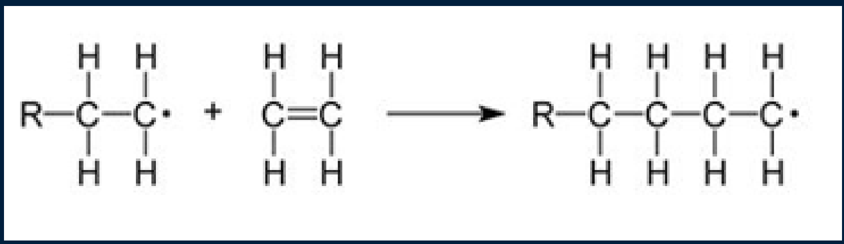
TERMINATION OF CHAINS USUALLY OCCURS BY RADICAL COUPLING OR DISPROPORTIONATION REACTIONS

04 | ADDITION POLYMERIZATION OF POLYETHYLENE

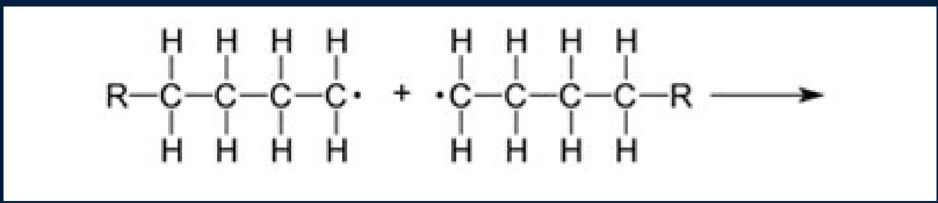
INITIATION STEP

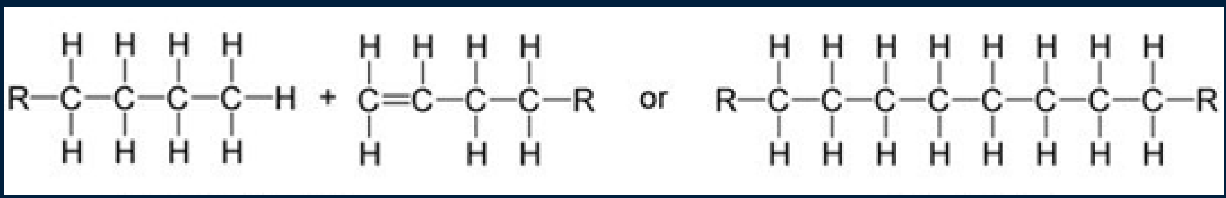


PROPAGATION STEP



TERMINATION STEP





DISPROPORTIONATION

COMBINATION

04 | COMPARISON ADDITION VS CONDENSATION POLYMERIZATION

	ADDITION POLYMERIZATION	CONDENSATION POLYMERIZATION
POLYMER GROWTH MECHANISM	CHAIN REACTION	STEP BY STEP REACTION
INITIATOR NEEDED	YES	NO
TYPE OF MONOMER	CARBON-CARBPN DOUBLE BOND	REACTING BIFUNCTIONAL GROUPS ON THE ENDS
BY PRODUCT FORM	NO	YES
POLYMER CHAIN CHARACTERISTICS	A FEW, LONG CHAINS	MANY NOT VERY LONG CHAINS
BRANCHING	POSSIBLE	UNLIKELY

5 Calculation

Calculation

DEGREE OF POLYMERIZATION

The degree of polymerization (DP) is defined as the average number of repeating units (monomers) in a polymer chain. It provides a measure of the size of the polymer and is an important factor in determining its properties, such as strength, viscosity, and thermal behavior.

Formula
The degree of polymerization can be calculated using the following formula:

$$DP = \frac{M_w}{M_m}$$

DP = degree of polymerization
Mw = Molecular weight of the polymer
Mm = Molecular weight of the monomer

Significance

- **Influence on Properties: A higher degree of polymerization generally leads to increased molecular weight, which can enhance the physical properties of the polymer, such as tensile strength and melting point.**
- **Structure-Property Relationships: Understanding the DP helps predict how a polymer will behave in different applications and processing conditions.**
- **Control of Polymerization: In industrial processes, controlling the degree of polymerization is crucial for producing polymers with desired characteristics.**

In summary, the degree of polymerization is a key concept in polymer science, as it directly relates to the size and properties of the polymer material.

Calculation

EXAMPLE 1

Calculate the molecular weight of the polythene polymer given DP is 100.
(CH2 – CH2)n polyethylene here 'n' is the DP.

Molecular weight of the polyethylene
= DP X Molecular weight of polyethylene

Molecular weight of ethylene CH2 – CH2
= (12 g/mol x 2) + (1 g/mol x 4)
= 28 g/mol
= 100 X 28
= 2800 g/mol

EXAMPLE 2

1.A high-molecular-weight polyethylene has an average molecular weight of 410,000 g/mol. What is its average degree of polymerization?

Molecular weight of the polyethylene
= DP X Molecular weight of polyethylene

Molecular weight of ethylene CH2 – CH2
= (12 g/mol x 2) + (1 g/mol x 4)
= 28 g/mol
= 410 000 / 28
= 14 642.86 g/mol

Exercise

Please answer ALL the question below:

1. A nylon 6,6 has an average molecular weight of 12,000 g/mol. Calculate the average degree of polymerization. M.W. (mer) = 226 g/mol
2. An injection molding polycarbonate material has an average molecular weight of 25,000 g/mol. Calculate its degree of polymerization. M.W. (mer) = 254 g/mol
3. If a particular type of polyethylene (CH_2 – CH_2)nhas a molecular mass of 150000, what is its degree of polymerization.
4. If a type of polyethylene has an average degree of polymerization of 10,000, what is its average molecular weight?
5. An ABS copolymer consists of 25 wt% polyacrylonitrile, 30 wt% polybutadiene and 45 wt % polystyrene. Calculate the mole fraction of each component in this material.

Calculation

NUMBER AVERAGE MOLECULAR WEIGHT

The average molecular weight of a polymer is a measure of the mass of the polymer chains, calculated as the average of the molecular weights of the individual chains in a sample. Since polymers are typically composed of chains of varying lengths, their molecular weight can vary significantly.

Formula

$$Mn = \Sigma\, xi\, Mi$$

Mn = number molecular weight of the polymer

xi = fraction of the total number of chains within each range

Mi = mean molecular weight of each size range of polymer chains

Importance:

- **The average molecular weight helps in understanding the properties of the polymer, such as its viscosity, mechanical strength, and thermal behavior.**
- **It is critical for processing and application, as it influences factors like solubility and the ability to form films or fibers.**

Calculation

WEIGHT AVERAGE MOLECULAR WEIGHT

The weight molecular weight of a polymer is calculated by giving more weight to larger chains, which provides a better representation of the polymer's behavior in bulk.

Formula
Mn = Σ xi Mi

$$\bar{M}_m = \frac{\sum f_i M_i}{\sum f_i}$$

Mm = weight molecular weight of the polymer
fi = weight fraction of the polymer chains
Mi = mean molecular weight of each size range of polymer chains

Polymers often have a broad distribution of chain lengths, which is why both number average and weight average molecular weights are important for characterizing a polymer sample.

In summary, the average molecular weight is a crucial parameter in polymer science, helping to define the material's properties and guide its applications.

Calculation

EXAMPLE 1

Calculate the weight average molecular weight for a thermoplastic material that has the mean molecular weight fractions fi for the molecular weight ranges listed in the following table:

Molecular Weight Range, g/mol	**Molecular Weight Fractions, *fi***
5 000 - 10 000	**0.13**
10 000 – 15 000	**0.15**
15 000 – 20 000	**0.23**
20 000 – 25 000	0.22
25 000 – 30 000	0.16
30 000 – 35 000	0.11

Calculation

SOLUTION

Molecular weight range, g/mol	**Molecular weight fractions, *fi***	**Mi**	**fiMi**
5 000 - 10 000	0.13	7500	975
10 000 – 15 000	0.15	12 500	1875
15 000 – 20 000	0.23	17 500	4025
20 000 – 25 000	0.22	22 500	4950
25 000 – 30 000	0.16	27 500	4400
30 000 – 35 000	0.11	32 500	3575
	1.00		19 800

Weight average molecular weight, M = 19 800/1.00
= 19 800 g/mol

Calculation

EXAMPLE 2

Laboratory synthesis of poly (methyl methacrylate) homopolymer generated the following polymerization data

Molecular Weight Range (g/mol)	Weight Fraction, fi	Number Fraction, Xi
8000 – 20,000	**0.02**	**0.05**
20,000 – 32,000	**0.08**	**0.15**
32,000 – 44,000	**0.17**	**0.21**
44,000 – 56,000	**0.29**	**0.28**
56,000 – 68,000	0.23	0.18
68,000 – 80,000	0.16	0.10
80,000 – 92,000	0.05	0.03

SOLUTION

Molecular weight range (g/mol)	Weight fraction, fi	Number fraction, Xi	Mean of molecular weight, Mi	XiMi	fiMi
8000 – 20,000	0.02	0.05	14,000	700	280
20,000 – 32,000	0.08	0.15	26,000	3,900	2,080
32,000 – 44,000	0.17	0.21	38,000	7,980	6,460
44,000 – 56,000	0.29	0.28	50,000	14,000	14,500
56,000 – 68,000	0.23	0.18	62,000	11,160	14,260
68,000 – 80,000	0.16	0.10	74,000	7,400	11,840
80,000 – 92,000	0.05	0.03	86,000	2,580	4,300
	1.00			47,720	53,720

i) The number – average molecular weight = 47,720 g/mol

ii) The weight - average molecular weight = 53,720 g/mol

iii) The number average and weight average degree of polymerization

Molecular weight of PMMA (C5O2H8)n =
(5 C atoms x 12 g/mol) + (2 O atoms x 16 g/mol) + (8 H atoms x 1 g/mol) =
100 g/mol

Number average degree of polymerization = 47,720 / 100 = 477.2
Weight average degree of polymerization = 53,720 / 100 = 537.20

6

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