

Polymer Chemistry (Chem 3121)

Debre markos university

Chapter one: Synthesis of polymer

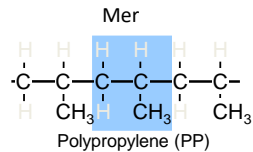
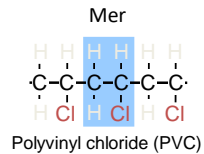
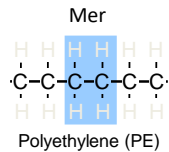
1. Introduction
 - 1.1 Classification of polymer
2. Synthesis of Polymers
 - 2.1. Types of polymerization
 - 2.2. Condensation Polymerization
 - 2.3. Addition Polymerization
 - 2.3.1. Free radical polymerization
 - 2.3.2. Ionic Polymerization
 - 2.3.3. Coordination Polymerization
 - 2.3.4. Ring opening polymerization

Chapter one: Synthesis of polymer

1. Introduction

- What is a polymer?
- Polymers are substances whose molecules have high molar masses and are composed of a large number of repeating units, called monomer.

Poly mer
many repeat unit



3

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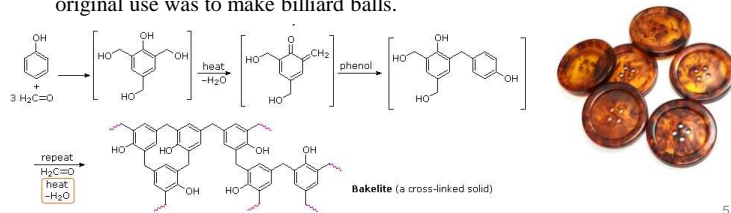
- They are naturally occurring and synthetic polymers.
- Naturally occurring polymers are proteins, starches, cellulose, and latex....etc.
- Synthetic polymers are formed by chemical reactions.
- Polymers are generally classified as natural and synthetic and partitioning rubber at the middle.
- Natural polymers are found in many forms such as horns of animals, tortoise shell, shellac (from the *lac* beetle), rosin (from pine trees), asphalt, and tar from distillation of organic materials.
- One of the most useful of the natural polymers was rubber, obtained from the sap of the *hevea* tree.



4

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- Natural rubber had only limited use as it became brittle in the cold and melted when warmed.
- In 1839, Charles Goodyear discovered, through a lucky accident, that by heating the latex with sulfur, the properties were changed making the rubber more flexible and temperature stable. That process became known as **vulcanization**.
- The first **synthetic polymer**, a phenol-formaldehyde polymer, was introduced under the name "Bakelite", by Leo Baekeland in 1909. Its original use was to make billiard balls.



Cont...

- Rayon, the first synthetic fiber was developed as a replacement for silk in 1911. Today, polymers are commonly used in thousands of products as plastics, elastomers, coatings, and adhesives.
- They make up about 80% of the organic chemical industry with products produced at approximately 150 kg of polymers per person annually in the United States.

➤ Polymer Composition

- Most polymers are hydrocarbons
 - i.e. made up of H and C
- How ever there are also some polymer which contains nitrogen, oxygen and sulfur

6

1.1 Classification of Polymers

- **Nature of Repeat Units**
 - **Structural Characteristics**
 - **Stereochemistry**
 - **Molecular (Functional Group) Classification**
 - **Trade names**
 - **Physical properties**
 - **End Uses**
 - **Polymerisation Process (Chain or Step Growth)**
- All highlight certain aspect or property of the polymer.

7

Nature of Repeat Units

Homopolymer- A-A-A-A-A-A-A-A-A-A-
(identical repeat units)

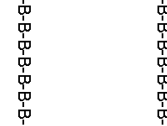
Copolymer - Different repeat units

Alternating Copolymer- A-B-A-B-A-B-A-B-A-B

Block Copolymer - AAAAAAAAA-BBBBBBBBB

Random Copolymer- AA-B-A-B-B-A-A-A-B-B-A

Graft Copolymer- -A-A-A-A-A-A-A-A-A-A-A-A-A-A-

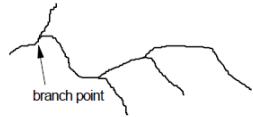


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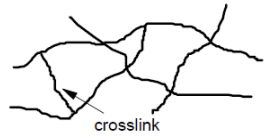
Structural characteristics-closely related to materials properties



linear (uninterrupted straight chain)



branched (occasional branches off longer chain)

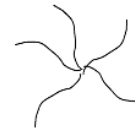


networked (many interconnected linear chains; one giant molecule)

9

Structural characteristics

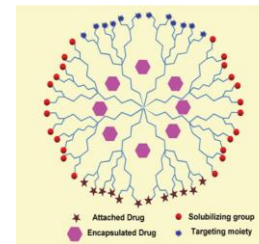
Dendrimers polymer



Combed polymers



Star Polymers

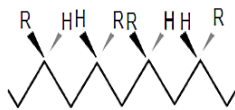


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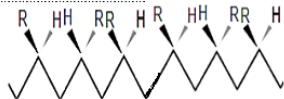
Stereochemistry of Linkages



ISOTACTIC – R groups on same side of backbone



SYNDIOTACTIC – R groups on alternating sides of backbone



ATACTIC — Random (most common)

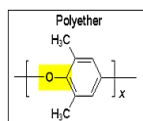
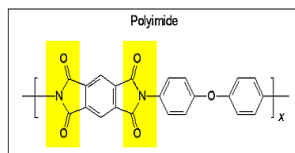
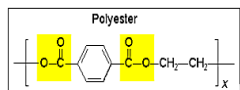
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Molecular (Functional Group) Classification

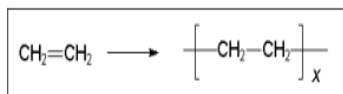
- Polymers are conveniently represented by the repeating chain formula, which shows the arrangement of bonds and atoms.
- The repeat units contain functional groups that describe the polymer.
- This terminology emphasizes the functional groups involved in the synthesis of the polymer from its monomers, although the usage is seldom exact.

12

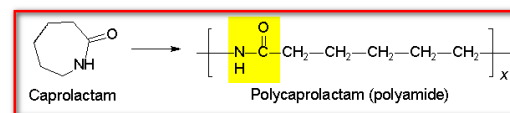
Examples



A polymer is often named according to the monomer that was used to form it. This is why the polymer consisting of only a long chain of CH₂ groups is called *polyethylene*, not *polymethylene*.



13

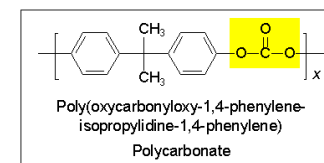
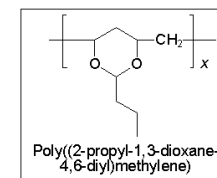


A polyamide containing 6 carbons is known as polycaprolactam.

Of course, there are systematic rules for polymer nomenclature set forth by the IUPAC, but for polymers with any complexity, the names are too cumbersome for common usage. IUPAC Polymer Nomenclature: see examples

• *Pure Appl. Chem.* **1976**, *48*, 373.

• *Macromolecules* **1973**, *6*, 149

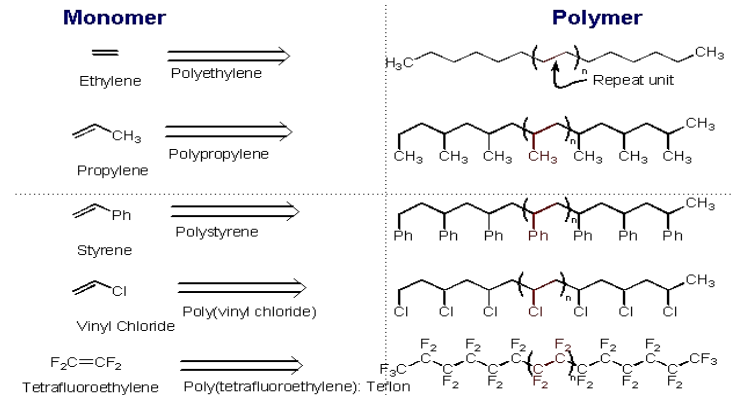


14

Polymer Families

- Polyolefins: made from olefin (alkene) monomers
- Polyesters, Amides, Urethanes, etc.: monomers linked by ester, amide, urethane or other functional groups
- Natural Polymers: Polysaccharides, DNA, proteins

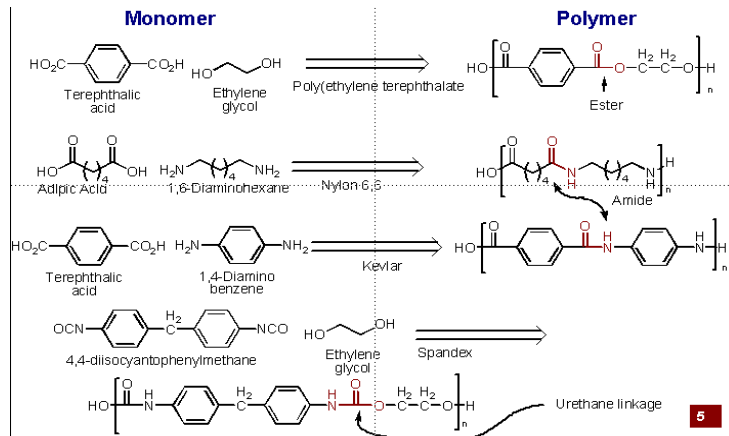
Common Polyolefins



15

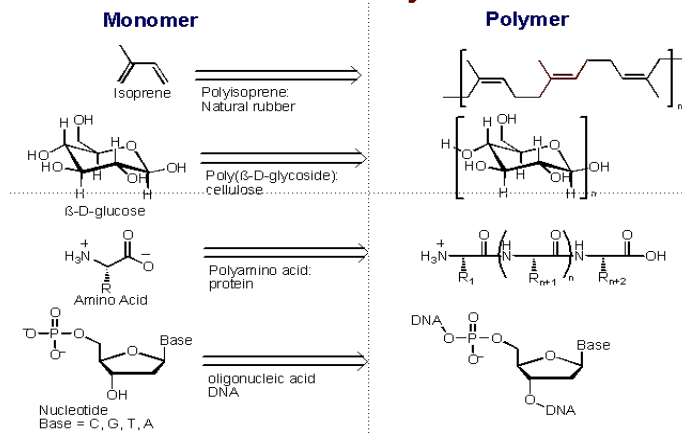
16

Polyesters, Amides, and Urethanes



17

Natural Polymers



18

Slang and Trade Names

The two polymers named by the IUPAC systematic rules above are good examples. **Poly((2-propyl-1,3-dioxane-4,6-diyl)methylene)** is known as "**polyvinylbutyral**," probably because it is synthesized for poly(vinyl alcohol) and butyraldehyde.

Poly(oxycarbonyloxy-1,4-phenylene-isopropylidene-1,4-phenylene) is an even worse case. Because it contains the carbonate linkage (highlighted), it is a kind of polycarbonate, for which there are infinite possible variations. However, because it is by far the most common commercial polymer of its kind, the term "**polycarbonate**" has come to refer to this particular member of the polycarbonate family.

19

Trade Names

Trade names were invented by marketing people in industry, who did not care about chemistry but wanted to have short, snappy-sounding names that could be easily remembered.

Butvar (TMMonsanto)----- polyvinyl butyral (PVB) resin

Dacron (TMDuPont)----- polyethylene terephthalate, polyester

Lexan (TM General Electric)--polycarbonate

Nylon 6 (TM DuPont)-----polycaprolactam

Noryl (TM General Electric)—polyphenylene ether

Kapton (TM DuPont)-----polyimide

Dowlex (TM Dow)-----polyethylene resin

Rayon (Viscose, Artificial Silk), Terylene, Plexiglass (perspex),
Celluloid,

20

Compositional Features (Nature of repeat Units)

Taking a slightly coarser view, one can classify the chain by the number of different repeat units and their sequence (i.e., homopolymer and copolymer).

Chain Architecture Features (Structural characteristics)

Again looking at the chains in decreasing detail, there is an infinite variety of chain architectures (i.e., linear, branched, crosslinked).

21

Physical Property Classifications

Looking at polymers as materials rather than from a chemical point of view, several classifications are widely used. -**Temperature**

- 1) **Thermoplastics** (plastics) — linear, or branched architecture can be melted and reformed on heating. Soluble in organic solvents
 - a) **Amorphous**—no ordered structure-soften over a relatively wide temperature range (always lower than T_m) known as the glass transition (T_g). Above these temperatures, polymers are liquids
Eg. polystyrene and poly(methyl methacrylate).
 - b) **Semi-crystalline**—composed of microscopic crystallites—domains of crystalline structure. Can be ordered.
Semicrystalline polymers have true melting temperatures (T_m) at which the ordered regions break up and become disordered.
Eg: polyethylene. **Fibers** (nylon, PET polyester)

22

2) **Thermosets**—(resins)—massively cross-linked

very rigid; degrade on heating. Insoluble in solvents. Usually synthesised in mold, then shaped by machining (grinding, drilling). E.g (tires, rubberbands)

Physical property

3) **Elastomers** (rubbers) — moderately cross-linked

can be stretched and rapidly recover their original dimension

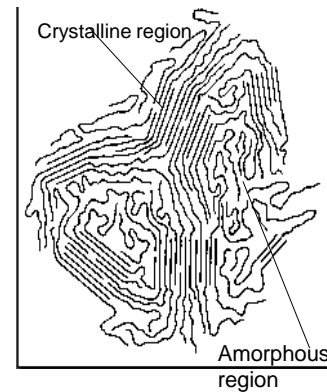
Structure

4) **Thermoplastic elastomers**: Elastic polymers that can be melted (soles of tennis shoes)

5) **Dendrimers**—multiply branched—multiple consecutive (regular) branches.

23

Morphology-Crystalline & Amorphous Polymers



In polymers, the degree of crystallinity ranges:

- from 0% (amorphous glasses)
- to >90% (highly crystalline)

and is affected by:

- structure
- temperature
- molecular weight
- stereochemistry
- processing conditions

A few special polymers show intermediate phases. Such materials are *liquid crystals*, *Liquid-crystalline Polymers*, R. A. Weiss and C. K. Ober, eds.; ACS Symposium Series No. 435, 1990.

• *Side-chain Liquid Crystalline Polymers*, C. B. McArdle, ed.; Blackie, 1989.

24

Thermoplastics & Thermosetting polymers

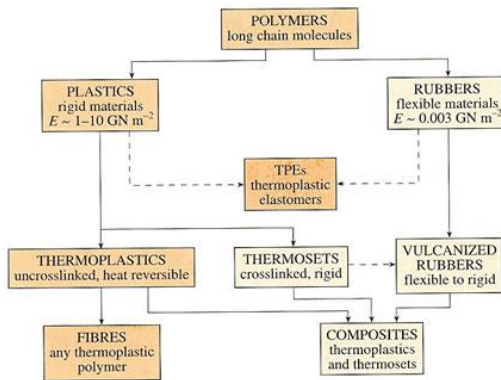
- **Thermoplastics** polymers: soften when heated and harden when cooled and vice versa
- **Structure Example:** linear, branched:
- Polyethylene, polystyrene, PVC, Poly (ethylene terephthalate)
- **Thermosetting** polymers: permanently hard (do not soften when heated)
- Made from network polymers: covalent bond resist motion at high temperature prevent.
- Epoxies, phenolics, and some polyester resins.

Range of Polymers

- Traditionally, the industry has produced two main types of synthetic polymer – plastics and rubbers.
- Plastics are (generally) rigid materials at service temperatures
- Rubbers are flexible, low modulus materials which exhibit long-range elasticity.

Range of Polymers

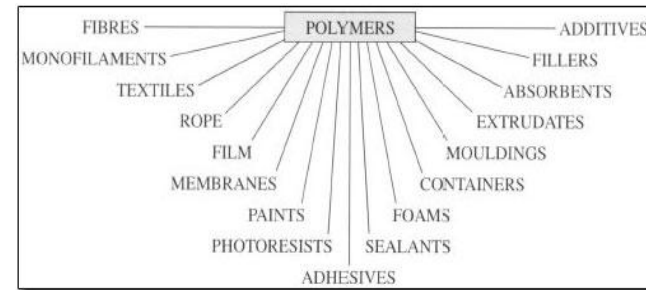
- Plastics are further subdivided into thermoplastics and thermosets



27

Range of Polymers

- Another way of classifying polymers is in terms of their form or function



28

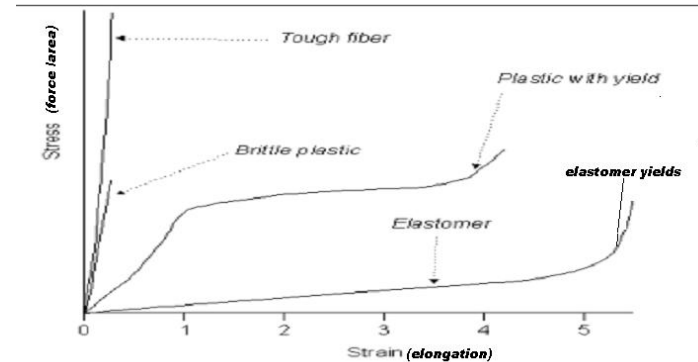
End Use

Rubbers:-have long range elasticity
 low molecular cohesion
 tensile strength 300-1000 psi (lbs/sq inch)

Plastics:- stronger than rubbers
 tensile strength 4000-13000 psi (lbs/sq inch)
 types -hard and stiff or soft and flexible

Fibres: Strongest of the three types of polymer
 tensile strength 20000-150000 psi (lbs/sq inch)

Tensile testing-produce distinctive shapes for different physical classes of polymers



Area under curve a measure of the energy required to make the sample fail. Note plastics are intermediate in properties to fibres and elastomers

Learning Outcome

1. Assign within a polymer family based on functional group (polyolefin, polyester, polyamide etc) and -polymerization process used (addition or step)
2. Assign the stereochemistry of a polymer structure –(Atactic, Isotactic etc)
3. Assign compositional features- homo, copolymer etc
4. Assign chain architecture- linear, branched, dendrimer
5. Identify some trade names in regard to polymer families or common names
6. Identify chain structure to its physical properties (amorphous, crystalline) and end uses (fibre, rubber etc)

2. Synthesis of polymer /Type of polymerization /

- Synthetic polymers are produced commercially on a very large scale and have a wide range of properties and uses. The materials commonly called plastics are all synthetic polymers.
- Synthetic polymers are formed by chemical reactions and hence polymers can be classified by the characteristics of the reactions by which they are formed.
- If all atoms in the monomers are incorporated into the polymer, the polymer is called an *addition polymer*(see table 1) , and the processes is called addition polymerization.
- If some of the atoms of the monomers are released into small molecules, such as water, the polymer is called a *condensation polymer* (see table 2), and the processes is called condensation polymerization.

Table1 of common addition polymer



Polymer name	Monomer(s)	Polymer	Use
Polyethylene	$\text{CH}_2=\text{CH}_2$ (ethene)	$-\text{CH}_2-\text{CH}_2-$	Most common polymer. Used in bags, wire insulation, and squeeze bottles
Polypropylene	$\text{CH}_2=\text{CH}$ $\quad $ CH_3 (1-propene)	$-\text{CH}_2-\text{CH}-$ $\quad $ CH_3	Fibers, indoor-outdoor carpets, bottles
Polystyrene	$\text{CH}_2=\text{CH}$ $\quad $  (styrene)	$-\text{CH}_2-\text{CH}-$ $\quad $ 	Styrofoam, molded objects such as tableware (forks, knives and spoons), trays, videocassette cases.
Poly(vinyl chloride) (PVC)	$\text{CH}_2=\text{CH}$ $\quad $ Cl (vinyl chloride)	$-\text{CH}_2-\text{CH}-$ $\quad $ Cl	Clear food wrap, bottles, floor covering, synthetic leather, water and drain pipe
Polytetrafluoroethylene (Teflon)	$\text{CF}_2=\text{CF}_2$ (tetrafluoroethene)	$-\text{CF}_2-\text{CF}_2-$	Nonstick surfaces, plumbing tape, chemical resistant containers and films
Poly(methyl methacrylate) (Lucite, Plexiglas)	CO_2CH_3 $\quad $ $\text{CH}_2=\text{C}$ $\quad $ CH_3 (methyl methacrylate)	CO_2CH_3 $\quad $ $-\text{CH}_2-\text{C}-$ $\quad $ CH_3	Glass replacement, paints, and household products

Table1 of common addition polymer



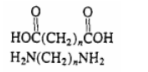
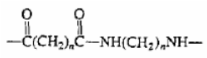
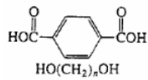
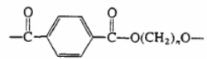
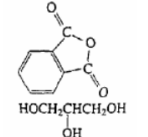
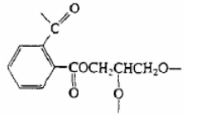
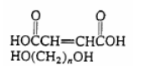
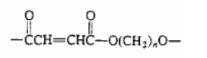
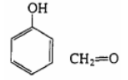
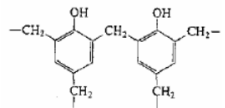
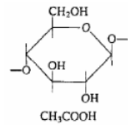
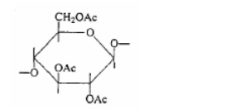
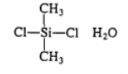
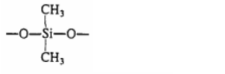
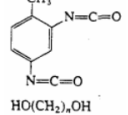
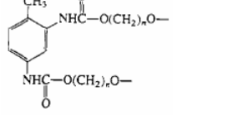
Polyacrylonitrile (Acrilan, Orlon, Creslan)	$\text{CH}_2=\text{CH}$ $\quad $ CN (acrylonitrile)	$-\text{CH}_2-\text{CH}-$ $\quad $ CN	Fibers used in knit shirts, sweaters, blankets, and carpets
Poly(vinyl acetate) (PVA)	$\text{CH}_2=\text{CH}$ $\quad $ OOCCH_3 (vinyl acetate)	$-\text{CH}_2-\text{CH}-$ $\quad $ OOCCH_3	Adhesives (Elmer's glue), paints, textile coatings, and chewing gum
Natural rubber	CH_3 $\quad $ $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$ (2-methyl-1,3-butadiene)	CH_3 $\quad $ $-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2-$	Rubber bands, gloves, tires, conveyor belts, and household materials
Polychloroprene (neoprene rubber)	Cl $\quad $ $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$ (2-methyl-1,3-butadiene)	Cl $\quad $ $-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2-$	Oil and gasoline resistant rubber
Styrene butadiene rubber (SBR)	$\text{CH}_2=\text{CH}$ $\quad $  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	$-\text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_2-$ $\quad $ 	Non-bounce rubber used in tires

Table2 of common condensation polymer

Polymer name	Monomers	Polymer	Use
Polyamides (nylon)	 $\text{HOC}(\text{CH}_2)_n\text{COH}$ $\text{H}_2\text{N}(\text{CH}_2)_m\text{NH}_2$	 $-\text{C}(\text{CH}_2)_n\text{C}-\text{NH}(\text{CH}_2)_m\text{NH}-$	Fibers, molded objects
Polyesters (Dacron, Mylar, Fortrel)	 $\text{HOC}-\text{C}_6\text{H}_4-\text{COOH}$ $\text{HO}(\text{CH}_2)_2\text{OH}$	 $-\text{C}(\text{C}_6\text{H}_4)-\text{C}-\text{O}(\text{CH}_2)_2\text{O}-$	Linear polyesters, fibers, recording tape
Polyesters (Glyptal resin)	 $\text{HOCH}_2\text{CH}_2\text{OH}$	 $-\text{COCH}_2\text{CH}_2\text{O}-$	Cross-linked polyester, paints
Polyesters (Casting resin)	 $\text{HOCCH}=\text{CHCOH}$ $\text{HO}(\text{CH}_2)_2\text{OH}$	 $-\text{CCH}=\text{CHC}-\text{O}(\text{CH}_2)_2\text{O}-$	Cross-linked with styrene and benzoyl peroxide, fiberglass boat resin, casting resin

35

Table2 of common condensation polymer

Phenol-formaldehyde (Bakelite)	 $\text{C}_6\text{H}_5\text{OH}$ $\text{CH}_2=\text{O}$		Mixed with fillers, molded electrical cases, adhesives, laminates, varnishes
Cellulose acetate (cellulose is a polymer of glucose)	 $\text{C}_6\text{H}_{10}\text{O}_5$ CH_3COOH		Photographic film
Silicones	 $\text{Cl}-\text{Si}(\text{CH}_3)_2-\text{Cl}$ H_2O		Water-repellent coatings, temperature-resistant fluids and rubber
Polyurethanes	 $\text{N}=\text{C}=\text{O}$ $\text{HO}(\text{CH}_2)_n\text{OH}$		Foams, rigid and flexible, fibers

36

Cont...

- molecular weight (MW). By definition,
- $MW(\text{Polymer}) = DP \times MW(\text{Repeat Unit})$
- the number of repeating units strung together in the polymer chain (molecule). This is known as the degree of polymerization (DP).
- It specifies the length of the polymer molecule.

Example

- Polystyrene, with a degree of polymerization of 7, is a viscous liquid (not of much use), whereas commercial grade polystyrene is a solid and the DP is typically in excess of 1000. It must be emphasized, however, that no clear demarcation has been established between the sizes of oligomers and polymers.

Example 2

- What is the molecular weight of polypropylene (PP), with a degree of polymerization of 3×10^4 ?

Solution: $(MW_{\text{Structure of the repeating unit for PP}}) \times DP =$

- Polydispersity is also another property of polymer

$$\text{Polydispersity} = \frac{\overline{M}_w}{\overline{M}_n}$$

- That is, this ratio is (>1) a measure of polydispersity, and consequently it is often referred to as the heterogeneity index.

Example 3:

- Nylon 11 has the following structure
- If the number-average degree of polymerization, X_n , for nylon is 100 and $M_w = 120,000$, what is its polydispersity?

Methods of Polymers Synthesis

- There are a number different methods of preparing polymers from suitable monomers, these are
 - Chain-growth (or addition) polymerization
 - Step-growth (or condensation) polymerization
 - insertion polymerization.

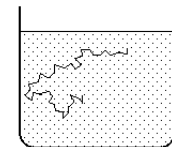
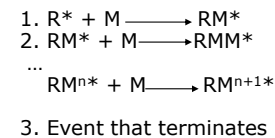
39

Polymerization process

Chain (addition)

Monomer decreases throughout reaction,

- In chain growth, a monomer is activated and polymerization propagates by activating neighboring monomers. The process is rapid & high MW polymers are achieved quickly.
- The following describes the chain growth reaction in which * represents the activated monomer M. This can be a free radical, negative charge, or positive charge:



chain growth

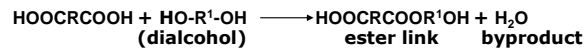
Step (condensation)

Monomer consumed early in reaction

- In step growth, bifunctional monomers are added systematically to form covalent bonds. It generally involves 2 (or more) functional groups: "a" and "b." Molecular weight increases "slowly" as dimers become trimers, which in turn become tetramers.
- Examples of polymers formed by step growth: nylons, polyesters, polypeptides (proteins)

$a + b \longrightarrow c + d$ where; $c =$ covalent link, $d =$ byproduct

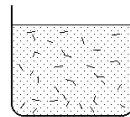
- 1. $a-a + b-b \longrightarrow a-c-b + d$



- 2. $a-c-b + a-a \longrightarrow a-c-c-a$

- 3. $a-c-c-a + b-c \longrightarrow a-c-c-a$ $a(c)_6a + d$

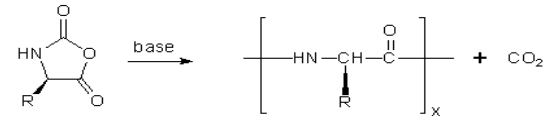
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step growth

Exceptions

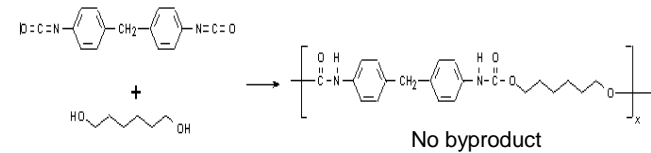
Chain (addition)



No initiator-initiator & monomer the same

No termination step

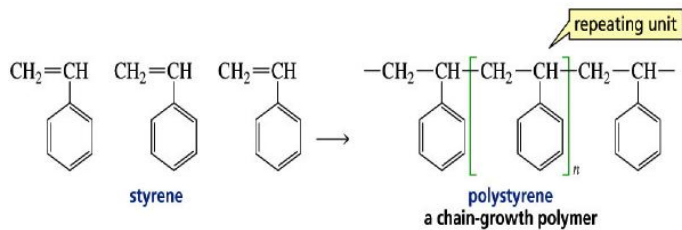
Step (condensation)



No byproduct

2.1 Types of Polymerization

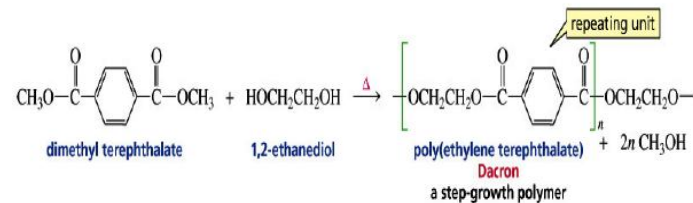
- Chain-growth polymers, also known as addition polymers, are made by chain reactions.
- There are different types of addition polymerization; Free-radical chain polymerization, Ionic Polymerization, Coordination Polymerization, and Ring opening polymerization are some.



43

Types of Polymerization

- Step-growth polymers, also called condensation polymers, are made by combining two molecules by removing a small molecule



Addition Vs. Condensation Polymerization

- polymerization reactions can generally be written as

$$x\text{-mer} + y\text{-mer} \longrightarrow (x+y)\text{-mer}$$
- In a reaction that leads to **condensation polymers**, x and y may assume any value
- i.e. chains of any size may react together as long as they are capped with the correct functional group

45

Addition Vs. Condensation Polymerization

- In **addition polymerization** although x may assume any value, y is confined to unity
- i.e. the growing chain can react only with a monomer molecule and continue its growth

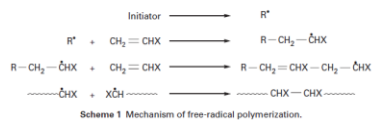
46

2.3 addition polymerization

1) Free-radical chain polymerization

- Involves the continuous addition of monomer units to a growing free radical chain.
- average degree of polymerization X_n

$$x_n = \frac{[\text{Monomer}]}{\sqrt{[\text{Initiator}]}} \quad (1)$$



Scheme 1 Mechanism of free-radical polymerization.

- Example of initiators: 2, 2'-azo-bisisobutyronitrile (AIBN),



Scheme 2 Thermal decomposition of the initiator AIBN.

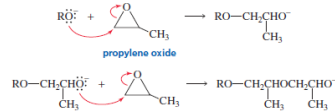
addition polymerization

2) Ionic Polymerization,

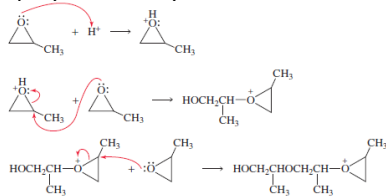
- Although the mechanism is a chain-growth process, as for free-radical polymerization above, anionic polymerization exhibits marked differences in terms of control of structure, tacticity, and molecular weight.
- such polymerizations are those that can stabilize a negative and positive charge. Monomers that may be polymerized this way include, styrene, methacrylate, acrylate esters, and butadiene.
- The cyanoacrylate esters, which by virtue of two powerful electron-withdrawing groups are extremely reactive to very weak nucleophiles, have found commercial exploitation as adhesives.

Cont....

- For example, epoxides undergo chain-growth polymerization reactions.
- If the initiator is a nucleophile such as OH^- or RO^- polymerization occurs by an anionic mechanism.



- If the initiator is a Lewis acid or a proton-donating acid, epoxides are polymerized by a cationic mechanism.

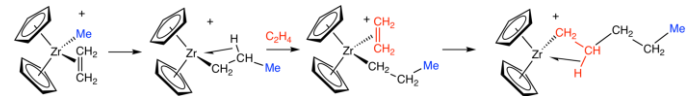


49

addition polymerization

3) Coordination Polymerization

- This is the role of transition metal compounds in the formation of polymers, that is, coordination catalysts.
- A **coordination polymer** is an inorganic or organometallic polymer structure containing metal cation centers linked by Ligands.
- Of these probably the best known and most commercially successful are the Ziegler–Natta catalysts. It used to manufacture a wide range of commercial polymers including **high-density polyethylene** and **isotactic polypropylene**.
- Because of the commercial importance of these polymers, an enormous range of catalysts has been developed.

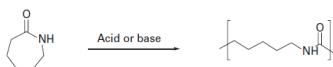


50

Addition polymerization

4) Ring opening polymerization

- The ring-opening polymerizations of heterocyclic compounds are important,
- The best-known examples include Nylon 6, which is produced from ϵ -caprolactam as shown in Scheme 16; poly(ethylene oxide) produced by ring-opening polymerization of ethylene oxide (or oxirane), a route to which is described in Protocol 14 (Scheme 17), and poly(dimethylsiloxane) which is formed from a cyclic tetramer produced on hydrolysis of dimethylsilyldichloride in a way similar to that described in Protocol 15.



Scheme 16 Synthesis of Nylon 6 from ϵ -caprolactam.

51

Assignment (1)

- What is/are elastomer,
- What are type of elastomers,
- What are the methods used to synthesize elastomer?

Do it in your previous group!

Answer it with maximum of 8-10page!

Submit it in 02/04/2020

52

Chapter two:

2. Reactions of Polymers

- 2.1. Reactions involving the main chain
- 2.2. Reactions involving the side group- Graft polymerisation
- 2.3. Surface reactions of polymers

53

Chapter 2. Reactions of Polymers

INTRODUCTION

- Chemical reactions of polymers have received great attention during the last two decades.
- Many fundamentally and industrially important **reactive and functional polymers** are prepared by the reactions of linear or crosslinked polymers and by the introduction of reactive, catalytically active or other groups onto polymer chains.
- The term "functional polymer" has two meanings: (A) a polymer bearing functional groups (such as hydroxy, carboxy, or amino groups) which make the polymer reactive, (B) a polymer performing a specific function for which it is produced and used. The function in the latter case may be either a chemical function such as reactivity or a physical function like electrical conductivity.

54

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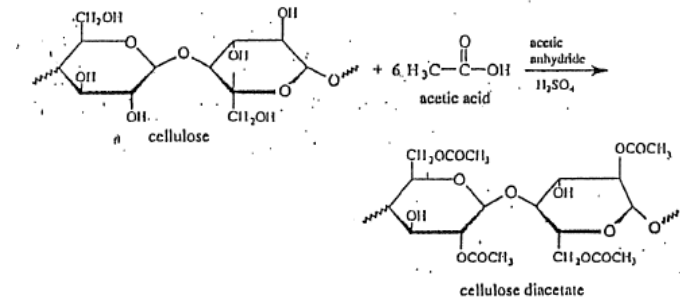
- **Characteristics of polymer reactions are appreciably different from those of low-molar-mass compounds and polymerization reactions.**
- In many case a polymer can be **chemically modified** to improve some property, such us biocompatibilty, fire resistance, adhesion, or to provide specific functional group for ion exchange or other application.
- Fore example 1) bromination is sometimes used to improve fire resistance of polymer.
- 2) chlorination of PVC to increase its softening tamprature or to improve its ability to blend with other polymer.
- Chemical modification includes
 - Chloromethylation
 - Surface modification
 - lone exchange resins

55

Chapter 2. Reactions of Polymers

2.1. Reactions involving the main chain

- Acylation: **Cellulose acetate** is **used** as a film base in photography, as a component in some coatings, and as a frame material for eyeglasses; it is also **used** as a synthetic fiber in the manufacture of cigarette filters and playing cards.



56

Chapter 2: Reactions of Polymers

2.2. Reactions involving the side group- Graft polymerization

- **Chloromethylation** (generally haloalkylation)

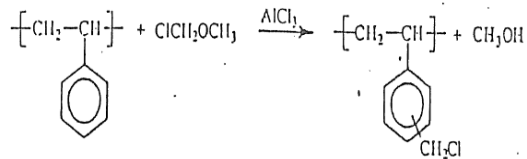


Figure 2.8. Chloromethylation of polystyrene.

57

- A) Sulfonation: ione exchange resins

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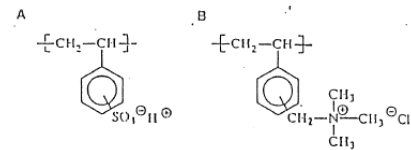


Figure 2.9. Example of a strongly acidic cation-exchange resin (A) and a strongly basic anion-exchange resin (B) prepared from polystyrene.

- B) **Chloromethylation** of polymeric membranes followed by an amination reaction has been widely used for preparation of **anion exchange membranes (AEMs)**.
- Significant efforts have been made to prepare AEMs from insoluble polymeric films such as polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF).
- Such AEMs are typically prepared by grafting vinyl monomers such as styrene onto polymeric films and subsequent chloromethylation and amination modifications.

58

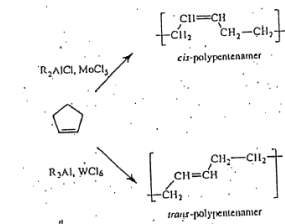
Chapter 2: Reactions of Polymers

2.3. Surface reactions of polymers

- **surface grafting**
- A process in which a polymer surface is chemically modified by generation of active sites that can lead to initiation of a graft polymerization or a grafting reaction.
- *Note*
- Peroxidation, ozonolysis, and high-energy irradiation are typical methods of generating active sites on a polymer surface.

Special topics 1) polymer synthesis

- It is not always polymers are synthesised through the known methods rather there are some other special method of synthesis
- These are : 1) metathesis, cyclic olefines => elastomer



2) group transfer polymerization,

3) macromer in polymer synthesis,

Special topic 2) FUNCTIONAL POLYMERIC MATERIALS

1) Biodegradable polymer

- A polymer susceptible to degradation that is accompanied by a lowering of its molar mass due to the interaction with enzymes, bacteria, or other biological systems.

2) Conducting polymer

- A polymer that exhibits electric conductivity similar to that of metals or solutions of electrolytes.
- 1. The electric conductivity of a conjugated polymer is markedly increased by doping it with an electron donor or acceptor, such as in the case of polyacetylene doped with iodine.
- 2. A polymer showing a substantial increase in electric conductivity upon irradiation with ultraviolet or visible light is called a **photoconductive polymer**; an example is poly(*N*-vinylcarbazole).

61

3) electroluminescent polymer

- A polymeric material that shows luminescence when an electric current passes through it such that charge carriers can combine at luminescent sites to give rise to an electronically excited state of luminescent groups or molecules.

Note

- Electroluminescent polymers are often made by incorporating luminescent groups or dyes into conducting polymers.

4) ferroelectric polymer

- A polymer in which spontaneous polarization arises when individual dipoles become arranged parallel to adjacent dipoles.

Note

- Poly(vinylidene fluoride) is an example of a ferroelectric polymer showing strong piezoelectricity after poling.

62

5) polymer drug

- A polymer that contains either an ionically or covalently bonded molecules of a drug or pharmacologically active groupings and moieties.
- *Note*
- A polymer drug is usually used to provide targeted drug delivery to and controlled release of active drug at the target sites of an organism.

6) polymer gel

- A polymer network, including a physical one, swollen or capable of being swollen in a liquid.

7) polymer membrane

- A thin piece of polymeric material that acts as a barrier permitting selective mass transport.

63

Special topic 3) REACTIVE POLYMERIC MATERIALS**1) chelating polymer**

- A polymer composed of molecules containing ligand groups capable of forming chelates through two or more coordination bonds with a central metal ion.

Note

- Chelating polymers mostly act also as ion-exchange polymers specific to ions that form chelates with chelating ligands of the polymer.

2) ion exchange polymer**ion-exchange resin**

- A network polymer possessing fixed ionic groups (polyanion or polycation) that are able to exchange counterions (cations or anions) with the ionic components of a solution.

64

3) living polymer

- A polymer with stable polymerization-active sites formed in a chain polymerization in which irreversible chain transfer and chain termination are absent.

4) macromonomer

- A polymer or oligomer that has one reactive group, often at the end, which enables it to act as a monomer; each macromonomer molecule is attached to the main chain of the final polymer by reaction of only one monomeric unit in the macromonomer molecule.

Notes

- 1. Homopolymerization or copolymerization of a macromonomer yields comb or graft polymers