

# **Egyptian Journal of Chemistry**

http://ejchem.journals.ekb.eg/



# **Polymers and Polymerization Mechanisms for Textile Industry** Fedaa Saad a, Mohamed M. Mosaad b, Hanan A. Othman b, and Ahmed G. Hassabo c\*



- <sup>a</sup> Textile Printing, Dyeing and Finishing Department, Faculty of Applied Arts, Tanta University, Tanta, Egypt
- <sup>b</sup> Textile Printing, Dyeing and Finishing Department, Faculty of Applied Arts, Benha University, Benha, Egypt <sup>c</sup> National Research Centre (Scopus affiliation ID 60014618), Textile Research and Technology Institute, Pre-
- treatment, and Finishing of Cellulose-based Textiles Department, 33 El-Behouth St. (former El-Tahrir str.), Dokki, P.O 12622, Giza, Egypt

#### **In Loving Memory of Late Professor D**octor " "Mohamed Refaat Hussein Mahran

#### Abstract

Polymers play an influential role in several field of textile industry. Textile research has concentrated on the production of fiber/fabric based on polymer as well as textile fabric coated with polymers. Polyester, Polyamide, polypyrrole, polyaniline, polyacrylonitrile, polyurethane, polyacrylamide, polyvinyl chloride, polyvinyl fluoride, polyvinyl alcohol, rayon, etc., have been specified as textile service polymers. Polymers are essential chemicals for the production of textile. Polymers are used in every step of textile manufacturing from fiber manufacturing to textile coloration and finishing. Different Nanoparticles and Nano carbons have also been utilized in polymeric composites for textile-related objectives. The possibilities and combination of polymer and textile materials are endless depending on the purpose of final use. Keywords: Polymers, textile production, textile coloration, Nanoparticles

#### Introduction 1.

Polymer came from the Greek word "poly" and "meros", where "poly" means many and "meros" means part. Polymers are macromolecules or giant substances made from the interlinking of many small units. Polymerization is the process of creating polymers. During polymerization, smaller molecules, called monomers or building blocks, are chemically combined to create larger molecules or a Different macromolecule. polymerization techniques are applied to obtain polymers with unique properties suitable for various applications.

Basically, two types of reactions are involved in polymerization. Monomers are either linked together without any elimination; this type of reaction is called addition reaction or chain polymerization. Or reaction between the reactive groups of the monomers where elimination of low molecular compound is involved, this type of reaction is called condensation reaction or step polymerization. [2]

Textiles and polymers are interconnected materials and all textile fibres are polymers. Polymers are essential chemicals for the production of textile. Polymers are used in every step of textile manufacturing from fiber manufacturing to textile

coloration and finishing. [3-8] Apart from this, polymers play an important role in textile processing and are utilized for various applications like sizing agents, thickeners for textile printing, finishing chemicals, coating chemicals, etc. All textile materials are polymeric except the metal, glass, and inorganic fiber woven fabric. Polymers have been used as fiber materials as well as for coating in the textile. [9, 10]

In the case of fibers, polymers have been spun using various spinning techniques such as fiber spinning, melt spinning, solution spinning, and electro spinning. The fibers then can be woven or stitched into the form of textile cloth or fabric A wide range of polymers, thus, have been identified in the textile industry. Polymer science and textile technology work together for the development of polymer-based textile materials. [11, 12]

#### Polymers 2.

The Polymers are very large molecules, or macromolecules, formed by the union of many smaller molecules. These small units from which polymers are formed are known as a monomer, which means a single part. The process by which individual monomers are linked together to form polymers is known as "polymerization" The

Receive Date: 24 December 2023, Revise Date: 11 January 2024, Accept Date: 28 January 2024

<sup>\*</sup> Corresponding author: aga.hassabo@hotmail.com, Tel. 00201102255513.

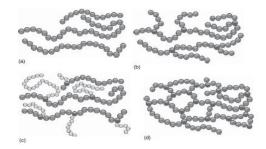
polymer can be formed from one type of monomer. The polymer formed from one type of monomer is known as a homo-polymer. For examples, polyethylene is formed only from ethylene monomer. On the other hand, the polymer formed from more than one type of monomers is called copolymer. Polyester can be taken as an example here, two types of monomers—acid and alcohol are used for the polyester polymer-formation. [13]

# 2.1. Classification of Polymers

There are many polymers with a variety of different behaviors. They can be classified in different ways based on their origin, physical properties, and thermal behavior. [14]

- 2.1.1. Based on Sources: Source of origin is the easiest way to classify a polymer. Based on their origin polymers are classified into natural and synthetic.
- I. Natural Polymer: Polymers have been found naturally existing in natural sources like vegetable and animals are known as natural polymers. Some examples include cellulose and starch present in vegetables, the protein present in animals and rubber from plant's latex.
- II. Synthetic Polymer: Polymers that are produced artificially in labs from lower molecular weight compound are known as synthetic polymers. They are produced commercially by the industries according to the demand. Commonly produced synthetic polymers that we used in our day-to-day life are Polyethylene, PVC, Polyester, Nylon, etc.
- III. Semi-synthetic Polymer: Polymers obtained by the modification of natural polymers. These types of polymers also are commercially important like vulcanized rubber, where the rubber is treated with sulfur for cross-linking between the polymers. Cellulose acetate is another example of a semi-synthetic polymer. Naturally occurring cellulose polymers are acetylated to produce a cellulose derivative known as cellulose acetate. [15]
- 2.1.2. Based on Polymer Structure: Based on the structure polymers are classified as follows:
- I. Linear Polymer: These polymers are straight and long chain polymer. These are the highdensity polymer as polymers are straight a compact structure is possible to obtain. Polymers' melting temperature is generally

- very high due to high density. PVC is a straight-chain polymer.
- II. Branch Chain Polymer: As the name suggests, polymers have a branch chain at random point of the main chain. Branching does not allow polymers to be packed closely; as a result, low-density polymer with lower melting temperature is obtained.
- III. If the branches are formed by repeating units (monomer) different from those forming the main chain, the branched polymer is a graft copolymer
- IV. Cross-linked Polymer: Polymers are internally linked with each other are known as cross-linked polymers. Monomers with trifunctional groups are prone to form a cross-linked network. Cross linked polymers are rigid and brittle. Urea and Melamine formaldehyde are examples of cross linked polymers figure 1. [16]



**Figure 1** Different polymer chain topologies: (a) linear polymer; (b) branched polymer; (c) graft copolymer; and (d) crosslinked polymer.

- 2.1.3. Based on Type of Polymerization: The process by which monomers are linked together to form a polymer is called polymerization. Based on polymerization types polymers are classified as follows:
  - Addition Polymers: Polymers that are produced by addition polymerization process is called addition polymers. Monomers linked together without any elimination in this process. In this case, double or triple bonds present in the chemical structure of the monomers work as functional group. Monomer and polymer have the same composition as no elimination of chemical species of monomer take place. Polyethylene, PVC, etc., are addition polymers as shown in table 1.
  - II. Condensation Polymers: Polymers produced by the combination of monomers with the elimination of small molecules like water, methanol etc. Active reactive sites present in the monomer work as functional groups here. Polyester, Nylon is the examples of

condensation polymers as shown in table 2. [17]

# 2.1.4. Based on Thermal Behavior: Polymers behave differently when the heat is applied. Based on the behavior of heating polymers are classified as follow:

- I. Thermoplastic: Polymers without crosslinking soften on heating and can be given any shape. These polymers on cooling become hard again and retain its shape. Polymers those soften on heating and stiffen on cooling are known as thermoplastic polymers. This process can be repeated several times without any deterioration of the properties of the polymers. PVC, Nylon, Polyester are common examples of thermoplastic polymer.
- II. Thermosetting: Polymers those generally undergo chemical changes during heating known as thermosetting polymers. These are generally low molecular weight semi-liquid substance, on heating; they start crosslinking with each other and become hard, insoluble and infusible masses. They form three-dimensional linking on heating which is irreversible. Urea, melamine–formaldehyde, and Bakelite are the common examples. [18]

# 2.1.5. Based on Ultimate Form and Use: Intramolecular forces are the forces that hold the atom in a polymer chain whereas intermolecular forces are the forces between the molecules. The form of a polymer ultimately depends on these two forces. Based on the form and uses polymers are classified as follows

- I. Plastics: These polymers are long-chain polymers where intermolecular forces hold them together. They do not have any cross bonds and can be shaped into hard and tough when pressure and heat is applied. Polystyrene and PVC are examples of polymers used as plastic.
- II. Elastomers: Polymers that are elastics in nature and rubber-like solid material are known as elastomers. Polymers are cross-linked with each other so that they can recover to original shape after releasing from stress. Polymers that easily stretched and come back to their original shape after releasing stress are called elastomers. Vulcanized rubber and synthetic rubber are examples of elastomers.
- III. Fibers: Polymers have strong intermolecular forces results in high strength and less elasticity can be used as fiber. Fibers are a

finer, flexible, and thread-like substance that can be woven easily. Fiber has a high melting temperature with a sharp value. Nylon66 and Polyester are common examples of fiber. [19]

# 2.1.6. Based on Homopolymer and Copolymer

- I. If only one type of monomer or repeating unit constitutes the macromolecule (without considering the chain ends) then the polymeric substance is termed a homopolymer.
- II. If, on the other hand, more than one type of repeating unit is present in the macromolecule, the polymeric substance is a copolymer.
- III. The macromolecule produced in the specific case of a reacting mixture containing three different monomers or monomer units is termed terpolymer.
- IV. Depending on the randomness or order in which two or more types of repeating units are present in the macromolecule, there are different types of copolymers: random, block, alternate, and so on. [20]

**Table 1:** Examples of Common Addition Polymers

Addition Polymers	Repeating Unit
Polyacrylonitril e	—CH₂-CH—     CN
Polybutadiene	—CH₂ CH₂— CH=CH
Polyethylene	CH <sub>2</sub> CH <sub>2</sub>
Poly(methyl methacrylate	CH₃ — CH₂-C— CO₂CH₃
Polypropylene	CH₃ —CH₂-CH—
Polystyrene	—CH₂-CH—
Poly(vinyl chloride)	—CH₂-CH—       CI

Polymer	Synthesis Reaction → Repeating Unit				
Polyamide	$H_2N-R_1-NH_2+HO_2C-R_2-CO_2H \longrightarrow H-NH-R_1-NHCO-R_2-CO-1-OH+H_2O$				
Polyester	$HO-R_1-OH+HO_2C-R_2-CO_2H \longrightarrow H-LO-R_1-OCO-R_2-CO-\frac{1}{n}OH+H_2O$				
Phenol- formaldehyde	OH + CH <sub>2</sub> O → CH <sub>2</sub> ] <sub>n</sub> +H <sub>2</sub> O				
Urea- formaldehyde	$H_2N$ — $CO$ — $NH_2$ + $CH_2O$ ————————————————————————————————————				
Polyurethane	$HO-R_{\Gamma}OH + OCN-R_{2}-NCO \longrightarrow \{O-R_{\Gamma}OCO-NH-R_{2}-NH-CO\}_{T}$				

Table 2 Examples of Common Condensation Polymers

# 2.1.7. Based on Biodegradability

- I. Biodegradable polymers are those that degrade by the action of biological agents (e.g., microorganisms, bacteria or fungi) in ambient or mild conditions, and in relatively short times. In order to be more specific, it is necessary to set a time frame for degradability, to define the environmental conditions under which degradation is supposed to occur, and also to what extent the polymer must degrade in order to be considered biodegradable.
- II. Most of the commodity polymers are not biodegradable: polyethylenes, poly(ethylene terephthalate) (PET), PVC, polystyrene, and so on. The development and commercialization of biodegradable polymers in significant amounts is relatively recent (since around the, but an accelerated growth of this industry is expected because of worldwide growing environmental concerns. Some examples of biodegradable polymers are poly(lactic acid) (PLA), poly(hydroxy-alkanoates) (PHA) and polycaprolactones. [21]

# 2.1.8. Based on Production Volume

T. polymers can be classified by production volume. Large production volume polymers are commodities, and they are usually produced by continuous processes with very low profit margins per weight unit. Mostly, mature technologies are used to produce them, and the investment in R&D that is used to improve the production processes or products tends to be relatively low. Main examples of commodities are polyethylene (LDPE and HDPE), polypropylene, PVC. PET. polystyrene, and derivatives. These five families of polymers constitute those produced in largest volume. Estimated worldwide production of polymers in 2003 was around

- 200 million Tons, with an annual estimated global growth rate of 3.4%. About 80% of the total polymer production is composed of the five families of commodities mentioned above.
- II. On the other hand, specialty polymers are produced in smaller quantities, in batch or semibatch processes, and have high profit margins per weight unit. They require high investment in R&D in order to offer significant advantages over existing products for specific applications. [22]

# 2.2. Polymerization Mechanisms

Functionality refers to a repeating unit's capacity to create covalent connections with nearby molecules. The ability of the repeating units to interact with the surrounding molecules through certain reaction mechanisms might be influenced by their numerous functions. Each repeating unit with two or more functionalities has the potential to interact with nearby molecules to produce a wide range of chemical reactions. This generates a sizably huge number of potentially confusing reactions. Different polymerization processes are grouped into several groups for clarity purposes depending on their reaction mechanisms, such as addition, condensation, ring opening, and other mechanisms. [23]

# 2.2.1. Addition or Chain Polymerization

One of the most common mechanisms is addition polymerization. In addition polymerization the growth of the polymer chain proceeds exclusively by reaction(s) between monomer(s) and reactive site(s) on the polymer chain. The addition of new monomer units occurs one at a time via chain reaction. Each addition of a repeating unit to the growing chain regenerates reactive site at the end of each growth step and the polymerization

\_\_\_\_\_

proceeds through repeated addition process. In a simplified manor the process could be visualized as making a bicycle chain where each link is added one at a time on one or both ends of the chains. The more links are added to longer the chain grows

Monomers with double or triple bonds can react elimination. any This type polymerization involves joining of the monomers very rapidly. As no byproduct is formed in this type of polymerization the polymer and the monomer have the same elemental composition. The functionality of the monomers is provided by the double or triple bonds present in the monomer.

Common examples of addition polymerization are polyethylene, polyvinyl chloride (PVC), acrylics, polystyrene, polytetrafluoroethylene, and polyoxymethylene (acetal).

Schematic representation of addition polymerization is presented in Figure (2). it could be observed that the polymer on the right of the arrow sign is formed by addition of the repeating units on the left of the arrow. In this illustration, R1 and R2 represent functional groups or other group of atoms.

Figure 2: Addition polymerization

Functional groups are specific groups of atoms that determine the characteristics and chemical reactivity of the polymer influencing processability and application of plastic products. In the example of a bicycle chain, a necklace, or even a charm bracelet, let us consider that each link in the chain has a hanging pendant or a charm. These pendants could be different in structure and could be attached distinctly to the chain providing unique characteristics and appearance. Similarly, functional groups are attached to the polymer backbone providing unique features to the polymer and plastics application. In addition polymerization the polymerization reaction occurs through three distinctive steps as:

1. Chain initiation: In this step the polymerization reaction is initiated usually by means of an external initiator which creates a reactive site. The initiator could be a radical (free radical polymerization), cation (cationic polymerization, applicable to monomers with electron donating groups such as isobutylene), anion (anionic polymerization, applicable to monomers with electron withdrawing groups such as styrene, acrylonitrile, butadiene, acrylates, ethylene oxide, and lactones), and

- organometallic complex (coordination polymerization with Ziegler Natta catalysts).
- 2. Chain propagation: In this step monomers or repeating units attach to the molecular chain, propagating the chain length.
- 3. Chain termination: In this step the chain growth is terminated through neutralization of the reactive center. Three major steps involved in chain polymerization: initiation, propagation, and termination. The chain polymerization process can be brought by free radical, ionic or coordination techniques. Depending techniques involved in the polymerization, chain polymerization can be classified as Freeradical, Ionic, and Coordination polymerization.

The simplest type of addition polymerization is free radical polymerization in which a polymer is formed by successive addition of free radical building block. [24]

#### 2.2.2. Free-Radical Polymerization

A free radical is a molecule with a free electron that can be paired with electron from another molecule. Using the examples of polyethylene polymerization the three steps of polymerization could be explained as follows:

#### 2.2.2.1. Chain Initiation

In this phase the chain is initiated by a free radical Ra\_ which creates a free radical building block. The initiation phase usually involves monomers with a double or triple bond (unsaturated carbon-carbon). The chain initiation phase starts when an external initiator disintegrates into a reactive group (free radicals Ra-) and stimulates the double bond of the ethylene monomer to open up creating a molecule with an unpaired electron or active center. The (-) represents the active center with a free electron that got transferred from the radical to the ethylene monomer, making the ethylene monomer as the new radical. The initiation stage can be demonstrated as follows:

$$Ra^*+CH_2=CH_2\longrightarrow RaCH_2CH_2^*$$

#### Chain Propagation 2.2.2.2.

In this step the free radical building block of ethylene monomer reacts with other ethylene monomers to create a larger free radical building block. In order to stabilize the active centers the free radical building block bonds with neighboring monomers extending the length of the chain. The polyethylene chain is thus constructed by a series of addition reactions between the active center of the growing chain and available monomers. The reactive group can attach at either end of the

growing chain. Each new monomer unit addition creates an active site for the next attachment. The propagation step could be demonstrated as follows:

RaCH<sub>2</sub>CH<sub>2</sub>\*+ CH<sub>2</sub> = CH<sub>2</sub> → RaCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH\*

# 2.2.2.3. Chain Termination

In this phase the process of chain growth terminates (stops). Fundamentally the addition process will continue until all the monomers in the system are consumed (controlling the supply of ethylene monomers could control the total chain length). However, the chain growth usually stops by direct combination or disproportionation. Direct combination occurs when the chain growth is stopped as a result of combining of free electrons from two growing chains and creates a single chain. Disproportionation occurs when an impurity reacts with active groups and terminates the chain growth. To avoid termination due to impurities, extremely clean environments are needed to perform these reactions. Chain termination by direct combination could be demonstrated as [25]

$$Ra (CH_2)_m * + (CH_2)_n Ra \longrightarrow Ra(CH_2)_m (CH_2)_n Ra$$

# 2.2.3. Ionic Polymerization:

The ionic polymerization also involves attaching like chain polymerization. But this time monomer is attacked not by an unpaired electron but by either positive or negative ion. If the initiation and propagation are done by a positively charged ion is called cationic polymerization and if by a negative ion it is called anionic polymerization. Like free radical polymerization, cationic polymerization also has three steps: initiation, propagation, and termination.

Anionic polymerization also has two steps: initiation and propagation. But the termination of the anionic polymerization is not a simultaneous process unless strong cationic agents are present in the reactor. Ionic repeating structures are highly reactive and have the ability to combine even at low temperatures and pressures compared to free radical polymerization.

As the polymerization occurs very fast, ionic polymerization generally produces linear polymer chains. Controlling the amount of impurities or termination agents provides the means to control the average molecular weight of ionic polymerization reactions. Polymers produced by anionic polymerization are live polymers as they are active and can react anytime if a favorable condition is given. (Figure 3) shows an example of an ionic polymerization. [26]

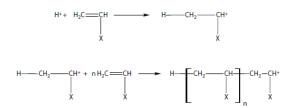


Figure 3: Ionic polymerization

# 2.2.4. Coordination Polymerization:

Chain polymerization started by a coordination bond and goes on through this coordination bond is known as coordination polymerization (Figure 4). In coordination polymerization the monomers with side groups are attached to the growing chain in a highly defined spatial arrangement (stereo regular). The significant feature of this mechanism is the ability to orient each monomer and join it to the growing polymer chain in a very specific configuration.

Olefins monomers form a complex with organometallic compounds in the first step. A coordination bond is involved between the metal and the carbon of the monomer in this complex. Afterward, more monomers keep successively adding to the polymer chain through this coordination bond. As the monomers are inserted between the metal and the carbon of the monomer this polymerization is also known as insertion polymerization. [27]

Figure 4: Coordination polymerization.

# 2.2.5. Condensation polymerizations or Stepgrowth Polymerization

Condensation polymerization (as the byproduct condenses out) is the second most common mechanism for polymerization. In this mechanism the reaction between the repeating units and the growing chain results in the release of a small molecule (condensate) such as water or hydrochloric acid as a byproduct.

The reaction progresses in a step-wise manner and thus the name step-growth polymerization. Common examples include polyesters, polyamides, polycarbonates, proteins, and polysaccharides. It should be noted that plastics such as polyesters and polyamides made via condensation polymerization, in which water is released, are susceptible to degradation when exposed to water at high

temperatures. Thus minimized moisture levels and dry conditions are necessary during melt processing of these polymers.

Monomers having reactive groups can react with themselves through a stepwise slow reaction to form a polymer. As this type of reaction, goes stepwise manner it is thereby slow, unlike chain polymerization. This type of reaction mostly accompanied by the elimination of small compound through step polymerization may proceed without any elimination.

Composition of the monomer and repeat unit will be the same or not depending on the elimination. If no elimination is involved in the polymerization the composition of the monomer and the repeat unit will be the same. If byproduct is formed then the composition of the monomer and the repeat unit will not be the same. Poly condensation, Polyaddition are the most common examples of step polymerization.

I. Polycondensation: Monomers containing reactive groups can be condensed by reacting with each other. Elimination of small molecules is known as condensation. As condensation is involved in every reaction during polymerization this polymerization is called Polycondensation (Figure.5). Monomers must have two functional groups for the Polycondensation to proceed. Only one type of reaction is involved in polymer formation. The polymer formed still have the two reactive groups at their chain end hence polymers are active.

Figure 5: Polycondensation polymerization.

II. Polyaddition: This type of polymerization is brought about by the migration of atom from one monomer to another. Monomers having double bonds or reactive groups as functional groups can undergo this type of reaction. Styrene can be polymerized by this method (Figure 6).

Hydrogen atom transfer from one monomer to another and simultaneously monomers keep adding with one another. Like chain polymerization monomers are added without producing any byproduct.

An interesting feature is that chain polymerization requires either free radicals or ions for polymerization to proceed, whereas styrene can be polymerized without any of them. But like in chain polymerization monomers here do not react

rapidly. As every reaction requires the transfer of an atom this type of reaction requires time.

Monomers having reactive functional groups can also undergo polyaddition polymerization without any byproduct. For example, polyurethane polymer is formed by the reaction between diisocyanates and diols where a transfer of atom is involved. Hydrogen from diol transfer to diisocyanates results from the addition of the two monomers.

$$H_2C = CH$$
 $H_3C = CH$ 
 $H_3C$ 

**Figure 6:** Polyaddition polymerization.

The differences between the step-growth and the chain polymerization mechanisms are summarized in Table 4. [28]

# 2.2.6. Ring-opening:

Ring-opening polymerization (ROP), as a variant of polymerization mechanism, yields higher molecular weight in relatively shorter time therefore this mechanism is preferred for industrial mass production. Monomers having a ring structure can be polymerized after the opening of the ring. Monomers after opening follow either polyaddition or Polycondensation type of polymerization. ROP is a superior method for making copolymers with tailored properties to support specific application such as coatings, fibers, elastomers, adhesives, and composites.

Some of the common examples include poly(propylene oxide), polyoxymethylene, poly(tetramethylene oxide), polycaprolactone, poly(dimethylesiloxane), Ethylene oxide and caprolactam. Where ethylene oxide follows polyaddition reaction and caprolactam follows Polycondensation polymerization after their ring is opened. Figure 7 is an example of a ring-opening polymerization.

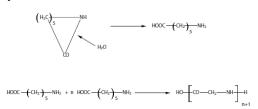


Figure 7: Ring-opening polymerization

Feature	Step-Growth Mechanism	Chain (Living)	Chain (with Termination)
Number and class of reactions	Only one between dissimilar groups	Two reactions: initiation and propagation	Three reactions: initiation, propagation, and termination
Reactive species	Two species of any size having dissimilar groups	Active species of any size with monomer	Active species of any size with monomer or among them (termination)
Monomer consumption	Monomer disappears early in the reaction	Monomer is present up to high conversion	Monomer is present up to high conversion
Conversion	On the basis of reacted functional groups	On the basis of polymerized monomer	On the basis of polymerized monomer
Average molecular weight versus	conversion	conversion	conversion

Table 4: Differences between the Step-Growth and the Chain Polymerization Mechanisms

ROP utilizes cyclic monomers. Cyclic monomers are monomers in which one or more series of atoms are connected in the form of a ring. Referencing to the example of bicycle chain, if the links are in the form of a circle then these circular rings are required to be opened to be polymerized. Once the circular link arrangement is opened up it could be attached to the chain at either ends promoting chain growth .Similarly, ROP involves an initial step of opening the cyclic monomer ring as illustrated in Figure 8. Generally a catalyst or initiator is used to expedite the ring-opening process.

**Figure 8:** Ring opening of a cyclic monomer (M) and "m" is the repeating unit derived from M

The strained cyclic monomer ring is opened to convert the monomer into an active center that can be further polymerized with another monomer or repeating unit to create a polymer as illustrated in Figure 9. After the cyclic ring is opened the polymerization proceeds according to one of the three different major reaction mechanisms as cationic, anionic, or coordination insertion mechanism. An important feature of this mechanism is that ROP systems are typically a living polymerization.

**Figure 9:** Elementary reaction of ring opening—chain-growth polymerization where m\_ denoted the active center, and kp and kd are rate constant of propagation and depropagation

The ring-opening reaction can be performed either as a bulk polymerization, or in solution, emulsion, or dispersion. A common example is production of polyamide PA6 polymer from cyclic caprolactam. As illustrated in Figure 10, ring opening of caprolactam is performed by water which produces a carboxylic acid end group (-COOH) and an amine end group (-NH2). The step polymerization of these functional groups develops the amide linkages (-NHCO-) that grow to form polyamide. [29]

$$\begin{array}{c} \text{HN} - (\text{CH}_{2})_{5} - \text{C} = \text{O} + \text{H}_{2}\text{O} & & \\ & & \\ & & \\ \text{H}_{2}\text{N} - (\text{CH}_{2})_{5} - \text{COOH} & & \\ & & \\ & & \\ \text{H}_{2}\text{N} - (\text{CH}_{2})_{5} - \text{COOH} & \\ & & \\ & & \\ \text{H}_{2}\text{N} - (\text{CH}_{2})_{5} - \text{COOH} & \\ \end{array} \\ \begin{array}{c} \text{H}_{2}\text{N} - (\text{CH}_{2})_{5} - \text{COOH} \\ & & \\ \text{H}_{2}\text{N} - (\text{CH}_{2})_{5} - \text{COOH} \\ \end{array}$$

**Figure 10:** Hydrolytic ring-opening polymerization of caprolactam to produce nylon 6

# 2.2.7. Other Mechanisms

Other mechanisms such as chain transfer and plasma polymerization are also applied in the production of various polymers. All these mechanisms produce polymers with unique properties.

# 2.2.7.1. Chain Transfer

In chain transfer mechanism the active center of the growing chain is transferred to another molecule. The transferred active center is not terminated during migration and has the potential to initiate either another polymer chain or a branch on an existing polymer chain. Chain transfer is a chain breaking step and decreases the average length of the propagating chain, significantly applicable to biomedical drug delivery application. The molecule receiving the active center may or may not initiate growth of another polymer chain depending on its reactivity. Chain transfer mechanism is very helpful in the formation of graft copolymers. [30]

# 2.2.7.2. Plasma Polymerization

In plasma polymerization the polymer is produced by using the influence of plasma (partially ionized gas). A plasma sources are used to generate gas discharge. The energy from the gas discharge is then used to activate the monomer for polymerization. The polymers created from plasma polymerization are highly branched and crosslinked with the capacity to adhere to solid surfaces. Because of their efficient adhesive characteristics, these polymers are significantly used in creating smooth coatings on metal surfaces. Insoluble polymers are used to create microscopic films of about  $100 \, \text{pm}$  to  $1 \, \mu \text{m}$  thicknesses on the metal surfaces. [8, 31-36]

# 2.2.7.3. Catalytic polymerization

Catalytic polymerization also called the Ziegler-Natta polymerization technique, employs catalysts that are transition metal-based coordination complexes derived from transition metal halides and organometallic reagents. This technique allows better control over the configuration of polymers synthesized from terminal alkenes and also facilitates the production of unbranched and high molecular weight compounds, hence, stronger polyolefins at relatively lower temperature and pressure than required by other addition polymerization methods. The polymerization of ethene using a titanium-based Ziegler-Natta catalyst is shown in Figure 11. [37]

$$\begin{array}{c|c} CI & & \\ H_3C - C & AI \\ H_2 & H_3C - CH_3 \\ CI & & \\ CI$$

**Figure 11:** Catalytic polymerization of ethene using a Ziegler-Natta catalyst.

### 3. Fund

The authors have no fund

# 4. Conflict of interest

The authors have no conflict of interest

# 5. Acknowledgment

The authors are gratefully-grateful to acknowledge the Faculty of Applied Arts, Benha University. Furthermore, the authors are gratefully

grateful to acknowledge the Central Labs Services (CLS) and Centre of Excellence for Innovative Textiles Technology (CEITT) in Textile Research and Technology Institute (TRTI), National Research Centre (NRC) for the facilities provided.

# 6. References

- [1]. S.K. Šimunković, S. Čimić, Polymers and polymerization, Expert Editor (2022) 218.
- [2]. M. Tirrell, R. Galvan, R.L. Laurence, Polymerization reactors, Chemical reaction and reactor engineering, CRC Press2020, pp. 735-778.
- [3]. N. Ahmed, A. Shahin, H. Othman, A.G. Hassabo, Neem tree extracts used in textile industries, Egy. J. Chem. (2024) -.
- [4]. E. El-Sayed, E. Abd El-Aziz, H. Othman, A.G. Hassabo, Azo dyes: Synthesis, classification and utilisation in textile industry, Egy. J. Chem. (2024) -.
- [5]. N. Khalid, H. Othman, A.G. Hassabo, Manufacturing and usage of lyocell fabric, Egy. J. Chem. (2024) -.
- [6]. S. Shaker, H. Ghazal, A.G. Hassabo, Synthesis of carbon dots and their functional impact on natural and synthetic fabrics, Egy. J. Chem. (2024) -.
- [7]. M. Zaied, E. Abd El-Aziz, H. Ghazal, H. Othman, A.G. Hassabo, Construction of intelligent bio-pcm matrix for cotton fabrics to improve thermal comfortability and human protection, Egy. J. Chem. (2024) -.
- [8]. N. Zakaria, A. Shahin, H. Othman, A.G. Hassabo, Enhancing the properties of textile fabrics using plasma technology, Egy. J. Chem. (2024) -.
- [9]. S. Chatterjee, P. Chi-leung HUI, Review of stimuli-responsive polymers in drug delivery and textile application, Molecules 24(14) (2019) 2547.
- [10]. A. Lund, N.M. van der Velden, N.-K. Persson, M.M. Hamedi, C. Müller, Electrically conducting fibres for e-textiles: An open playground for conjugated polymers and carbon nanomaterials, Materials Science and Engineering: R: Reports 126 (2018) 1-29.
- [11]. R. Hufenus, Y. Yan, M. Dauner, T. Kikutani, Melt-spun fibers for textile applications, Materials 13(19) (2020) 4298.
- [12]. A. Kumar, S. Sinha-Ray, A review on biopolymer-based fibers via electrospinning and solution blowing and their applications, Fibers 6(3) (2018) 45.
- [13]. Y. Yang, M.W. Urban, Self-healing of polymers via supramolecular chemistry, Advanced Materials Interfaces 5(17) (2018) 1800384.
- [14]. S.A. Varghese, S.M. Rangappa, S. Siengchin, J. Parameswaranpillai, Natural polymers and the hydrogels prepared from them, Hydrogels based on natural polymers, Elsevier2020, pp. 17-47.
- [15]. A. Mignon, N. De Belie, P. Dubruel, S. Van Vlierberghe, Superabsorbent polymers: A review on the characteristics and applications of synthetic, polysaccharide-based, semi-synthetic

- and 'smart'derivatives, European Polymer Journal 117 (2019) 165-178.
- [16]. E. Saldívar-Guerra, E. Vivaldo-Lima, Introduction to polymers and polymer types, Handbook of polymer synthesis, characterization, and processing (2013) 1-14.
- [17]. J. Li, D. Han, Q. Zhang, Z. He, Y. Lu, Synthesis and properties of fluorinated benzotriazole-based donor-acceptor-type conjugated polymers via pd-catalyzed direct c□ h/c□ h coupling polymerization, Journal of Polymer Science 59(3) (2021) 240-250.
- [18]. R. Hamzaoui, F. Muslim, S. Guessasma, A. Bennabi, J. Guillin, Structural and thermal behavior of proclay kaolinite using high energy ball milling process, Powder Technology 271 (2015) 228-237.
- [19]. J.P. Pascault, R.J. Williams, Thermosetting polymers, Handbook of Polymer Synthesis, Characterization, and Processing (2013) 519-533
- [20]. X. Lu, X. Wang, N. Brown, Slow fracture in a homopolymer and copolymer of polyethylene, Journal of materials science 23 (1988) 643-648.
- [21]. N.T. Dintcheva, F. La Mantia, Durability of a starch-based biodegradable polymer, Polymer Degradation and Stability 92(4) (2007) 630-634.
- [22]. G. Braunegg, R. Bona, M. Koller, Sustainable polymer production, Polymer-plastics technology and engineering 43(6) (2004) 1779-1793.
- [23]. A. Kumar, R.K. Gupta, Fundamentals of polymer engineering, CRC press2018.
- [24]. A. Jain, S. Dhiman, A. Dhayani, P.K. Vemula, S.J. George, Chemical fuel-driven living and transient supramolecular polymerization, Nature Communications 10(1) (2019) 450.
- [25]. K. Matyjaszewski, T.P. Davis, Handbook of radical polymerization, (2002).
- [26]. S. Kobayashi, Ionic polymerization, John Wiley & Sons2000.

- [27]. J.M. Asua, Introduction to polymerization processes, Polymer reaction engineering (2007) 1-28.
- [28]. M. Kade, M. Tirrell, Free radical and condensation polymerizations, Monitoring polymerization reactions: From fundamentals to applications (2013) 1-28.
- [29]. P. Dubois, O. Coulembier, J.-M. Raquez, Handbook of ring-opening polymerization, John Wiley & Sons2009.
- [30]. M. Liu, Y. Li, J. Han, X. Dong, Synthesis of tetracycline-imprinted polymer microspheres by reversible addition—fragmentation chain-transfer precipitation polymerization using polyethylene glycol as a coporogen, Journal of separation science 37(9-10) (2014) 1118-1125.
- [31]. C. Noël, Plasma polymerisation: Study and application, Durham University, 2009.
- [32]. A.G. Hassabo, M. Bakr, M. Zayed, H.A. Othman, Review on some fabric pretreatment via plasma to improve their printability using various types of colorants and dyes, Materials International (Accept 2022).
- [33]. A. Hassabo, E. El-Sayed, Recent advances in the application of plasma in textile finishing (a review), J. Text. Color. Polym. Sci. 0(0) (2021) 0-0.
- [34]. E. El-Sayed, A.G. Hassabo, Recent advances in the application of plasma in textile finishing (a review), J. Text. Color. Polym. Sci. 18(1) (2021) 33-43.
- [35]. E. El-Sayed, A.G. Hassabo, Recent advances in the application of plasma in textile finishing, J. Text. Color. Polym. Sci. 18(1) (2021) 33-43.
- [36]. D.M. Hamdy, H.A. Othman, A.G. Hassabo, A recent uses of plasma in the textile printing J. Text. Color. Polym. Sci. 19(1) (2022) 1-10.
- [37]. M.R. Buchmeiser, Polymeric materials in organic synthesis and catalysis, John Wiley & Sons2006.