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Université MOULAY Tahar, Saida

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قسم الكيمياء
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Synthesis and characterization of biopolymer in presence of homogeneous and heterogeneous catalysis

Présentée par :

- Mlle : Boutaleb jihad

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Devant le jury composé de :

Présidente	Mme. Mostéfai Asmaa	Pr Université UMTS
Rapporteur	Mme. Miloudi Safiya	MCB Université UMTS
Examinatrice	Mme. Ayat Oum el kheir	MCA Université UMTS
Examinatrice	Mme. Chabani Malika	MCB Université UMTS

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Dedications:

With great pleasure ,an open heart and immense joy , we guide this work to my very dear respectful and magnificent parents :AHMED may god have mercy on him , MERIEM who have supported me throughout my life .

To our sisters and brother for all the love affection with which you have always surrounded me .

To my niece ASSIL

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Wise advice.

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Abreaviation list :

US : unitate states

PE : polyethylene

PP : polypropylene

PET : polyethylene terephthalate

PS : polystyrene

PHAs :polyhydroxy alcanoate

$\overline{\mathbf{Dp}}$: degree of polymerization

TPA : terephthalic acid

F : formaldehyde

D-g : D-glucose

$\mathbf{m_{poly}}$: masse of polymer

$\mathbf{m_{mono}}$: masse of monomer

Y: Yeild

Sr : swelling rate

Ws: weight of solid polymer

Wg: weight of swollen

cond: conductivity

Ph: potential hydrogen

TDS: total dissolved solids

Turb: turbidity

OD: dissolved oxygen

General introduction

Green chemistry is an alternative perspective of the field of chemistry and chemical ingeneering , it is a concept with eco-friendly principles that focus on the environmental impact of chemical approaches to prevent pollution. This concept emphasizes the use and production of renewable resources, including various chemical products such as macromolecules, which play a crucial role in all areas of life.

A macromolecule is a very large molecule typically composed of repeating units. It includes organic and inorganic compounds, both non-degradable and biodegradable, encompassing polymers and biopolymers. The latter are particularly relevant to green chemistry concepts. However in our work we mainly study biopolymers which are natural, semi-synthetic, or synthetic polymers made from non-hazardous reactants. They possess unique properties such as compatibility and biodegradability. Biopolymers find diverse applications across various domains, including the treatment of wastewater, a significant challenge in daily life.

This work is divided into two parts: a bibliographical review and an experimental section.

- The first part presents important reviews covering green chemistry, macromolecules in green chemistry, generalities about polymers and biopolymers, concluding with an overview of water and its treatment.

- The second and more significant part is dedicated to the synthesis and characterization of several products leading to the production of our main bio-product.

- Finally, we close our work with conclusion which summarizes results and discussions of synthesized our product.

Part I : Bibliographic Reviews

I. Overview of green chemistry:

I.1.History:

It all started in the United States in 1990. The U.S. Environmental Protection Agency (EPA), following increasing pressure from environmental groups supported by a few senators, for the first time made the Senate amend a law called the Pollution Prevention Act. This landmark law is seen as a guideline for U.S. policy to prevent or reduce pollution at the source whenever possible, with the ultimate objective of protecting human health and the environment. Despite appearing paradoxical to some, green chemistry involves applying innovative solutions to real-life environmental pollution situations.

The 12 principles of green chemistry were originally developed by former EPA agents Paul Anastas and John Warner in "Green Chemistry: Theory and Practice". These principles outline the roadmap for chemists to integrate green chemistry logic into their actions.

I.2.Definition :

Green chemistry, also known as sustainable chemistry, is an area of chemistry and chemical engineering focused on designing products and processes that minimize or eliminate the use and generation of hazardous substances[1].

I.3.The twelve principales of green chemistry[2]:

In 1998, Anastas and Warner proposed twelve principles for putting green chemistry into practice, a modern, environmentally friendly chemistory. The reduction of discharges, material use (particularly non-renewable resources), energy consumption, and risks and dangers are the goals of all these principles[3]:

1-Prevention :

It is better to prevent waste than to treat or clean it up after it has been created.

2-Atom economy :

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3-Less hazardous chemical syntheses :

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

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[1] -Yogita S .Temak , PravinBalashebCholke , Nassir Taboli , Green Chemistry , IJCRT , Vol 10 ,2022.

[2] -Anastas, P. T. and Warner, J. C. Green Chemistry: Theory and Practice. Oxford University Press: New York, By permission of Oxford University Press;1998, p. 30.

[3]-P. T. Anastas, M. M. Kirchhoff, Acc. Chem. Res. 35, 686,2002.

4-Designing safer chemicals :
Chemical products should be designed to effect their desired function while minimizing their toxicity.

5-Safer solvents and auxiliaries:
The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6-Design for energy efficiency:
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7-Use of renaweble feed stocks :
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8-Reduce derivatives :
Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because -such steps require additional reagents and can generate waste.

9-Catalysis:
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10-Design for degradation :
Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11-Real-time analysis for pollution prevention :
Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12-Inherently safer of chemistry for accident prevention:
Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

We can see all its principles summarized in the figure below (fig I.1).

Figure I-1 :the twelveprinciples of green chemistry.

II.Macromolecule in green chemistry :

In the context of green chemistry, macromolecule plays a crucial role in promoting sustainable and environmentally friendly practices.

Macromolecules are giant molecules in which at least a thousand atoms are linked together by covalent bonds[4]. They are defined as polymers, biopolymers and other large-scale molecule with complex structures. Macromolecules may be linear, branched chains or three-dimensional networks. Their role is involved in this key aspect of green chemistry:

II.1.Biodegradable polymers:

Traditional plastics macromolecular generated from petrochemicals pose serious environmental risks due to their enduring nature. The goal of green chemistry is to create biodegradable polymers that degrade more quickly and cause less pollution, like PLA and PHA[5].

II.2.Renawable resources:

Green chemistry emphasizes the use of renewable resources for synthesizing macromolecules. For example, biopolymers like cellulose, starch, and chitosan are derived from plants and other

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[4]- K. Boudraa. Thèse de magister, Option : physique des polymères UABB Tlemcen, 2006.

[5]-Joanna Rydz, and Al.., Polyester-Based Biodegradable Polymers as Environmentally Friendly Materials for Sustainable Development, Int.J.Mol.Sci,16(1),pp564-596,2015.

biological sources, reducing reliance on fossil fuels and decreasing the carbon footprint of the materials[6].

II.3.Non-toxic synthesis:

The goal of green chemistry's macromolecule production is to employ non-toxic solvents and reagents in order to reduce exposure to and waste from hazardous materials. This method makes use enzymatic reactions and water-based process, both of which are safer and better for the environment[7].

II.4.Energy efficiency:

Energy-efficient methods for the synthesis and manipulation of macromolecules are the aim of green chemistry. This involves the creation of catalysts with softer operating environments, which use less energy during chemical reactions and have a less overall negative influence on the environment[8].

II.5.Recyclable and Reusable Materials:

Designing macromolecules for recyclability and reuse is a key principle. This involves creating polymers that can be easily broken down and reconstituted into new products, thus promoting a circular economy and reducing waste[8]

II.6.Functional Biomaterials:

Green chemistry explores the development of functional biomaterials that can replace harmful chemicals. For example, biocompatible polymers are used in medical applications such as drug delivery systems and biodegradable sutures, offering safer alternatives to conventional materials[9].

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[6] -Josef Kollar, and Al.., Functional polymers and polymeric material from renewable alpha-unsaturated gamma-butyrolactones, Polymer chemistry, Frontier article, Vol7,2019.

[7] -Saleh O.Alaswad,andAl..,Recent advances in biodegradable polymers and their biological application: A brief review,Polymers,14(22), p4924,2022.

[8] -Joanna Rydz, and Al.., Polyester-Based Biodegradable Polymers as Environmentally Friendly Materials for Sustainable Development, Int.J.Mol.Sci,16(1),pp564-596,2015.

[9] -Josef Kollar, and Al.., Functional polymers and polymeric material from renewable alpha-unsaturated gamma-butyrolactones, Polymer chemistry, Frontier article, Vol7,2019.

III. Overview of polymer:

III.1.History[10]:

The word “polymer” was introduced by the Swedish chemist J. J. Berzelius. He considered, for example, benzene (C_6H_6) to be a polymer of ethylene (C_2H_2). Later this definition underwent a subtle modification.[11]

Polymer science, a new discipline, is concerned with plastics, natural and synthetic fibers, rubbers, coatings, adhesives, sealants, and other materials, which have become increasingly common.

One of the most significant concepts of the 20th century, polymers emerged in the 1920s during a period of prolonged controversy and is closely associated with H. Staudinger, whose Nobel Prize was awarded in 1953.

Synthetic polymers have multiple examples: some common, like polyesters or nylons, and some less known, such as those used in medical applications for organs, degradable sutures, and so on.

In the next “Table 1”, we have selected some important dates that marked the advance of a field in many of them corresponding to the discovery of new materials followed by their elaboration.

Table I.1: The most important stations in the history of polymer[12]

1838	A.PAYEN succeeded in extracting from wood a compound with the formula ($C_6H_{10}O_5$),cellulose.
1844	C.GOODYEAR develops the vulcanization of natural rubber
1846	C.SCHONBEIN obtains nitrocellulose,the first artificial polymer by the action of a sulfo-nutritive mixture on cellulose
1866	Mr. BERTHLOT discovers that the ″styrene ″, heated to 200°C for a few hours, turns into a resin polymer.
1883	H.CHARDONNET obtains artificial silk by slaughtering collodion based on anitrocellulose.

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[10]-Dorel Feldman, Polymer History, Designed Monomers and Polymers 11 (2008) 1–15.

[11] - J. W. Nicholson, Educ. Chem. 28, 70 ,1991.

[12]-J-M Lehm «Chimie et physico –chimie des polymères », SNEL S.A France .2001.P :1,7 .

1907	A.HAFMANN produces the first synthetic rubber by polymerization to conjugate diennes.
1910	L.BEKLAND develops the first industrial process for the production of conjugated diennes. From a synthetic polymer, formophenolic polymers are produced under the name ″Bakelia″.
1919	H.STAUDURGER introduced the notion of macromolecule and then realized the polymerization of many ethylene monomers.He can be considered the father of macromolecular science.
1925	T.SVEDBERG proves the existence of macromolecules by measuring their molar mass by ultracentrifugation.
1928	K.MEYER and H.MARK link the chemical structure to the crystallographic polymerization structure.
1933	The engineers E.FAWCET and R.GIBSON from ICI (UK) perform the radical polymerization of high-pressure ethylene.
1938	W.CAROTHERS (du pont de Nemours) et son équipe prépare le premier synthétique les polyamides (nylon).
1942	P.FLORY and M.HUGGINS propose a theory of solutions.Micromolecular.
1943	O.BAYER synthesizes the first polyurethane.
1947	TALFREY and C.PRICE propose R discovers the polymerization of ethylene under low pressure.
1954	G.NATTA obtains and identifies isotactic polypropylene.
1955	M.WILLIAMS, R.LANDEL and J.FERRY propose a relationship between time and the environment.chain relaxations and glass transition temperatures.
1956	M.SZWARC establishes the principles of "living" polymerizations based on work on anionic polymerization on styrene.
1957	A.KELLER obtained and characterized the first macromolecular monocrystals.
1959	J.MOORE developssterile exclusion chromatography.
1960	Discovery of thermoplastic elastomers and discovery of corresponding morphology.
1974	Development of aromatic polyamides by the Ferme du pont Nemours.
1980	W.KAMINSKY and H.SINN discovered the effect of aluminoxane, metallocene–started the polymerization of olefins.

1982	A team from Du pont de Nemours led by O.WEBSTER discovers the group transfer polymerization of acrylic monomers and gives time to a multitude of research studies on the control of the polymerisation of these monomeres.
1982	T.OTSU introduced the concept of control of radical polymerizations, this concept will be applied by ERJZZARDO and D.SOLOMON(1985)and then by M.GEORGE(1992)to controlled polymerization of styrene.
1986	D.TOMALLIA realizes the synthesis of the first dendrimers.
1992	D.TIRREL engineered the first perfectly iso-molecular polymer by engineering.
1994	Polymerization in bridge M.SAWAMOTO and K.MATYJA SZEWESKJ controlled by atonia transfer.
2000	After more than twenty years of work on intrinsic conductive polymers, H.SHIRSKAWA.UNJ.HEEGER A.G.MCDIARMID receives the Nobel Prize in Chemistry.The theory of chain copolymerization.

III.2.Definition :

III.2.1.Monomer :

Monomer is an organic substance used to synthesis oligomers or polymers may contain one or more chemical functions that are likely to participate in the polymerization reactions[13].

III.2.2.Oligomer:

Oligomers are low molecular weight polymers comprising a small number of repeat units whose physical properties are significantly dependent on the length of the chain. Oligomers are essentially intermediates of the polymerization reaction[14] .

III.2.3.Polymer :

The term polymer is derived from the ancient Greek word “Polus” which means many and “meros” which means parts[15]. Polymer is a class of natural or synthetic substances composed of a very large molecules called macromolecule obtained by the repitition of a constituent unit , also called a repeating unit or monomer , comprising a group of atoms [16]. Monomers are joined by covalent bonds .

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[13] -Ben-Aim Roger , and al ..,L’indispensableen polymers ,p14,2008.

[14]-G. Klaerner, R. Padmanabhan,Multi-Step/Step-Wise Polymerization of Well-Defined Oligomers,Material Science and Material Engineering , 2016.

[15]-Attanayake N.A.B, Chandrasiri M.T.M.S, Asela A.U, Pitawala H.M.J.C, Senevirathna M.A.S.R, Biopolymer: Structure,properties, extraction methods and applications , Sri Lankan Journal of Applied Sciences , Vol 1.1, 2022.

[16]-Anonyme, Zeigler.k, Stoddart.J.F, Mark.H.F, Marvel.C.S, Kuhn.W, Science Tech,

III.3.Type of polymer[17]:

There are two types of polymer:

III.3.1. Homopolymer: is a polymer derived from one species of monomer, such as vinyl polymers

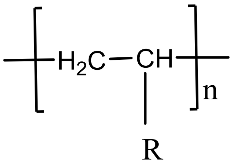


Figure I.2:example of homopolymer .

R: is a group that varies from one vinyl polymer to another.

III.3.2.Copolymer: is a polymer derived from more than one species of monomer,such as

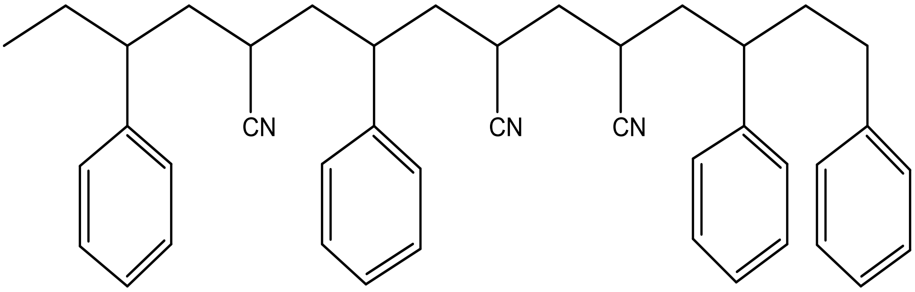


Figure I.3:example of copolymer (Poly (styrene-stat-acrylonitrile)

III.3.2.1.Block copolymer: block copolymer are linear copolymers in which the repeat units exist only in long sequences or block.

(– A – A – A – A – B – B – B – B – A – A – A – A – B – B – B – B –)

---

[17] -Robert.J ,Young , Petter.A ,level , Introduction to polymers ,Ed3,P(6 ,9) 2011.

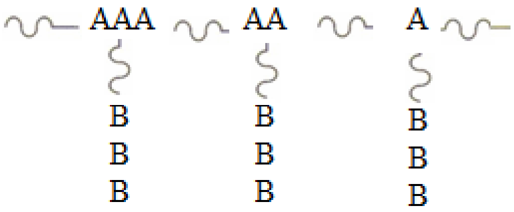
III.3.2.2.Statistical copolymers: are copolymers in which the sequential distribution of the repeat units obeys known statistical laws .

(– A – A – A – B – A – B – B – A – B –)

III.3.2.3.Alternate copolymers : Alternate copolymers consist of only two different types of repeat units arranged alternately along the polymer chain.

(– A – B – A – B – A – B – A – B –)

III.3.2.4.Graft copolymers: are branched polymers in which the branches have a different chemical structure to that of the main chain .



III.4.Structure of polymers:

III.4.1.Linear polymer:

Linear structure is the basic topological shape of polymer chains; the ensembly of linear polymers normally contains a specific distribution of chain lengths[18] .

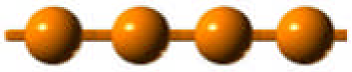


Figure I.4: linear polymer

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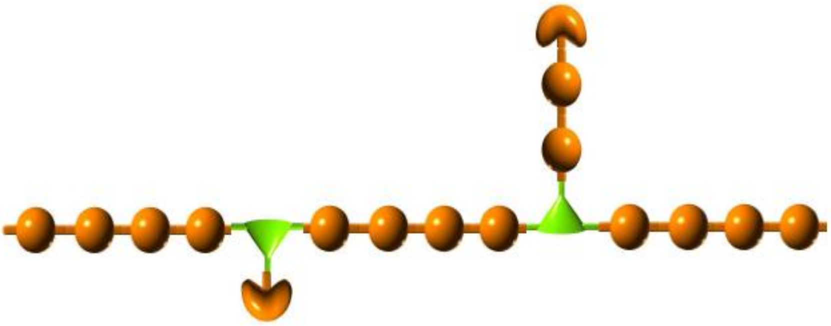
[18] -Wenbing.Hu , polymer physics A molucular approach , P 27,2013.

III.4.2.Branched polymers :

Branched polymers contain molecules having a linear backbone with branches emanating randomly from it. In order to form this class of material, the monomer must have a capability of growing in more than two directions, which implies that the starting monomer must have a functionality greater than 2[19].



FigureI.5:branched polymer

Linear and branched polymers are usually soluble in some solvent at normal temperatures .

III.4.3.cross-linking , network polymers :

When a multifunctional monomer is polymerized, the polymer evolves from a collection of linear chains to a collection of branched chains, ultimately forming a three-dimensional polymer that does not dissolve in any solvent, but it swells by incorporating molecules of the solvent into its own matrix[20].

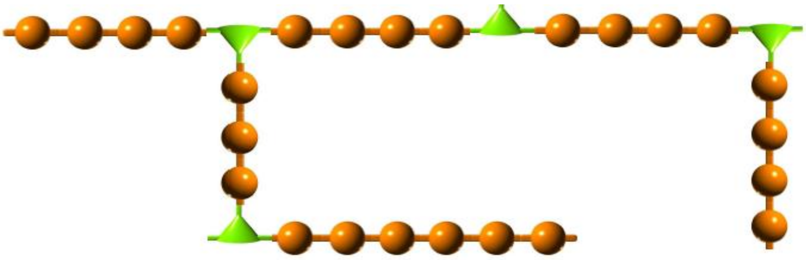


Figure I.6: cross-linking network polymer

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[19] -Anil Kumar, Rakesh.K.Gupta, Fondamental of Polymer Engineering,p5, New York ,Ed2, 2003.
[20] -Anil Kumar, Rakesh.K.Gupta, Fondamental of Polymer Engineering,p6, New York ,Ed2, 2003.

III.5.Classification of polymer :

III.5.1.Classification by nature of polymer[21]:

There are three types of classification under this category :

III.5.1.1.Natural polymers :

they are so numerous in nature ,so is common to divide them into plant, animal, or mineral origin .

III.5.1.2.Synthetic polymers :

Synthesis often produces structures that are similar to those of natural polymers even though monomer molecules do not exist in nature .

III.5.1.3.Semi-synthetic polymers:

The basic constituents are natural, but they are created through a chemical transformation of the functionc that carry the monomeric units .

For exemple : cellulose nitrate .

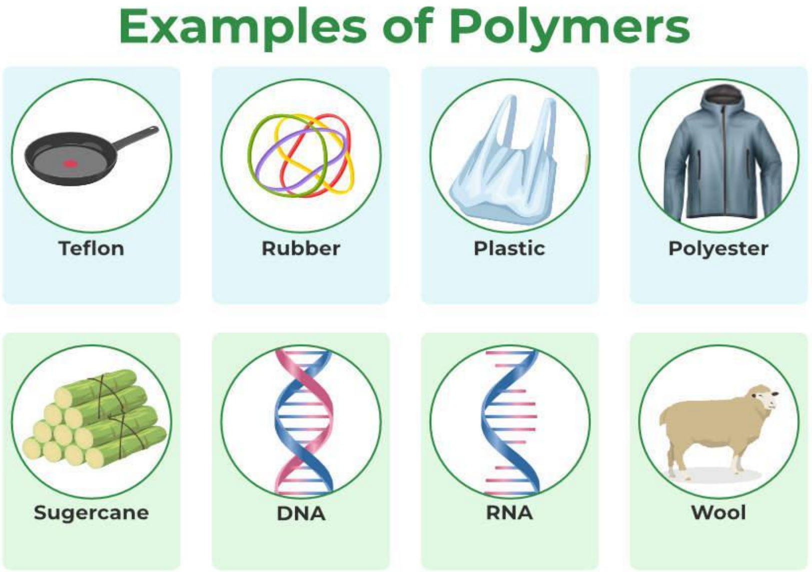

Figure I.7 :examples of natural and synthetic polymers

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[21]- C.Oudet , (Polymères, structures et propriétés , Introduction) , Masson, Paris,P1-3 , 1994.

III.5.2.Classification according chemical behavior:

III.5.1.Crystalline polymer:

A crystalline polymer is a highly ordered molecular structure that is stacked or aligned together[22],Completely crystalline polymers are rarely encountered.

III.5.2.Semi-crystalline polymer:

This term is used to refer to polymers that are partially crystalline[23], semi-crystalline polymers have crystalline and amorphous zones.

III.5.3. Amorphous polymer :

Amorphous thermoplastics are long-chain molecules that are oriented randomly, intertwined, and twisted. an amorphous polymer is in a glassy state, in which they are hard and brittle[24].

Both amorphous and semi-crystalline polymers are only degraded at extremely high temperatures.

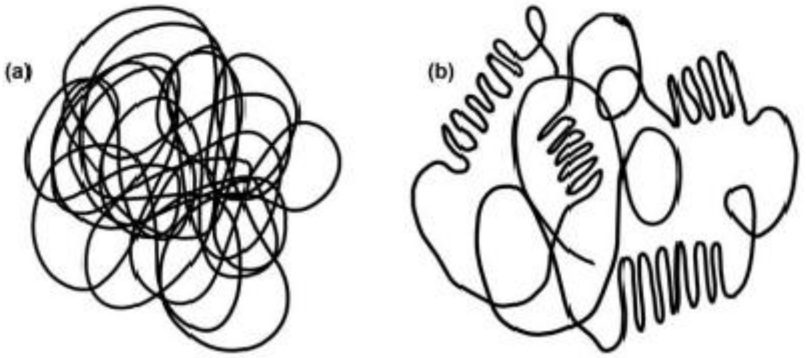

Figure I.8: (a) amorphous and (b) semi-crystalline polymer matrix .

III.5.3. Classification according thermal behavior:

III.5.3.1.Thermoplastics polymer[25] :

A thermoplastic is a polymer that softens and can be made to flow when it is heated. It hardens on cooling and retains the shape imposed at elevated temperature. This heating and cooling cycle can usually by repeated many times if the polymer is properly compounded with stabilizers.

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[22] -J. Wagner, E. Mount and H. Giles, in Extrusion, 2014, pp. 225–232.

[23] -George.Odian, Principales of polymerization, WeleyInterscience, New York, Ed4, p24,2004.

[24] - S. J. Dodd, J. V. Champion and A. S. Vaughan, Electrical breakdown of polymer glasses, in Encyclopedia of Materials: Science and Technology, Elsevier, pp. 7649–7654,2001.

[25] -AlfreidRudin, Phillip Choi, THE ELEMENTS OF POLYMER SCIENCE and ENGINEERING,Ed 3,P22,2013.

III.5.3.2.Elastomers polymer[26]:

Elastomers are a crosslinked rubbery polymers that can be stretched easily to high extensions and which rapidly recover their original dimensions when the applied stress is released. Thus extremely important and useful property is a reflection of their molecular structure in which the network is of low crosslink density. The rubbery polymer chains become extended upon deformation but are prevented from permanent flow by the crosslinks , and driven by entropy, spring back to their original positions on removal of the stress.

III.5.3.3.Thermosets polymer[27]:

A thermosetting plastic is a polymer that can be caused to undergo a chemical change to produce a network polymer, called a thermoset polymer. Thermosetting polymers can often be shaped with the application of heat and pressure, but the number of such cycles is severely limited .this polymer cannot be dissolved or heated to sufficiently high temperatures to permit continuous deformation, because chemical decomposition intervenes at lower temperature.

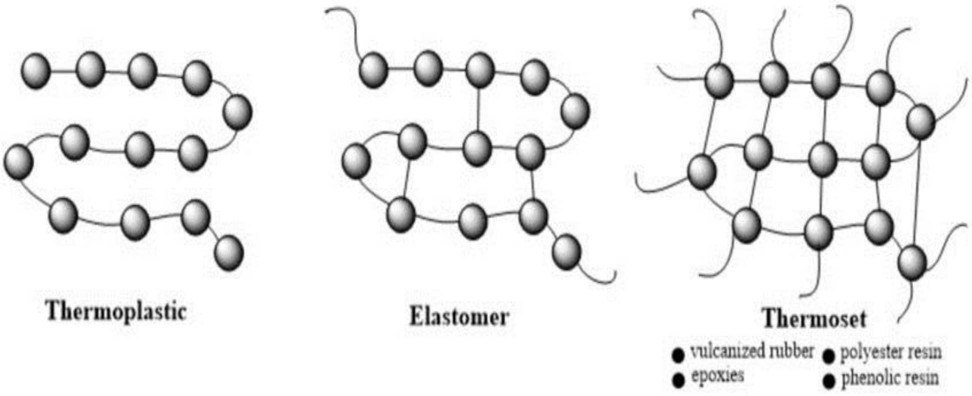

Figure I.9:thermoplastic, elastomer and thermoset polymer chain.

IV. Generalities of biopolymer:

IV.1.History :

Biopolymers are the organic substances present in natural sources. The term biopolymer originates from the Greek words bio and polymer, representing nature and living organisms. Large macromolecules made up of numerous repeating units are known as biopolymers[28].The

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[26]-Robert J.Young, Peter A.Lovell, Introduction to polymers, Ed3,P 10, 2011.

[27]-AlfreidRudin, Phillip Choi, THE ELEMENTS OF POLYMER SCIENCE and ENGINEERING,Ed 3,P22,2013.

[28] - T.A. Osswald, S.G. Rodrı´guez, History of sustainable bio-based polymers, in: S.K. Sharma, A. Mudhoo (Eds.), A Handbook of Applied Biopolymer Technology: Synthesis, Degradation and Applications, pp. 1-21,2011.

long chain of polymeric biomolecules is generally produced by living organisms like DNA, RNA . Cellulose and starch are the main building block materials of plants

These polymers have been on earth for billions of years as compared to synthetic plastics. Synthetic polymers have similar and random structures, whereas biopolymers are arranged in a well-defined structure. Hence, biopolymers involve the breakdown of large chains into smaller chains by the action of biological factors.[29]

Table I.2: some important dates that marked synthesis and advanced of biopolymers[30]:

1862	Alexander Parkes creates the first man-made polymer from an organic material derived from cellulose. It was a bio-based plastic and was called Parkesine.
1907	Leo Baekeland invents Bakelite and it will be described as a National Historic Chemical Landmark due to its importance. Bakelite was a synthetic plastic that was revolutionary for its electrical non conductivity and heat-resistant properties in electrical insulators, radio and telephone casings and such diverse products as kitchenware, jewelry, pipe stems, children's toys, and firearms.
1926	French scientist Maurice Lemoigne developed polyhydroxybutyrate (PHB) from bacterium Bacillus megaterium. The first bioplastics made from bacteria
1990	Imperial Chemical Industries (UK) developed a bioplastic that was biodegradable. It was called named Biopol. Commercial demand for bioplastics starts to develop, driven by oil price volatility and environmental concerns.

IV.1.Definition :

According to the International Union of Pure and Applied Chemistry (UIPAC), biopolymers are bio-macromolecules synthesized by living organisms and according to the definition of the ADEME (Environment and Energy Management Agency), they are natural polymers derived from renewable resources of plants, algae or animals[31].

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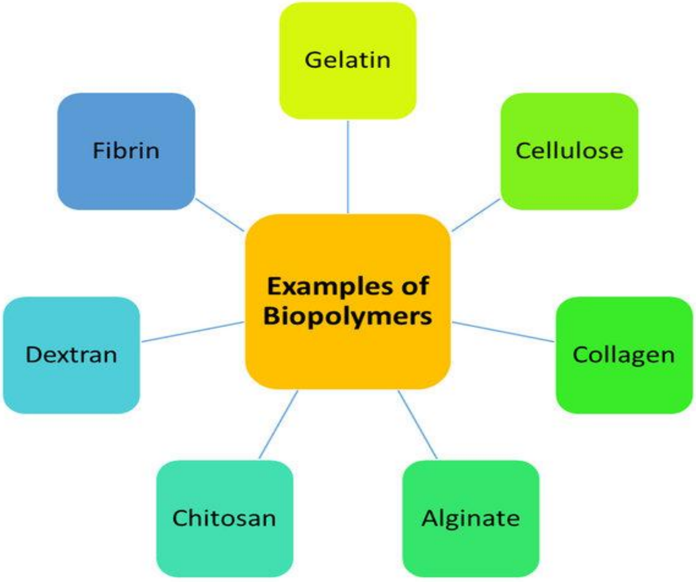
[29] - A. Guzman, N. Gnutek, H. Janik, Biodegradable polymers for food packagingefactors influencing their degradation and certification typesea comprehensive review, Chem. Chem. Technol. 5, 115-122,2011.

[30] -Bioplastics and Biopolymers. (2013, December 17). Bioplastics News. https://bioplasticsnews.com/bioplastics/

[31] - Boudouaia.N, Modification, caracterisation et valorization d'un materiaux d'origine naturelle le chitosane pour la dépollution des eaux , 2020.

Biopolymers are polymeric resins derived from bio-based raw materials, such as biomass like sugarcane or corn. They are biodegradable or compostable under environmental influences, and their biodegradability is directly correlated to the polymer's chemical structure[32][33].



FigureI.10: examples of biopolymers .

IV.2. Source of biopolymers:

Biopolymers can be found in various natural sources such as plants, animals, microorganisms, and agricultural wastes. Plant sources include rice, maize, wheat, sorghum, yams, cassava, potatoes, banana, tapioca, corn, cotton, and barley. Animal sources include cats, corals, sponges, fish, lobster, and shrimp. Microbiological sources include algae, fungus, and yeasts. Carbohydrate-rich biomass-based sources include agro leftovers, paper wastes, crops, green wastes, and wood waste. Vegetable oils, such as sunflower, soybean, safflower, jojoba, rapeseed, castor, and meadowfoam oil, are excellent alternatives for natural polymer synthesis. PHAs, secondary metabolites generated by microbes and plants, are stored as inclusion bodies in bacteria and can be melted and shaped like chemical and synthetic thermoplastics[34].

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[32] - Endres H.J., Siebert-Raths A., Engineering Biopolymers: Markets, Manufacturing, Properties ans Applications. Hanser, Munich; 2011.

[33]- Anonymous.Whatarebioplastics? Material types, terminology and labels-an introduction. www.european-bioplastics.org (Accessed Date: 22/11/2013).

[34]- Amit.K, Antonella.F, Brajesh.B, Jaya.B, Giovanna.L.D,Biopolymer: A Sustainable Material for Food Medical Application,polymers 2022,14(5),983.

IV.3.Classification of biopolymers :

Biopolymers include diverse materials that are classified in numerous ways. They can be classified according to their origin as either structure based or process based . Biopolymers classified according to their origin are plant origin such as alginate, starch polyisoprene and so on; animal origin such as polylactic, polybutylene succinate, polyhydroxyalcanoates (PHAs) and so on; bacterial fermentation products like chitosan, collagen, chitin, and sericin . The structure of monomer unit-based biopolymer classification is polysaccharides, polynucleotides, and polypeptides. Proteins can be classified as enzymes (such as polypeptide) and structural proteins(such as collagen and gelatin)[35]. polysaccharides such as cellulose, chitin, starch, and so on . polynucleotides such as DNA and RNA . Polysaccharides are biopolymers that consist of monosaccharide units linked together by glycosidic bonding. The four types of polysaccharide biopolymers are sugar-based, starch-based, cellulose-based, and lignin-based.

Sugar based biopolymer: biopolymers based on sugar can be produced by blowing, vacuum forming injection, and extrusion. Lactic acid polymers (Polyactides) are created from milk sugar (lactose) which is extracted from maize, potatoes, wheat and sugar beet. Polyactides, manufactured by methods like vacuum forming, blowing and injection molding, are resistant to water[36].

Starck based biopolymer: This polymer is naturally present as granules in plant tissue and is readily available in large quantities, originating from potatoes, maize, wheat, tapioca, and similar sources. The modification of starch can make it thermoplastic, making it suitable for conventional plastic-forming processes like injection molding and extruding[37][38].

Cellulose based biopolymer: for making packaging material , Glucose is the primary component of plant cellulose walls, and it is obtained from natural sources like cotton, wood, wheat, and corn[39].

Lignin biopolymer : Lignin comprises another important biopolymer but not of polysaccharide origin[40].

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[35]-Endres H.J., Siebert-Raths A., Engineering Biopolymers: Markets, Manufacturing, Properties ans Applications. Hanser, Munich; 2011.

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IV.3.Type of biopolymers :

IV.3.1.Conventional polymers:

These polymers are related to the conventional thermoplastic resins such as PE, PP, PET, PS or even Poly(vinyl chloride) (PVC). They are obtained from petrochemical raw materials (non renewable) and are not biodegradable[41][42].

IV.3.2.Biodegradable bio-based polymer made from renewable raw materials:

These polymers can be produced by either biological systems (microorganisms, animals,

and plants) or synthesized chemically from biological starting materials (e.g., corn, sugar, starch, etc.), they include:

- Synthetic polymers from renewable resources: such as poly (lactic acid) (PLA).

- Biopolymers produced by microorganisms: such as PHAs.

- Natural occurring biopolymers: such as starch or protein[43].

IV.3.3.Non-biodegradable bio-based polymers made from renewable raw materials:

These biopolymers can be produced from biomass or renewable resources and are non-biodegradable, they include :

- Renewable resource’s synthetic polymers such as specific polyamides from castor oil (polyamide 11), bio polyethylene (bio-LDPE, bio-HDPE), bio polypropylene (bio-PP), or bio poly (vinyl chloride) (bio-PVC), etc.

- Natural occurring biopolymers such as natural rubber or amber[44].

IV.3.4.Biodegradable polymers made from fossil fuels:

These biopolymers are produced from fossil fuel, such as synthetic aliphatic polyesters made from crude oil or natural gas, and are certified biodegradable and compostable. PCL, poly (butylene succinate) (PBS), and certain “aliphatic–aromatic” copolyesters are at least partly fossil fuel-based polymers, but they can be degraded by microorganisms[45].

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[41]- Endres H.J., Siebert-Raths A., Engineering Biopolymers: Markets, Manufacturing, Properties ans Applications. Hanser, Munich; 2011.

[42]-. [3] Endres H.J., Siebert A., Kaneva Y., Overview of the current biopolymers market situation. Bioplastics Magazine. 2007; 2.

[43]- Niaounakis M. Biopolymers: Reuse, Recycling, and Disposal. [chapter 2]; section 2.5. 1st ed. Plastics Design Library (PDL); Access Online via Elsevier.p. 432 .2013.

[44]- Vroman I., Tighzert L., Biodegradable polymers. Materials, 2, 307–344 ,2009.

IV.4.Biopolymer properties:

IV.4.1.Biodegradation of biopolymers:

The term 'biopolymers' refers to polymers made of organic matter that can naturally decompose after use. With the assistance of microorganisms like bacteria, algae, and fungi in the natural environment, these polymers break down or fragment into their basic constituent compounds, including water, carbon dioxide (CO_2), humic materials, biomass, and minerals. This decomposition process alters the polymer's chemical structure, physical characteristics, and mechanical properties. The factors that facilitate this conversion includethe ideal temperature, humidity, and oxygen content. The process is sometimes called ultimate aerobic biodegradation[45].

Table I.3: Factors affecting biodegradation of biopolymers 46.

Factors affecting biodegradation process		
Environmental conditions		Physical properties of polymers
Abiotic factors	Biotic factors	Molecular weight ,Size and shape ,crystallinity functional groups ,cross-linking , blend, copolymers additives .
Temperature, pH, Moisture ,UV radiation .	Hydrophobicity, Extracellular,enzymes, Nuterients, Biosurfactants.	

IV.4.2.Copostability of biopolymer :

Composting is a predominantly aerobic process and can be considered as nature's way of recycling. ASTM defines composting as a process where biodegradable materials, such as manure and leaves, are decomposed and transformed into a humus-like substance called compost, CO_2 , water and minerals by microorganisms through a controlled biological process[47], meaning without leaving toxic substances to the atmosphere . thecompostale products can also degrade by the mechanism of enzymes . For exemple PLA is suitable for both methods to degrading completely[48] .

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[45]-Systems, P.,.Bioplastic Labels and tags, Portland: s.n .2012.

[46] -Basak N, Meena SS. Microbial biodegradation of plastics : challenges, opportunities, and critical perspective .Front Environ SciEng 2022;16:1–22.

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[48]-Jane Gilbert, M.R, An overview of the compostability of biodegradable plastics and its implications for the collection and treatment of organic wastes,s.l:ISWA-the international solid waste association, 2015 .

IV.4.3.Biocompatibility and bioresorbability of biopolymers :

Biocompatibility may be defined as :

“*ability of a biomaterial to perform its desired function with respect to a medical therapy, without eliciting any undesirable local or systemic effects in the recipient or beneficiary of that therapy, but generating the most appropriate beneficial cellular or tissue response to that specific situation, and optimizing the clinically relevant performance of that therapy*.[49]

The compatibility of a material with an organism is defined as its ability to coexist without causing adverse effects. This is becoming increasingly important in the evaluation of dental and medical materials and equipment. Biocompatibility encompasses physical, mechanical, chemical, as well as potential cytotoxic, mutagenic, and allergenic effects. Studies in pharmaceutics, biology, chemistry, and toxicology are necessary to determine the biocompatibility of materials. Clinical trials and in vitro assays must be conducted until these propertiesare established.[50][51][52]

IV.4.4.Chemical properties:

Molecules derive their properties from their chemical activities, in addition to their ability to engage in molecular interactions. They can react due to functional groups such as alcohols, acids, amines, or aldehydes, which provide nucleophilic and electrophilic sites. Specific chains containing unsaturations and hydroxyl groups, such as alkyls and triglycerides, can facilitate the production of polymers such as polyamide, polyurethane, or polyester. Subsequent modifications can alter the physical characteristics and mechanical properties of these polymers, influencing their applications.[53]

IV.5. Biopolymers application :

IV.5.1.Synthesis of nanomaterials[54]:

Nanotechnology focuses on synthesizing nanoparticles using eco-friendly processes, shifting from physical and chemical methods to "green" chemistry and bioprocesses. Metal nanoparticles have unique properties but pose environmental risks due to toxic reducing agents. Green chemistry approaches are desirable for waste minimization and sustainable processes.

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[54]-SnehaMohan,and All.,Biopolymers:Application in Nanoscience and Nanotechnology,Recent Advances in Biopolymer,2016.

Biopolymers like chitosan, heparin, and gelatin can replace toxic regents in nanoparticle synthesis.

IV.5.2.Medecine:

Biopolymer-based composites have been used for the delivery of drugs against various diseases. Their excellent characteristics due to biocompatibility, biodegradability, hemocompatibility, nonimmunogenicity, stability in physiological conditions, and nontoxicity makes them a potent candidate for drug delivery. Biopolymers have the capability to functionalize with specific ligands and encapsulate hydrophobic as well as hydrophilic drugs to achieve a controlled and targeted release of drug at the desired site of action [55]. Besides, they have the ability to protect the integrity of the drug and provide stability because of their structure and complexity.

Biopolymers are used in various medical applications such as gene therapy, tissue engineering, including bone, cartilage, skin, vascular graft, implantable devices inclusive of barrier membrane, stents, and encapsulated medicines [56].

IV.5.3.Agriculture:

Biopolymers can be used as an excellent alternative to synthetic pesticides. They can be used in fertilizers, pesticides, and biocides by incorporating biodegradable polymers. They can be used for forest fire lighting formulation, fishing lines, traps, artificial baits, cures and aquaculture [57]. Certain synthetic polymers tend to affect the soil characteristics, therefore the primary concern is the use of polymers that could be sustainable and keep intact the properties of soil.

IV.5.4.Cosmetics:

In the modern era, biopolymers find wide applications in cosmetics, for example, soy meal-based particles provide improved color profiles. Similarly, biopolymers can be incorporated in cleaning products, sunscreen, manicure preparation, biodegradable packaging, scrubbing agents, and so on. The main advantage of using biopolymers in cosmetics is that they are nontoxic and nonskin irritant[58].

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[55]-S.S.D. Kumar, N. N Houreld, H. Abrahamse, Biopolymer-based composites for medical applications, in: S. Hashmi, I.A. Choudhary (Eds.), Encyclopedia of Renewable and Sustainable Materials,United States, pp. 20e28,2020.

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[58]-M. Niaounakis, Cosmetics, Biopolymers: Applications and Trends, first ed., William Andrew Publishing, United States, 2015.

IV.5.5.Papermaking and textile:

In the papermaking industry, biopolymers are used to enhance the strength of paper sheets, provide strong bonding, improve antibacterial activity, and increase brightness and tensile strength. In the textile industry, biopolymers serve as eco-friendly materials aimed at enhancing the durability of fabrics[59].

IV.5.6.Food packaging[60] :

In recent years, significant advancements have been made in utilizing nanomaterials to modify polymers, enhancing mechanical strength, flexibility, heat resistance, barrier properties, and other attributes of natural or synthetic polymers used in food packaging. Various types of nanocomposite materials have been developed for this purpose, including starch nanocomposites, montmorillonitenanocomposite films, cellulose nanocomposites, protein nanocomposites, and poly(lactic acid) nanocomposites. These materials improve the antimicrobial properties, mechanical strength, flexibility, heat resistance, and barrier properties of food packaging.[61]

IV.5.8.Water purification:

Safe drinking water is a significant yet simple indicator of development. Biopolymers offer numerous advantages in water treatment due to their biocompatibility, biodegradability, and versatility. They exhibit excellent adsorption capacities, flocculation abilities, and antimicrobial properties, making them suitable for various water treatment processes. Recently, researchers have focused on biopolymeric nanocomposite materials, which show promise in diverse water treatment applications. These materials combine biopolymers derived from renewable resources with nanofillers, enhancing performance and efficiency. Incorporating nanofillers into biopolymers opens new opportunities to improve their mechanical strength, increase surface area, enhance stability, and customize functionalities. These synergistic combinations enable biopolymeric nanocomposites to address specific water treatment challenges, such as the removal of heavy metals, organic pollutants, and microorganisms[62].

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[59]-M.B. Kasiri, Application of chitosan derivatives as promising adsorbents for treatment of textile wastewater, in: S. ul-Islam, B.S. Butola (Eds.), The Impact and Prospects of Green Chemistry for Textile Technology, Woodhead Publishing, United States, pp. 417e469,2019.

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V. Polymer and biopolymer synthesis:

V.1.Chain growth polymerization (polyaddition)[63]:

The monomers must contain at least one double bond in order to perform addition polymerization. Furthermore , polymerization produces no by-product and does not destroy any molecules, the molecular weight of the formed polymer is exactly the same as the sum of all monomers inclThe monomers must contain at least one double bond to undergo addition polymerization. Furthermore, this process produces no by-products and does not destroy any molecules; the molecular weight of the resulting polymer is exactly the sum of all monomers involved in the polymerization. There are three steps in normal chain-growth polymerization: initiation, propagation, and termination. However, in many cases, a fourth step, namely chain transfer, is also included.uded in the polymerization .there tree steps in normal chain growth polymerization : initiation, propagation and termination. However , in many cases a fourth step namely chain transfer also included.

Initiation :during initiation, the monomer acquires an active site to become a free radical, the addition of initiators or other approaches such as absorption of heat, light or irradiation can trigger the initiation process .

$$I + M \longrightarrow M^*$$

I :initiator.

M: monomer.

Propagation :propagation involves the quick addition of new monomers by the initiated monomers , this process keeps going until the active site which is constantly moved to the end of the developing chain during propagation is deactivated through chain termination or chain transfer.

$$M^* + (M)_n \longrightarrow (M)_n\,M^*$$

Termination :this step involves the reaction of polymer chain radical with another free radical .

$$(M)_n\,M^* \longrightarrow (MM)_n$$

Chain transfer : in chain transfer the growing activity of a polymer chain is transferred to previously inert species.

Chain polymerizations are also classified according to the type of chain carrier or active site:

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[63] -Min Wang, Lin Guo, HaoranSun , Manufacture of biomaterials, Enclopedia Of Biomedical Engenering,1,2019.

V.1.1.Radical polymerization[64]:is a type of addition polymerization , where the polymer is formed by successive addition of building block to propagating radical chain. the process can be initiated in a number of ways, but most commonly involves the presence of species which decompose into radicals, known as initiators.

V.1.2.Ionic polymerization[65]:ionic chain polymerization is a chain-growth reaction where the active center is charged, either negatively (anionic), or positively (cationic). Anionic polymerization is essentially limited to those monomers bearing electron-withdrawing groups, whereas cationic polymerization to those monomers possessing electron-releasing substituents.

V.1.3.Coordination polymerization [66] :are used to obtain polymers with a high stereospecificity, using special catalysts like Zeigler-Natta .

V.1.4.Living polymerization[67]:a form of addition polymerization employed for synthesis of block copolymers where two or more monomores are polymerized sequentially in which exact control over molecular weight are made possible by the active chain ends remaining active .

V.2. A step growth polymerization (polycondensation):

A Polycondensation reaction refers to a type of polymerization mechanism in which bifunctional or multifunctional monomers react to from first dimers, then trimers, longer oligomers, and eventually long-chain polymers[68]. This indicates the difficulty of controlling molecular hight weight. Large numbers of synthetic and naturally polymers are obtained by step-growth polymerization (SGP) such as polyamides, polyethers, polyesters, polyurea, polyurethanes and polyimides.[69]

There are two types of polycondensation :

V.2.1.Successive addition and elimination reactions:

These are reactions that occur with elimination of condensation product (by-product) such as synthesis of polyamid 6,6 .

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[64] -Konstantinov.I V, Broadbelt.JL,Computional Quantum Chemistry, P17-46,2019.

[65] -Pitsikalis.M, Ionic polymerization, molecular sciences and chemical engineering,2013.

[66] -Hasirci.V, YilgorHuri.P, EndoganTanir.T, Eke.G, Hasirci.N, Comprehensive Biomaterial II,Vol 1, P478-506,2017.

[67] -ToshinobuHigashimura, MitsuoSawamoto,Comprehensive Polymer Science and Supplements , Vol 3, P673-696,1989.

[68] -Bernard E.ObiPhD,Polymeric Foams Structure-property-performance , A Design Guide,pp17-40,2018.

[69] -T. Yokozawa and A. Yokoyama, Polymer journal, 2004, 36, 65-83.

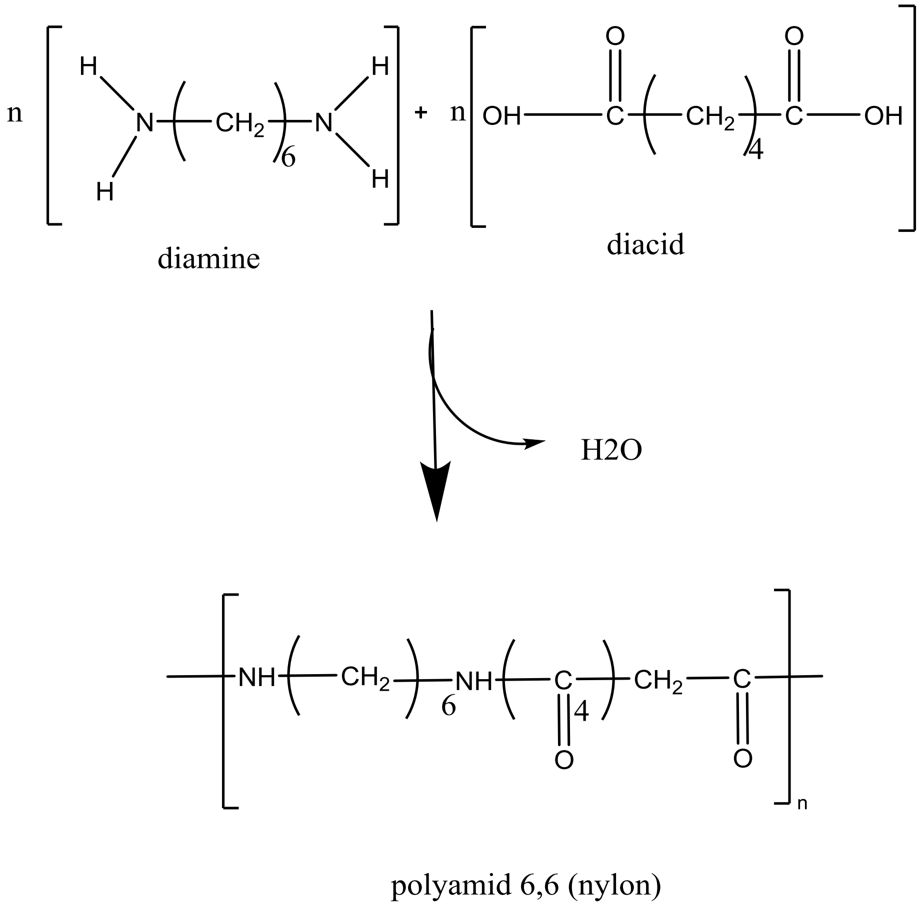

Figure I.11:synthesis of nylon 6,6.

V.2.2.Raction without elimination of a by-product :

Such as reaction of polyurethane :

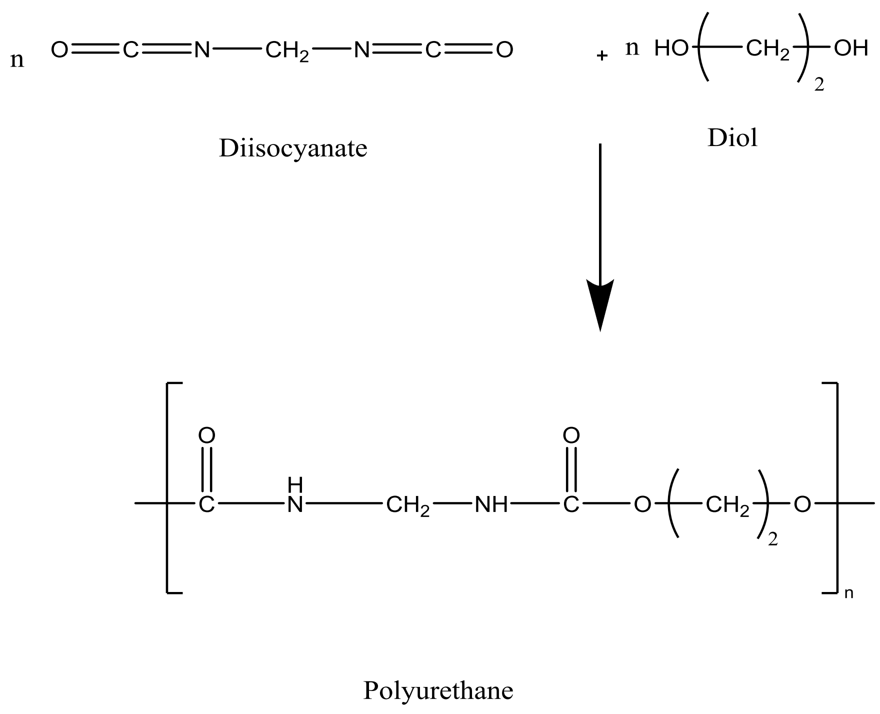

Figure I.12: Synthesis of polyurethane.

Table I.3: comparison of step-reaction and chain-reaction polymerization.70

Step polymerization	Chain polymerization
Growth occurs throughout matrix by reaction between monomers, oligomers, and polymers	Growth occurs by successive addition pf monomer units to limited number of growing chains
$\overline{DP}$ low to moderate	$\overline{DP}$ can be very high
Monomer consumed rapidly while molecular weight increases slowly	Monomer consumed relatively slowly, but molecular weight increases rapidly
No initiator needed; same reaction mechanism throughout	Initiation and propagation mechanism different
No termination step, end groups still reactive	Usually chain-terminating step involved
Polymerization rate decreases steadily as functional groups consumed	Polymerization rate increases initially as initiator units generated; remains relatively constant until monomer depleted

VI. Water pollution :

VI.1. Overview of water:

Water is one of the key elements of the environments that determine the survival of life;It dominates a majority of the space on our planet, covering about 71% of the total surface area of Earth. Water is a transparent colorless chemical substance with one oxygen atom covalently bonded to two hydrogen atoms[71].

Overseas and inland surface and sub-surface water systems play an incredible role in everyday life activities mainly for drinking, agricultural, Industrial, recreational, and other public uses. Our everyday lives depend on the availability and quality of water[72]. This implies the need to protect water, it must be treated whether to produce clean water for consumption or industrial uses or to limit releases in the natural environment[73].

VI.2.Water contamination:

VI.2.1.Chemical pollution[74]:

This type of pollution results from excessive amounts of products of mineral origin (such as heavy metals, cyanides, etc.), which are mostly soluble in water to some extent, and products of organic origin (like hydrocarbons, pesticides, etc.) that can be dissolved by bacteria present in the water. Alternatively, they may not dissolve, leading to the death of living organisms even at very low concentrations.

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[70]-Malcolm P.Stevens, Polymer Chemistry : An Introduction, New York, P15,1999.

[71]-P. Senthil Kumar, P.K. Yaashikaa, Water in Textiles and Fashion, pp1-20, 2019.

[72]-MamuyeTebebalEjigu, Overview of water quality modeling, CIVIL and ENVIRONMENTAL ENGENEERING,P2,2021.

[73]-Jerom Monod.

[74]-SuaadHadi Hassan Al-Tai,Water pollution its causes and effects, First International Virtual Conference on Environment & Natural Resources ,IOP Conf. Series: Earth and Environmental Science,2021.

VI.2.2.Physical pollution:

Both organic and inorganic materials suspended in water can cause physical pollution. The taste, smell, and color of water are all altered by these pollutants. The high temperature caused by dumping cool factory and nuclear reactor water into bodies of water is one type of physical pollution. It damages aquatic life and causes a drop in the amount of dissolved oxygen[75].

VI.2.3.Thermal pollution:

Thermal pollution is classified as a water pollutant when it is caused by heated industrial wastewater or anthropogenic (human) changes in coastal vegetation that increase water system temperatures due to solar radiation.

A common cause of thermal pollution is the use of water as a coolant in power plants and industrial producers[76].

VI.2.4. Radioactive pollution :

Nuclear activity and the attempt to dispose of nuclear waste increase the risk of this kind of pollution. It is possible for radioactive materials to leak into bodies of water, where they are then absorbed by living things and passed on to people, having a variety of genetic effects[77]. The natural radioactivity of the water is directly related to the geological nature of the terrain what cross-section, contact time, temperature, solubility, of the elements encountered,etc. epidemiological studies to date have not shown a link between levels of radioactivity in drinking water and increased risk of digestive cancer or leukemia[78].

VI.2.5.Heavy metals:

Lead, mercury, cadmium, and arsenic are the most prevalent heavy metals in the environment. It is possible to combine the compounds of the mineral mercury with both soil and water. Mercury compound contamination results in inflammation of the kidneys and gingivitis, sleeplessness, psychological depression, and forgetfulness in addition to disruptions in the central nervous system. Many industries, including the production of batteries and plastics, use cadmium. Chromium poisoning of water causes problems with the kidneys, lungs, heart, and bones. Lead factories that manufacture batteries are also one of the main causes of lead pollution[79].

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[75] -Ewaid, S.H., Abed, S.A., Water quality index for Al-Gharrafriver, southern Iraq. Egypt. J. Aquatic Res. 43 (2), 117–122,2017.

[76] -James G.Speight, Sources of water pollution, Natural Water Remediation, Chemistry andTechnology ,pp165-198,2020.

Technology, pp. 165-198,2020.

[77] -Ewaid, S.H., Abed, S.A.,Water quality index for Al-Gharraf river, southern Iraq. Egypt. J. AquaticRes. 43 (2), 117–122,2017.

[78] -Safiamiloudi. Activites Antibactérienne des Monomères et des Résines Phénoliques Synthétisées contenant des différents groupements fonctionnels, THESE DE DOCTORAT, p3, 2021.

[79] -Ewaid, S.H.; Abed, S.A.; Al-Ansari, N. Crop Water Requirements and Irrigation Schedules for Some Major Crops in Southern Iraq, 11, 756, Water 2019.

VI.2.6.Bio-pollution:

Biological contamination includes vital pollutants such as pathogenic bacteria, viruses, and parasites and protistas. The sources of these pollutants are human and animal excreta. They are transferred to the water when it mixes with sewage or agricultural drainage water, causing human infection with many diseases such as cholera[80].Biological organisms can enter to the body through drinking water. Water contamination by these organisms can be related to the contamination of the water itself or water may infect during the piping phase[81].

VI.3. Methods of treatment of contamined water:

Water treatment methods are broadly classifiable into physico-chemical and biological processes:

VI.3.1.Physico-chemical treatment:

VI.3.1.1.Sedimentation:

Sedimentation, a fundamental and widely used unit operation in contaminated water treatment, involves the gravitational settling of heavy particles suspended in a mixture. This process is used for the removal of grit, particulate matter in the primary settling basin, biological floc in the activated sludge settling basin, and chemical flow when the chemical coagulation process is used. Sedimentation takes place in a settling tank, also referred to as a clarifier. There are three main designs, namely, horizontal flow, solids contact and inclined surface[82].

VI.3.1.2. Flotation :

Flotation is a unit operation that involves the introduction of a fine gas, typically air bubbles, to remove solid or liquid particles from a liquid phase. The gas bubbles increase the buoyant force of the combined particle and gas bubbles because they either stick to the liquid or become trapped in the suspended solids' particle structure. This allows particles with a density greater than that of the liquid to rise. Flotation is primarily used to concentrate biological sludge and remove suspended matter in waste-water treatment processes. The main benefit of flotation over sedimentation is the faster and more thorough removal of very light or tiny particles. The particles can be skimmed out after they have floated to the top.

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[80] -Ewaid, S.H.; Abed, S.A.; Al-Ansari, N. Crop Water Requirements and Irrigation Schedules for Some Major Crops in Southern Iraq, 11, 756,Water 2019.

[81] -HiroBehnam, SoheilSaeedfar, FarzanehSabbaghMojaveryazdi, Biological Contamination of the Water and Its Effects, Technology, Education, and Science International Conference (TESIC),p2,2013.

[82] -AksheyBhargava, Physico chemical Waste Water Treatment Technologies: An Overview, International Journal of Scientific Research And Education,Vol5,p5311,2016.

VI.3.1.3.Filtration:

The filtration of effluents from waste-water treatment processes involves removal of suspended solids from waste-water effluents of biological and chemical treatment processes, in addition to the removal of chemically precipitated phosphorus. The complete filtration operation comprises two phases: filtration and cleaning or backwashing.

VI.3.1.4.Screening:

The screening of waste-water, one of the oldest treatment methods, removes gross pollutants from the Waste stream to protect downstream equipment from damage, avoid interference with plant operations and prevent objectionable floating material from entering the primary settling tanks. There are many types of screening; coarse screens (remove large solids, rags, and debris), finescreens (Reduce suspended solids to primary treatment levels), Very fine screens (Reduce suspended solids to primary treatment levels)and Micro screens(Upgrade secondary effluent to tertiary standards)[83].

VI.3.1.5.Ozonation:

Ozonation is a useful technique for pH-range water disinfection .Ozonation lowers the concentration of inorganic elements like sulfur, iron, and manganese, which eliminates the taste of water. Ozonation is rather costly and calls for advanced operational procedures and techniques[84].

VI.3.1.6.Chlorination:

The most popular, low-cost, and efficient chemical process for a variety of uses is chlorination, which can be used to deactivate pathogens like Rotavirus, Salmonella, Shigella, Escherichia coli, adenoviruses, and Pseudomonas aeruginosa species in wastewater, swimming pool water, and drinking water. The chemical chlorine is frequently used to disinfect water, and research has been done on what happens to it once it is in the water. Nonetheless, the only active disinfection method that is utilized worldwide is chlorination; chlorine's ability to disinfect water is dependent on both substitution reactions involving chlorine and the oxidizing power of free oxygen atoms. Certain pathogens, such as the protozoan parasites Giardia and Cryptosporidium, as well as protozoan cysts and eggs, have been found to be resistant to chlorine even at high concentrations CL, despite the fact that chlorine effectively disinfects a variety of microbes[85].

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[83] -AksheyBhargava, Physico chemical Waste Water Treatment Technologies: An Overview, International Journal of Scientific Research And Education,Vol5,p5310,2016.

[84] -Sabina Ziembowicz,Małgorzata_Kida, Science of the total environment, vol929,2024.

[85] -Mahendren.B, Bondili.JS, Pardhasaradhi.M, Water chlorination and his relevance to human health,vol 8,1,2015.

VI.3.1.7.Coagulation and flocculation[86]:

The chemical coagulation (conventional) is best method for removal of organic; if dose of the coagulant and adjustment of pH in optimal range. Thein creasing dose of the coagulant can achieve the best results for the removal of organic. Alum dose and pH are very important variables in industrial wastewater treatment process[87]. Coagulation-flocculation is particularly employed for effective removal of colloidal sized particles[88].

VI.3.1.8. Ion-exchange:

Ion-exchange is a major water treatment process where one or more than one ionic pollutants are eliminated from water by substitute with other less objectionable or non-objectionable ionic material. Both the substituted and contaminant material have to be softened plus have the equivalent electrical charge (negative or positive).A typical illustration of ion exchange Progressive Water Treatment is a procedure which is commonly known as water-softening which is used to eliminate magnesium plus calcium content. But, ion exchange is also resourceful in eliminating noxious metals from water[89].

VI.3.1.9.pH adjustment[90]:

The pH of the medium strongly influences on the solution of many substances. Low pH increases the solubility of heavy metals and hence their toxicity. So, increase in pH values leads to significant changes in solution composition as a result of the decreased solubility of many elements. Neutralization (or pH control) is the most common treatment of AMD. It means that metals precipitate from AMD as pH increases[91]. The pH plays a critical role in precipitation of heavy metals. Active and passive treatments are two approaches to remove pollutants in AMD remediation, both based on using an agent to precipitate metals by increasing pH and alkalinity[92].

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[86]-Panhwar.A, Kandhro.A, Qaisar.S, Gorar.M, Sargani.E, Khan.H, Chemical Coagulation: An Effective Treatment Technique for Industrial Wastewater,Turkish Journal of Agricultural Engineering Research,2(2),pp508-516,2021.

[87]-Sahu OP and Chaudhari PK, Review on chemical treatment of industrial waste. Journal of Applied Science and Environmental Management. 17(2): 241-257,2013.

[88]-Teh CY, Budiman PM, Shak KPY and Wu TY, Recent advancement of coagulation–flocculation and its application in wastewater treatment. Industrial Engineering Chemical Research,55(16): 4363-4389,2016.

[89]-Ahmadpari.H,Tavazoei.A, Taghavi.M, Parhamfar.M,Application of ion exchange technology in water treatment,2022.

[90]-Parissa Mehrpour,and al, Experimental pH adjustment for different concentrations of industrial wastewater and modeling by Artificial Neural Network,Environmental Technology & Innovation, Vol31,2023.

[91] -Favas P.J.C., et al.Acid mine drainages from abandoned mines: hydrochemistry, environmental impact, resource recovery, and prevention of pollution,Environmental Materials and Waste, Elsevier, pp. 413-462,2016.

[92]-Ighalo Joshua O., *et al.*A review of treatment technologies for the mitigation of the toxic environmental effects of acid mine drainage (AMD)ProcessSaf. Environ. Prot., 157, pp. 37-58,2022.

VI.3.2.Biological treatment:

Wastewaters contain parasites with potential zoonotic potential. The use of antibiotics in medicine increases antibiotic-resistant bacteria, which enter the environment through human feces and animal manure. These bacteria are emerging environmental pollutants, posing risks to aquatic ecosystems and food chains, for mitigating the spread of antibiotic-resistant bacteria and ensuring environmental safety. Various treatment methods have been studied for their effectiveness in reducing antibacterial agent and resistance genes[93]. Conventional treatment which includes the activated sludge systems; they consists of maintaining an active floc in a tank supplied with oxygen so that maximum contact is made between the incoming waste water and the microorganisms in the floc, this process can reduce some antibiotic concentrations but they are not sufficient to completely eliminate them[94], primary and secondary treatment; these stages remove partially antibiotic and antibacterial agents[95].Advanced oxidation processes which includes ozonation; ozone is An excellent disinfectant of drinking water, they have ability to inactivate even more resistant pathogenic microorganisms[96]. UV radiation can dismantle antibiotic molecules and inactivate bacteria cellules[97]. Fenton reaction for treating water with hydrogen peroxide and iron catalysts[98]. Membrane technologies(microfiltration, ultrafiltration, nanofiltration and reverse osmosis), conststructed weltands , bioaugmentation , biomediation and adsorption process , all of this techniques are effective for antibacterial activity.

VII.Over view of bacteria and anti-bacterial activity of biopolymer:

VII.1.Bacteria:

Bacteria are a large group of single-celled phylogenetically related prockaryotes distinct from archea. They are ubiquitous, growing in soil, water, extreme environments, and deep in the each crust[99].

VII.2.Bacteria structure[100]:

There are two major structural classes of cells:

VII.2.1. Eukaryotic cells: are found in the phylogenetic domain Eukarya. This group includes plants and animals as well as diverse microbial eukaryotes such as algae, protozoa, and fungi.

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[93]-Papajova.Ingrid,and al.., Effect of Wastewater Treatment on Bacterial Community,Antibiotic-ResistantBacteria and Endoparasites ,MDPI Journal , Vol19 ,2023.

[94]-Englande.A.J, Krenkel.Peter A, Waste water Treatment and Water Reclamation, Encyclopedia of Physical Science and Technology,Ed3,pp639-670,2003.

[95]-Al-Gheethi.A.A, and Al ..,Removal of pathogenic bacteria from sewage-treated effluent and biosolids for agricultural purposes,Applied water science ,Vol8,74,2018.

[96]-Ferdes.M, and Al..,effect of ozone treatment on three bacterial strains of drinking water, engineering for rural development, 23,2018.

[97]-Maria Turtoi, ultraviolet light potentiel for wastewater disinfection, Annals, Food science and Technologie,2013.

[98]-Saloua Biyada, Mohammed Merzouki,Earthworm Technology in Organic Waste Management,pp339-357,2024.

[99]-Ricardo.A ,and All.., Encyclopedia of Astrobiology, pp 137-139, 2011.

[100]-Madigan.M.T, Martinko.J.M ,Bender.K.S,Brock Biology of Microorganisms,Ed15,2018.

Eukaryotic cells contain an assortment of membrane-enclosed cytoplasmic structures called organelles. These include, most prominently, the DNA-containing nucleus but also mitochondria and chloroplasts, organelles that specialize in supplying the cell with energy, and various other organelles.

VII.2.2.Prokaryotic cells: are found in the domains Bacteria and Archaea. Prokaryotic cells have few internal structures, they lack a nucleus, and they typically lack organelles .The prokaryotic cell structure evolved prior to the evolution of the eukaryotic cell. While Archaea and Bacteria both contain exclusively prokaryotic cells, these groups have diverged greatly and we will see later that the Archaea actually share many molecular and genetic characteristics with cells of Eukarya.

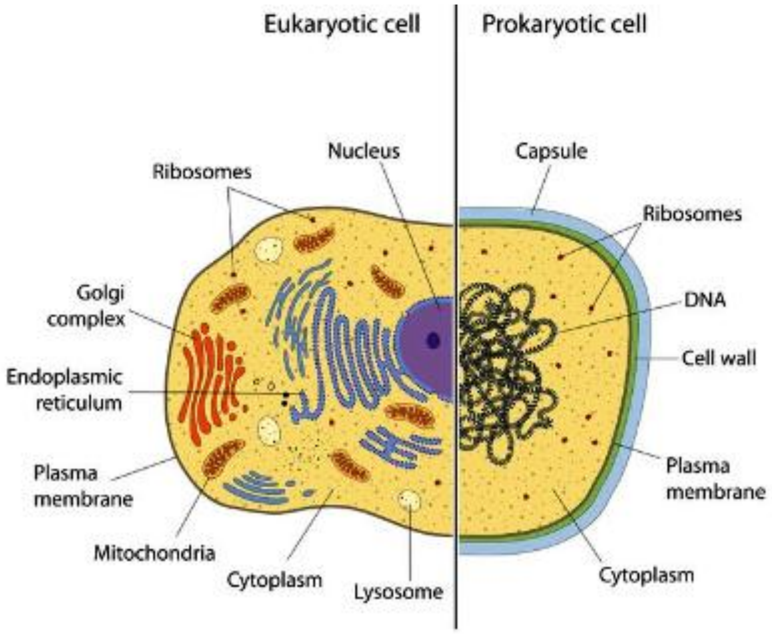

Figure I.13: Eukaryotic cell and Prokaryotic cell.

VII.4.Classification of bacteria:

Bacteria are classified by the following criteria:

VII.4.1.Morphologie[101]:

Bacteria have various shapes including; cocci (from kokkos meaning berry) are spherical or oval cells, bacilli (from baculus meaning rod) are rod shaped cells, vibrios are comma shaped curved rods and derive their name from theircharacteristics vibratory motility, spirilla are rigid spiral forms, spirochetes (from speira meaning coil and chaite meaning hair) are flexuous spiral forms, actinomycetes are branching filamentous bacteria, so called because of a fancied resemblance to the radiating rays of the sun when seen in tissue lesions (from actis meaning ray and mykes meaning fungus), and mycoplasmas are bacteria that are cell wall deficient and

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[101]- MoshtaqTalip Al-Mohanna, Bacterial introduction, 2016.

hence do not possess a stable morphology. They occur as round or oval bodies and as interlacing filaments.

VII.4.2.Staning:

Trough the interaction of bacteria with the gram stain, they are classified into two types: gram negative and gram positive bacteria .

VII.4.2.1.Gram negative:

The gram negative bacteria stain red when gram stain applied to them[102], they are usually highly adaptable organisms with strongly developed synthetic capabilities . They can often be grown on simple media containing a carbon source such as glucose, an inorganic source of nitrogen, and small quantities of suitable mineral salts. Their cytoplasm has a relatively low osmolarity since these bacteria do not strongly concentrate nutrients and metabolites [103].

VII.4.2.2.Gram positive:

The gram positive bacteria stain blue when gram stain applied to them[104], they tend to be more exacting in their nutritional needs. They have less well-developed synthetic abilities and require various amino acids, vitamins and accessory factors for growth. They are usually cultivated on rich, undefined broths or on fairly elaborate synthetic media. They concentrate amino acids, nucleotides and other metabolites of low molecular weight in their cytoplasm and consequently have a high internal osmolarity[105].

VII.4.3.Encapsulation[105]:

Some bacteria are enclosed in capsules; for some encapsulated bacteria (eg, Streptococcus pneumoniae, Haemophilusinfluenzae), the capsule helps protect them from ingestion by phagocytes. Encapsulation increases bacterial virulence.

VII.4.4.Oxigen requirement[106]:

Microorganisms have variable oxygen requirement for growth. Based on oxygen requirement, organisms are classified into four types:

VII.4.4.1.Aerobes :are capable of growing at full oxygen tension and many can tolerate elevated levels of oxygen (greater than 21%).

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[102]-Larry.M.Bush, Overview of Gram-positive Bacteria, MSD;MANUAL Consumer version,2023.

[103]-Franklin.T.J, Snow.G.A, Biochemistry of Antimicrobial Action , Ed2, p23-24,1975.

[104] - Larry.M.Bush, Overview of Gram-positive Bacteria, MSD;MANUAL Consumer version,2022.

[105]-Brian.J.Werth, Overview of Bacteria ,MSD;MANUAL Professional version,2022.

[106]-Singh.S.P, Kaur.S, Singh.D, Food Safety in The 21st Century, pp111-127,2017.

VII.4.4.2.Microaerophiles:are aerobes that can use oxygen if only it is present at reduced levels in air.

VII.4.4.3.Facultative organisms: under appropriate nutrient and culture conditions, can grow in either aerobic or anaerobic conditions.

VII.4.4.4.Anaerobes:lack respiratory systems and thus cannot use oxygen as the final electron acceptor. There are two types of anaerobes:

a.Aerotolerant anaerobes can tolerate oxygen and grow in its presence even though they cannot use it.
b.Obligate anaerobes are killed by oxygen. Obligate anaerobes are unable to detoxify some of the by-products of oxygen metabolism. Anaerobes lack the enzymes, which aerobes have that decompose toxic oxygen products.

VII.5.Antibacterial activity of biopolymer:

An antimicrobial agent can be defined as an agent that kills microorganisms or inhibits their growth,they emerge as a possible alternative to eliminate or reduce possible microorganisms. Biopolymer as a antimicrobial agent are essential to daily life as our human forms are based on them .These polymers are found widely in nature or extracted from plants or animals or synthesis them . they exhibit high biocompatibility, biodegradability, accessibility,stability, lack of toxicity, and low cost and They incorporate antimicrobial agents . Biopolymers have been extensively studied as carriers of antimicrobial agents. . The synergic union between antimicrobial agents and polymers can form new materials known as composites The most common fillers with antimicrobial activity are metals, chemicals, essential oils (EOs), natural extracts, and NPs, which make it used as drug carries, for food packaging because they are recognized as safe materials for food in coating in air contact and other application[107].

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[107]-Moises Bustamante-torres, and Al.. ,Antimicrobial Activity of Composites-Bases on Biopolymers,Macromol,2:(3),pp 258-283,2022.

Part II : Experimental part

The devices used

Bench kofler :

The kofler bench is an offline apparatus for microscopy in that the bench contains a metal strip With temperature gradient ranging from 50°C to 260°C The temperature is controlled by placing a sample at a certain location of the bench and after heating the sample is examined by a light microscopy.[108]

Figure II.1: apparatus of bench kofler

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[108] -Stephen R.Byen and All: Solid-state properties of pharmaceutical matarials,p 144,2017.

pH meter apparatus :

pH meter, electric device used to measure hydrogen-ion activity (acidity or alkalinity) in solution. Fundamentally, a ph meter consists of a voltmeter attached to a ph-responsive electrode and a reference (unvarying) electrode. The ph- responsive electrode is usually glass, and the reference is usually a silver-silver chloride electrode, although a mercury- mercurous chloride (calomel) electrode is sometimes used. When the two electrodes are immersed in a solution, they act as a battery. The glass electrode develops an electric potential (charge) that is directly related to the hydrogen-ion activity in the solution , and the voltmeter measures the potential difference between the glass and reference electrodes[109].

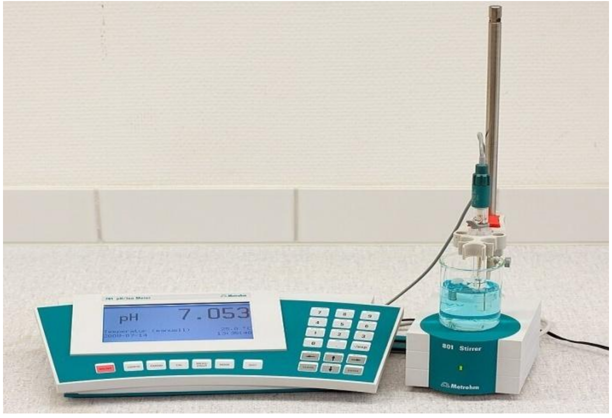

Figure II.2:pH meter apparatus

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[109] -Anonymous,https://www.britannica.com/science/hydrogen-ion

Product and materials

Table II.1: the main products used

Product	Molar mass	Melting point	Boiling point	Solubilityand miscibility
Terephthalic acid $C_8H_6O_4$ (ALDRICH sigma)	166.132 g/mol	402°C		Soluble in DMSO, DMF and bases
Formaldehyde CH_2O (BIOCHEM chemopharma)	30.026 g/mol	-92°C	-19.5°C, 98°C(solution 37%)	Soluble in Acetone , benzene ,ether , diethylique ,alcool
D-glucose $C_6H_{12}O_{60}$	180.155g/mol	146°C 150°C		Water
XyleneC_8H_{10}	106.16g/mol	-25°C	144.43°C	Soluble in Non-polar solvents
Potassium hydroxide KOH	56.105g/mol	380°C	1324°C	Soluble in Water
Sodium aluminate$NaAlO_2$	81.970g/mol	1650°C		Soluble in Water
ChlorhydriqueacidHCl (35-38%) (BIOCHEM chemopharma)	37.4 g/mol	-30°C (solution 37%	48°C	
MethanolCH_3OH	32.042g/mol	-97.6°C	64.7°C	Miscible with water
Ethanol C_2H_5OH	46.068g/mol	-144°C	79°C	Miscible with water , soluble in polar and non-polar solvents
AcetoneC_3H_6O	58.079g/mol	94.6°C	56.05°C	Miscible with water, ethanol, esters, chloroforme and most of oils

DMSOC_2H_6OS	78.133g/mol	18.5°C	190.85°C	Miscible with only organic solvents
THF C_4H_8O	72.105g/mol	-108.5°C	66°C	Miscible with water
DMF C_3H_7NO	73.093g/mol	-61°C	153°C	Miscible with water
Tetrachloromethane CCl_4	153.81g/mol	-22.92°C	76.72°C	Soluble in alcohol, ether chloroform, benzene formic acid, CS_2, Naphta
Chloroform $CHCl_3$	119.378g/mol	-64°C	62°C	
DichloromethaneCH_2Cl_2	84.933g/mol	-95.1°C	40°C	Miscible with acetone , ether and oher solvents , non-miscible in water
Cyclohexane C_6H_{12}	84.159g/mol	6.47°C	80.75°C	Soluble in alcohol, ether, acetone

The main material used

.Balance

.Becker

.Buret

.Erlenmeyer

.Filter paper

.Funnel

.Magnetic bar

.Heating mantle

.Magnetic stirrer with heating

.Spatula

.Stand

.Thermometer

.Morter and pestle

.Watch gals

.Bicol flask

.Petri dish

.Bromine funnel

.Crystallizer

.Graduated cylinder

.Condenser

.Ultrasonic cleaner

.Vials

I.Introduction :

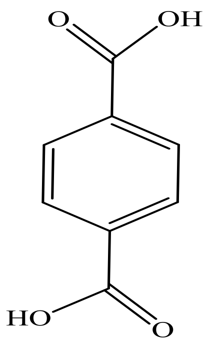
Green synthesis emphasizes following a reliable and eco-friendly pathway with mild reactions, utilizing nontoxic precursors, and producing a lower amount of wastes to ensure a sustainable environment. As a result of this green chemistry, the design and synthesis of novel products that are safe, reusable, and biodegradable are now taking place[110].

The focus of this section is on the study of synthesized products in the laboratory , starting with the synthesis of a toxic product (polymer) and progressing through all stages until obtaining a purely non-toxic product (biopolymer), taking into account the concept of green chemistry.

II. Review of uses product (monomers and bases):

II.1. Properties of terephthalic acid[111] :

Terephthalic acid (TPA) , also known as 1,4-benzenedicarboxylic acid. Terephthalic acid is made by air oxidation of p-xylene .it is a white crystalline , density= 1.519g/cm”3, acidity(pKa)=3.54,4.34[112].



FigureII.3 : molecular structure of TPA.

1,4-benzenedicarboxylic acid is the main component in the polyester industry for the production of polyester terephthalate . the production of PET uses In great proportion of the terephthalic acid produced worldwide, terephthalic acid has other applications such as in textiles, in polyester staple fibers and filament yarns, as a carrier in paints, a coating resin, and as a raw material in the pharmaceutical industry.

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[110] -Chitra Devi Venkatachalam, and al ..,Nanomaterials Application in Biofuels and Bioenergy Production Systems, Pages 79-96,2021.

[111] -Hugo M.Lapa, LuissaM.D.R.S.Martins, p-Xylene Oxidation to TerephthalicAcid : New Trends,Molecule,p1,2023.

[112] -anonymous :https://en.wikipedia.org/wiki/Terephthalic _acid

II.1.1. Solubility test of TPA.

0.0002g of terephthalic acid in 1ml of solvent

Table II.2: Solubility test of terephthalic acid

Water	Methanol	Ethanol	Aceton	Chloroform	Cyclohexane	Dichloromethane	DMSO	DMF	THF
Insoluble	Insoluble	Insoluble	In-Soluble	Insoluble	insoluble	insoluble	soluble	soluble	insoluble

II.2. Properties of formaldehyde:

Formaldehyde is an organic compound also known as Methanal, is a pungent, colourlessgaz who stored as aqueous solution .methanal is the simplest of the aldehydes with a chemical formula CH_2O, density 0.815 g/cm^3, acidity (pKa) 13.27(hydrate).

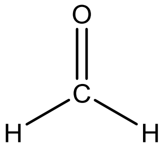

Figure II.4: molecular structure of formaldehyde

Formaldehyde is used in the production of formaldehyde resins, particleboard, paper, plywood, and urea-formaldehyde foam. It is an important precursor to other chemical compounds, especially polymers. Formaldehyde is used extensively in the cabinet-making industry as well as wood-working. The major industrial consumers of formaldehyde resins are molded plastic parts, decorative laminates and photographic film[113].

II.3. Properties of D-glucose:

Glucose, also called dextrose, belongs to a group of carbohy-drates known as simple sugars (monosaccharides). Glucose is a white crystalline with a sweet taste, it has the molecular formula $C_6H_{12}O_6$ (isomers) with linear or cyclic structure.

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[113]-Abdollahi, M., Hosseini, A., Formaldehyde. In: Wexler, P. (Ed.), Encyclopedia of Toxicology, ed3,vol 2. Elsevier Inc., Academic Press, pp. 653–656,2014.

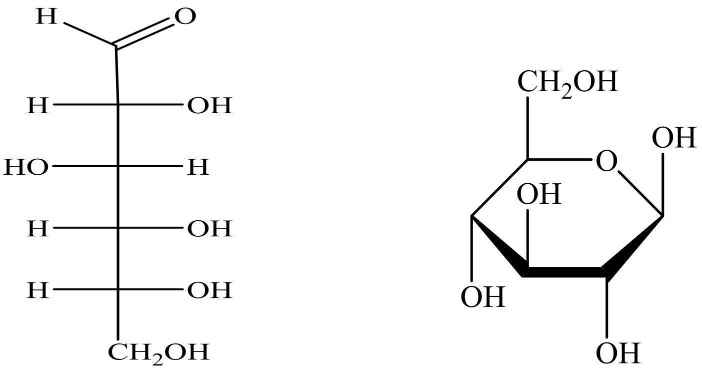

Figure II.5: linear and cyclic molecular structure of D-glucose

D-glucose is found in fruits and honey and is the major free sugar circulating in the blood of higher animals. It is the source of energy in cell function, and the regulation of its metabolism is of great importance[114].

II.4. Properties of KOH :

Potassium hydroxide is an inorganic compound which is denoted by the chemical formula KOH. Potassium hydroxide is an alkali metal hydroxide is a very powerful base. The aqueous form of potassium hydroxide appears as a clear solution. In its solid form, KOH can exist as white to slightly yellow lumps, flakes, pellets, or rods. No characteristic odour can be attributed to this compound in its solid state[115].

II.5. Properties of $NaAlO_2$:

Sodium aluminate,also known as sodium dioxoalumanuide is an odorless white powdered solid with molar mass 81.970 g/mol.Toxic by ingestion and corrosive to tissue. Used in water purification[116].

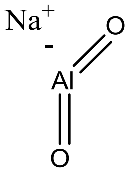

Figure II.6:molecular structure of $NaAlO_2$

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[114] -Shendurse A.M., and KhedkarC.D.,Glucose: Properties and Analysis. In: Caballero, B., Finglas, P., and Toldrá, F. (eds.) The Encyclopedia of Food and Health vol. 3, pp. 239-247. Oxford: Academic Press,2016.

[115] -Anonymous, http://byjus.com/chemistry/potassium/hydroxide

[116] -Anonymous,https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-aluminate

Table II.3: Solubility test of NaAlO2

Water	Acetone	methanol	ethanol	Chloroform	DMSO
Soluble	Insoluble	insoluble	insoluble	Insoluble	Insoluble

III. Study synthesis of polymer TPA/F:

III.1.Study of molar ratio factor and temperature on the polymer TPA/F reaction:

III.1.1. Syntheses with temperatureAt 25°C ,50°C and 80°C:

At 25°C ,50°C and 80°C no reaction occurred .

III.1.2. Synthesis with temperature increase of more than 80°C of polymer TPA/F:

In clean and dry vial , we put in each one a mixture of tarephthalic acid , formaldehyde and KOH , mix them with a magnetic stirrer with heating for a well defined time .

The product is washed with solvent to eliminate monomer ,filtred then allowed to dry .

III.1.3. Variation of molar ratio with temperature increase of more than 80°C of polymer:

In clean and dry six vials, we put in each one a mixture of tarephthalic acid , D-glucose and KOH, mix them with a magnetic stirrer with heating for a well defined time .

The product is washed with solvent to eliminate monomer ,filtred then allowed to dry .

Yield = $(m_{poly}/m_{mono})100$

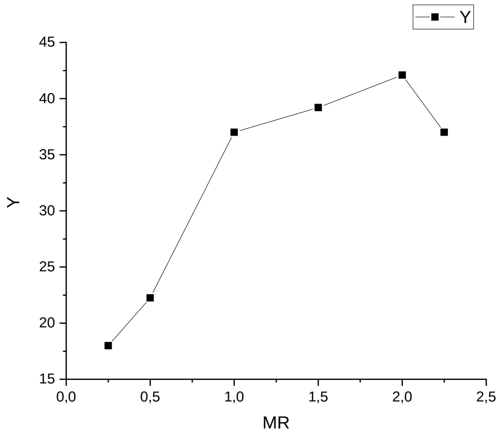


Figure II.7: yeild evolution of tests according to molar ratio

III.1.2. Synthesis with temperature increase of more than 80°C of polymer ATP/F with changing of percentage of the base (KOH):

In clean and dry six vials, we put in each one a mixture of tarephthalic acid , formaldehyde and KOH , mix them with a magnetic stirrer with heating for a well defined time .

The product is washed with solvent to eliminate monomer ,filtred then allowed to dry .

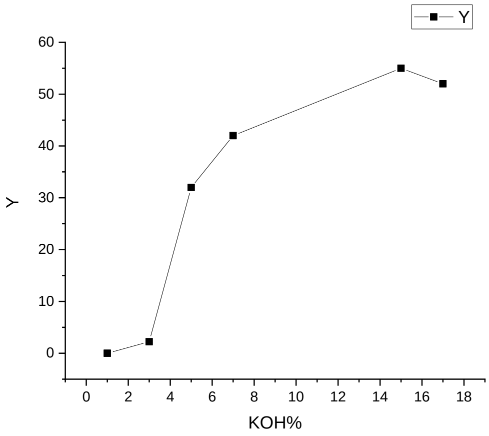


Figure II.8 :yeild evolution of tests according to the percentage of KOH

Yeild = $(m_{poly}/m_{mono})100$

IV. Synthesis of polymer :

IV.1. Synthesis of polymer TPA/F with homogeneous base (KOH):

To a mixture of 0.013 mol of terephthalicacid , formaldehyde and Potassium hydroxide in a bicol flask fitted with a dean-starck are refluxed in an inert medium at 120°C . after a moment of reaction add 20ml of p-xylene using a dropping funnel , increase the temperature and let it heat up for a while (5hours of reaction).

The product is washed with solvent to eliminate impurities ,filtred then allowed to dry .

A. Reaction schema :

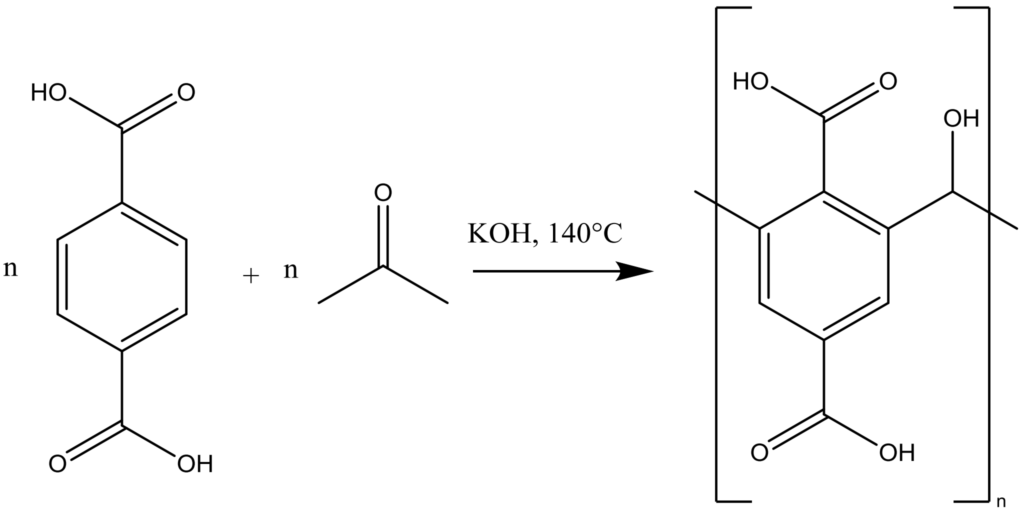


Figure II.9: reaction schema of polymer TPA/F with homogeneous base

B.Solubility test :

Table II.4: solubility test of the product obtained :

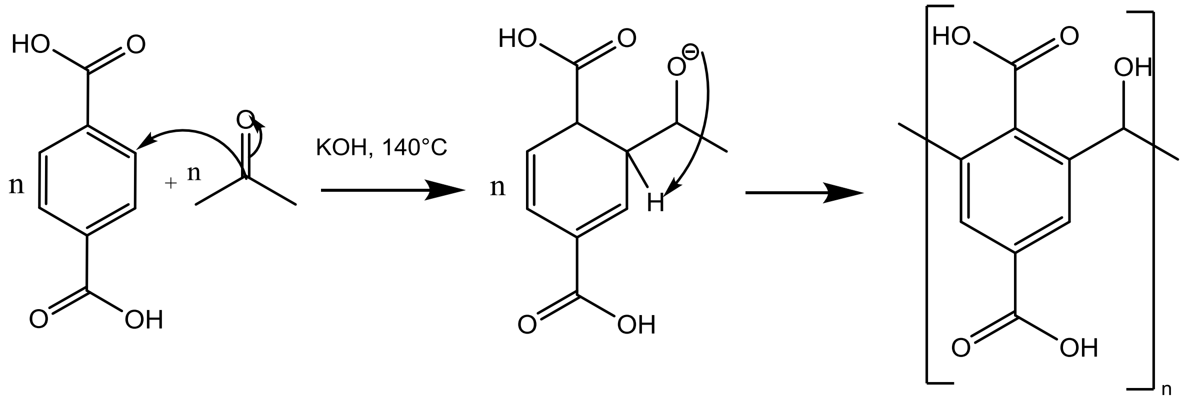
Water	Acetone	Ethanol	methanol	CCl_4	$CHCl_3$	CH_2Cl_2	DMSO	THF
Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	insoluble	Insoluble

Yield obtained :

$Y = (m_{exp}/m_{theo})100$

Y=77.83%

C.Mechanism reaction :



FigureII.10 : mechanism reaction of polymer TPA/F with homogeneous base(KOH)

V.Synthesis of polymer in green chemistry :

V.1.Synthesis of polymer TPA/F with a heterogeneous base ($NaAlO_2$) :

To a mixture of 0.013 mol of terephthalicacid ,3.5 ml of formaldehyde and Sodium aluminate in a bicol flask fitted with a dean-starck are refluxed in an inert medium. after a moment of reaction add 10ml of p-xylene using a dropping funnel , increase the temperature and let it heat up for a while .

The product is washed with solvent to eliminate impurities ,filtred then allowed to dry .

Table II.5: yield of synthesis with heterogeneous base $NaAlO_2$

Percentage of $NaAlO_2$	1%	3%	5%	7%	10%	15%
Yield %	2%	7%	66%	69%	70.9%	73%

$$Yeild = \left(\frac{m_{poly}}{m_{mono}}\right).100$$

A.Reaction schema:

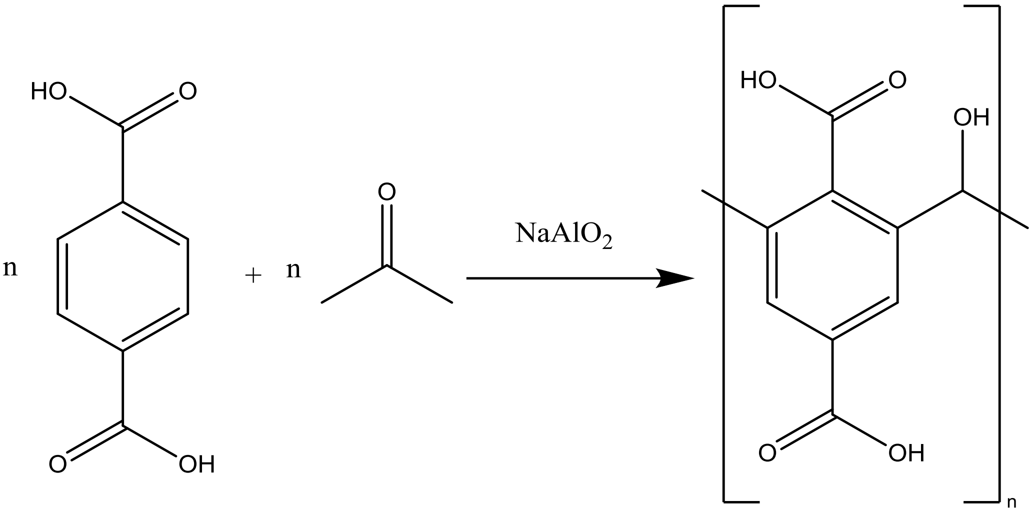


Figure II.11 : reaction schema of polymer TPA/F with a heterogeneous base $NaAlO_2$

B. Solubility test:

Table II.6: solubility test of product obtained TPA/F with $NaAlO_2$

Water	**Methanol**	**Ethanol**	**Acetone**	**CCl_4**	**$CHCl_3$**	**CH_2Cl_2**	**DMSO**
Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble

C.Mechanism reaction:

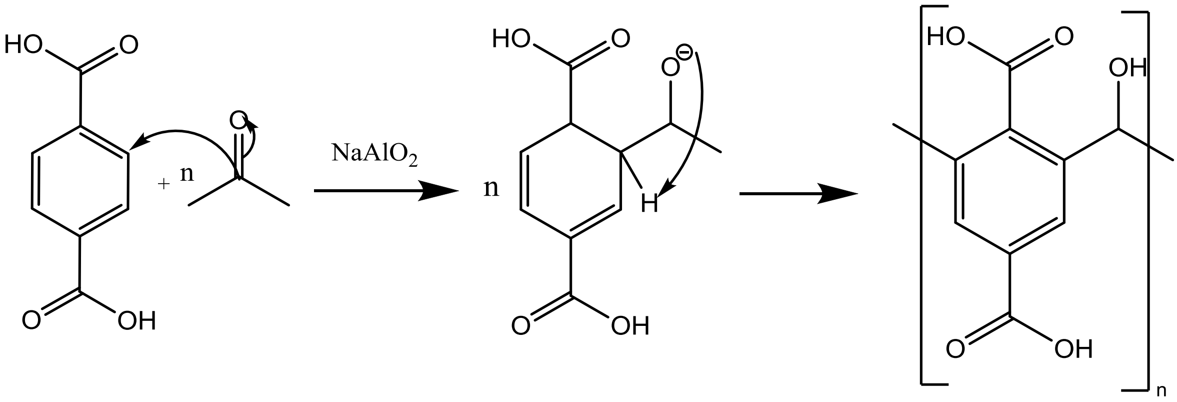


Figure II.12:mechanism reaction of polymer TPA/D-g with heterogenous base($NaAlO_2$)

V.2.Syntheses of polymer TPA/D-g with HCl :

V.2.1. Synthesis with HCl as a excess catalyst :

To a mixture of 0.01 mol of terephthalicacid , 0.004 mol of D-glucose in a bicol flask fitted with a dean-starck are refluxed in an inert medium. after a moment of reaction add 7ml of hydrolic acidusing a dropping funnel , increase the temperature and let it heat up for a while .

The product is washed with solvent to eliminate impurities ,filtred then allowed to dry

V.2.2. Synthesis with HCl as a catalys:

To a mixture of 0.005mol of terephthalicacid , 0.0024 mol of D-glucose and one drop of HCl in a bicol flask fitted with a dean-starck are refluxed in an inert medium. after a moment of reaction increase the temperature and let it heat up for a while .

The product is washed with solvent to eliminate impurities ,filtred then allowed to dry .

Solubility test :

Table II.7: solubility test for polymer obtained TPA/D-g with HCl:

Water	Insoluble	**CH_2Cl_2**	Insoluble
Ethanol	Insoluble	**CH_3Cl**	Insoluble
Methanol	Insoluble	**Cyclohexane**	Insoluble
Acetone	Insoluble	**DMSO**	Insoluble
CCl_4	Insoluble	**DMF**	Insoluble
$CHCl_3$	Insoluble	**THF**	Insoluble

Yield obtained :

$Y = (m_{exp}/m_{theo})100$

$Y = 11.88\%$

V.2.3. Reaction schema:

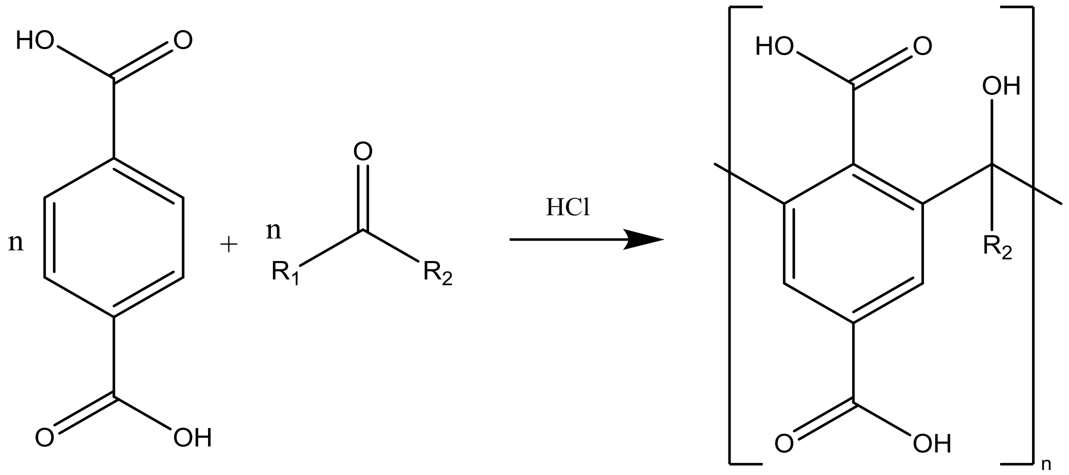


Figure II.13 : Reaction schema of polymer TPA/D-g with HCl as a catalyst

V.2.4.Mechanism reaction:

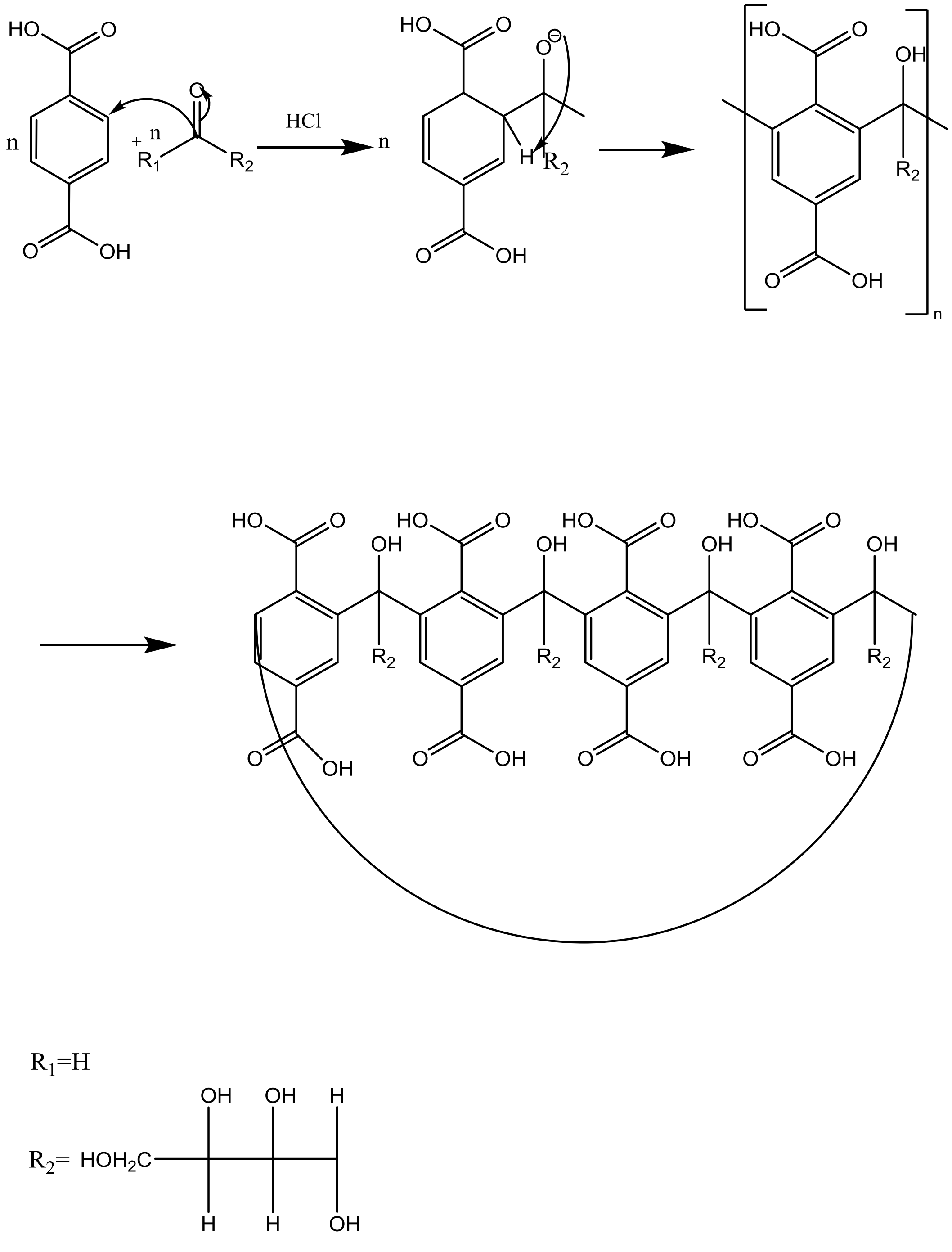


Figure II.14: mechanism reaction of polymer TPA/D-g with HCl as a catalyst

V.3.Synthesis of polymer TPA/D-g with KOH:

To a mixture of 0.005mol of terephthalicacid , 0.0024 mol of D-glucose and Potassium hydroxide in a bicol flask fitted with a dean-starck are refluxed in an inert medium. after a moment of reaction increase the temperature and let it heat up for a while .

The product is washed with solvent to eliminate impurities ,filtred then allowed to dry .

A.Reactionschema:

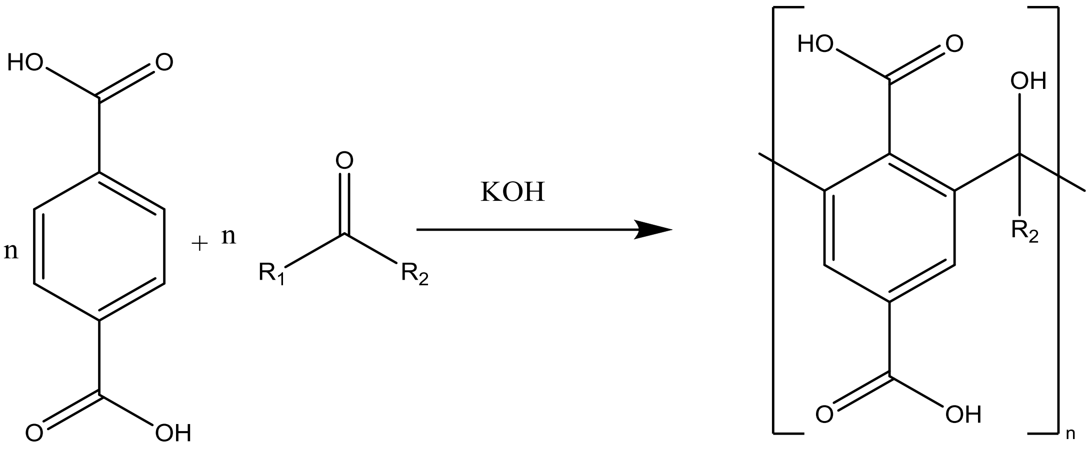


Figure II.15 : reaction schema of polymer TPA/D-g with homogenous base (KOH)

B. Solubility test:

Table II.8: solubility test of polymer obtained TPA/D-g with KOH

Water	**Methanol**	**Ethanol**	**Acetone**	**CCl_4**	**$CHCl_3$**	**CH_2Cl_2**	**DMSO**
Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	Insoluble	soluble

Yield obtained :

$$Yeild = \left(\frac{m_{poly}}{m_{mono}}\right).100$$

$$Y = 50.44\%$$

C. Mechanism reaction:

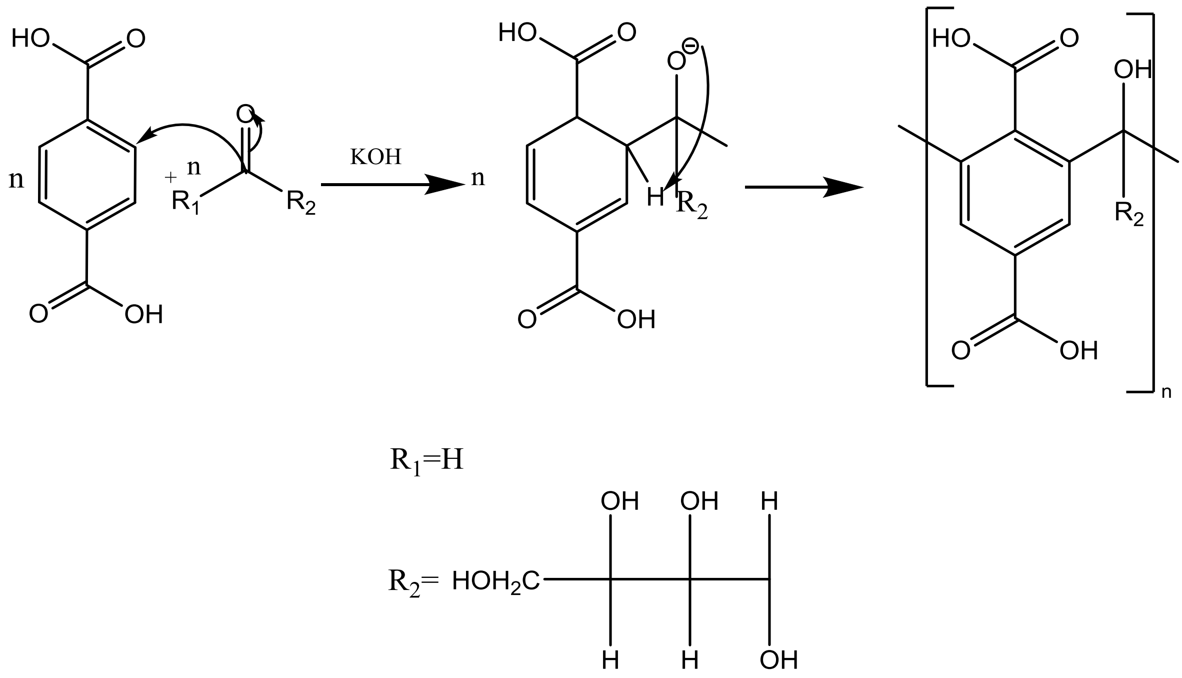


Figure II.16 : mechanism reaction of polymer TPA/D-g With homogenous base (KOH)

V.4.Synthesis of biopolymer TPA/D-g with heterogeneous base ($NAAlO_2$):

To a mixture of 0.005mol of terephthalic acid , 0.0024 mol of D-glucose and Sodium aluminate in a bicol flask fitted with a dean-starck are refluxed in an inert medium. after a moment of reaction increase the temperature and let it heat up for a while .

The product is washed with solvent to eliminate impurities ,filtred then allowed to dry .

Table II.9: yield of syntheses with different percentage of $NaAlO_2$

Percentage of $NaAlO_2$	1%	5%	7%
Yield %	0.21%	43.29%	79.41%

$$\rightarrow Yeild = \left(\frac{m_{poly}}{m_{mono}}\right).100$$

Swelling rate of p TPA/D-g with $NaAlO_2$(5%):

$$S_r = \frac{W_g - W_s}{W_s}$$

$$S_r = 0.45$$

Swelling rate of this product is 45%

A.Reaction schema :

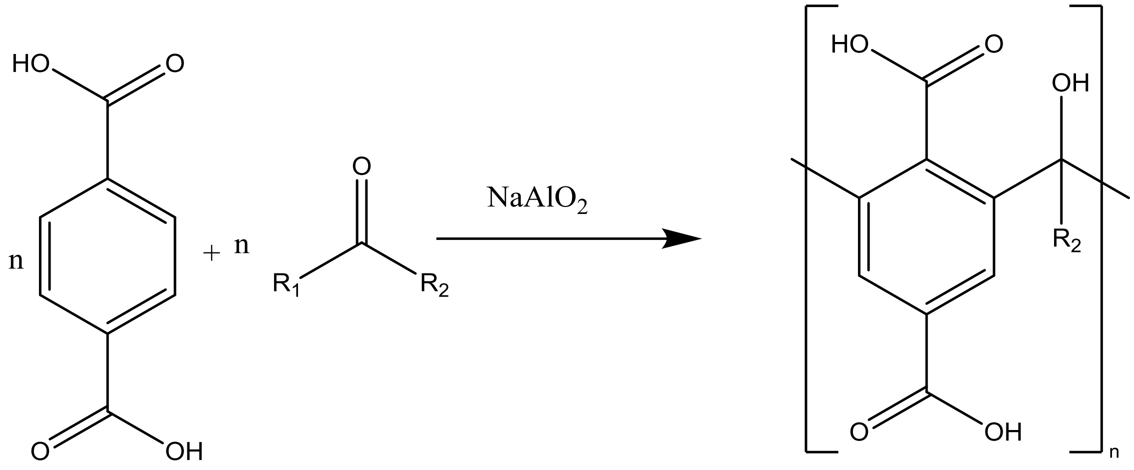


Figure II.17: **r**eaction schema of polymer TPA/D-g with heterogenous base $NaAlO_2$

B. Solubility test :

TableII.10 : solubility test of biopolymer obtained TPA/D-g with $NaAlO_2$

Water	Insoluble	**CH_2Cl_2**	Insoluble
Ethanol	Insoluble	**CH_3Cl**	Insoluble
Methanol	Insoluble	**Cyclohexane**	Insoluble
Acetone	Insoluble	**DMSO**	Insoluble
CCl_4	Insoluble	**DMF**	Insoluble
$CHCl_3$	Insoluble	**THF**	Insoluble

C.Mechanism reaction:

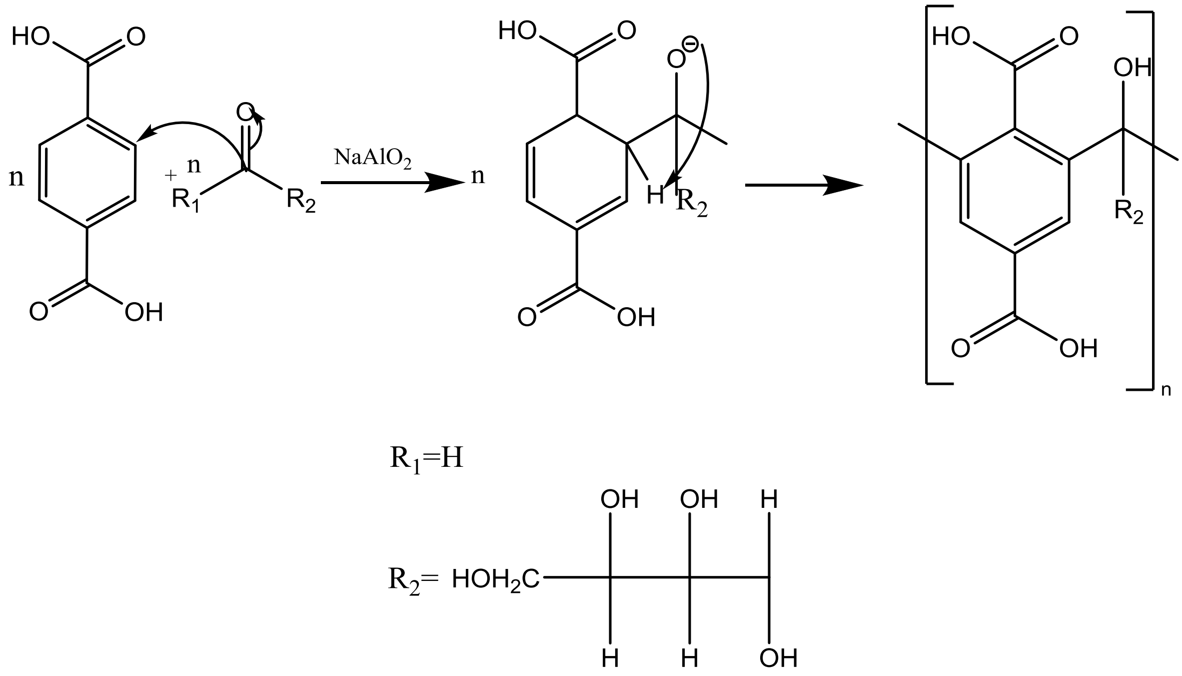


Figure II.18: Mechanism reaction of polymer TPA/D-g with heterogenous base $NaAlO_2$

V.5.Synthesis of biopolymer TPA/D-g with Maghnit:

V.5.1. Synthesis pf ATP/D-g with maghnit H^+:

V.5.1.1.Maghnit activation at laboratory :

In an becker add 500ml of distilled water to 60g of crushed maghnit and leave it with stirring .After 2 hours , prepare a solution of sulphuric acid (0.5M) and added to the previous mixture and leave it for two days . filtering, washing, drying and grinding the mixture with manganese agitation should be kept in bottles well sealed in the oven against humidity .

V.5.1.2.Synthesis of polymer ATP/D-g with maghnit H^+:

A. Operational procedure :

To a mixture of 0.003 mol of terephthalic acid , 0.0015 mol of D-glucose and maghnit H^+ a bicol flask fitted with a dean-starck are refluxed in an inert medium. after a moment of reaction increase the temperature and let it heat up for a while .

The product is washed with solvent to eliminate impurities ,filtred then allowed to dry .

B. Solubility test:

Table II.11: test of solubility of ATP/D-g with maghnit H^+:

Water	Insoluble	**CH_2Cl_2**	Insoluble
Ethanol	Insoluble	**CH_3Cl**	Insoluble
Methanol	Insoluble	**Cyclohexane**	Insoluble
Acetone	Insoluble	**DMSO**	Insoluble
CCl_4	Insoluble	**DMF**	Insoluble
$CHCl_3$	Insoluble	**THF**	Insoluble

Yield obtained :

$$Yeild \ = \left(\frac{m_{poly}}{m_{mono}}\right).100$$

$$Y = 5.42\%$$

V.5.2.1. Maghnit activation at laboratory :

In an becker add 500ml of distilled water to 60g of crushed maghnit and leave it with stirring .After 2 hours , prepare a solution of sulphuric acid (0.5M) and added to the previous mixture and leave it for 48 hours , then add a solution of cupric chloride that it was already prepared filtering, washing, drying and grinding the mixture with manganese agitation should be kept in bottles well sealed in the oven against humidity .

V.5.2.2.Synthesis of polymer ATP/D-g with maghnitCu^{2+}:

A. Operational procedure :

To a mixture of 0.003 mol of terephthalic acid , 0.0015 mol of D-glucose and maghnit Cu^{2+} a bicol flask fitted with a dean-starck are refluxed in an inert medium. after a moment of reaction increase the temperature and let it heat up for a while .

The product is washed with solvent to eliminate impurities ,filtred then allowed to dry .

B. Solubility test:

TableII.12 : test of solubility of ATP/D-g with maghnitCu^{2+}

Water	Insoluble	**CH_2Cl_2**	Insoluble
Ethanol	Insoluble	**CH_3Cl**	Insoluble
Methanol	Insoluble	**Cyclohexane**	Insoluble
Acetone	Insoluble	**DMSO**	Insoluble
CCl_4	Insoluble	**DMF**	Insoluble
$CHCl_3$	Insoluble	**THF**	Insoluble

Yield obtained :

$$Yeild\ = \left(\frac{m_{poly}}{m_{mono}}\right).100$$

$$Y = 5.2\%$$

Rq: there is a problem of separation between the base and the product in this two syntheses.

V.6.Synthesis with ultrasonic cleanser :

V.6.1. Synthesis with base ($NaAlO_2$):

Add a mixture of 0.0025mol terephthalic acid, 0.0012mol D-glucose and $NaAlO_2$ in a vial and we put it in this device and let it for 30min .

We observe that there is a reaction after this moment .

Yeild obtained :

$$Yeild\ = \left(\frac{m_{poly}}{m_{mono}}\right).100$$

$$Yeild\ = \%$$

V.6.2. Synthesis without base :

Add a mixture of 0.0025mol terephthalic acid and 0.0012mol D-glucose in a vial and we put it in this device and let it for 30min .

V.7.Synthesis with the pressure effect :

V.7.1. Synthesis of ATP/F with KOH :

In a vial we put 0.0006 mol of ATP , formaldehyde and 5% of base (KOH) and we press them for a moment (in our case we used the mortar and pestle for 30min).

Filter the product after washing with solvent .

Yeild obtained:

$$Yeild \ = \left(\frac{m_{poly}}{m_{mono}}\right).100$$

$$Y \ = \ 60.2\%$$

V.7.2.Synthesis of ATP/Dg with NaAlO$_2$:

In a vial we put 0.0006mol of ATP ,0.00027mol D-glucose and 5% of base (NaAlO$_2$) and we press them for a moment (in our case we used the mortar and pestle for 30min).

Filter the product after washing with solvent .

Yield obtained:

$$Yeild \ = \left(\frac{m_{poly}}{m_{mono}}\right).100$$

$$Y \ = 2.4\%$$

VI. Bio-synthesis of polymer :

According to the studies of Louis Armand Victor AmedéeCailliot the first who has come to discover this acid(from nature), he studied on the chemical composition of therebenthine oil . AmedéeCailliot found a serval molecules which are already discovred until he arrived at a new structure that he named terephthalicacid .

VI.1. Extraction of terebenthine oil from pine :

. Experimental protocol of distillation:

Make the simple distillation mount show in the figure :

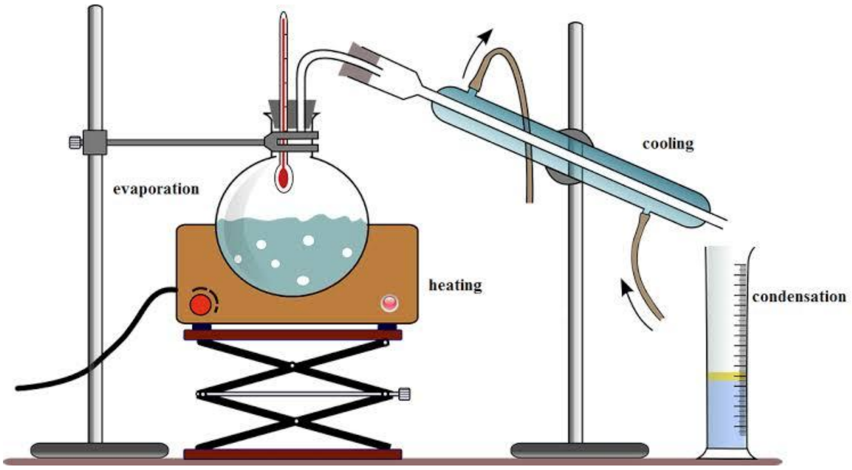


Figure II.19: Schema of distillation mount

Add 100g of pine and 200ml of water distillated in the flask of 500ml , we start distillation by observing the temperature with each distilate tau .

The temperature is stabilized at 97.4°C , we notice the recovery of distilate (water+oil) 95.5ml.

VI.2. Synthesis of biopolymer from degradation of oil :

In this synthesis we used two modes :

A.Operational procedure 1:

In monocol flask fitted with dean-starck add 100ml of distilate , 0.05g D-glucose and 5% of $NaAlO_2$, this mixture is refluxed at higher temperature for a well time .

We notice that we have a recovery product in dean starck (75ml) and a new liquid product is formed in flask.

We put This product in wash glass and we put it on a hot plate , the product is passed directly to cross-linking state (solid)

We notice that we have 2 product one is soluble in solvent and the other one is insoluble .

B.Operational procedure 2:

In biocol flask fitted with dean-starck add 100ml of distillate refluxed at higher temperature for a well time.we have a recovery product in dean starck (75ml) and rest a very small quantity of distilate in flask , we add 0.05g D-glucose and 5% of $NaAlO_2$and we refluxed them at 140°C for 3hours.

This product are also in the cross-linking state .

Table II.13: Solubility test of the product :

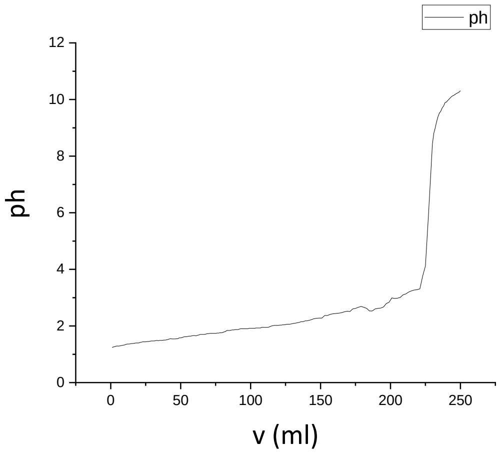
Water	Insoluble	**CH_2Cl_2**	Insoluble
Ethanol	Insoluble	**CH_3Cl**	Insoluble
Methanol	Insoluble	**Cyclohexane**	Insoluble
Acetone	Insoluble	**DMSO**	Insoluble
CCl_4	Insoluble	**DMF**	Insoluble
$CHCl_3$	Insoluble	**THF**	Insoluble

VII. Gran method :

The Gran method is using to determinate the acid functions that exist in resin . It consists to deprotonate the carboxylic groups of the resin with solution of $NaNO_3$(0.01M), then the carboxylic functions are dosed with HNO_3(0.01M) solution for protonation , and the excess of free protons in the solution is dosed with NaOH(0.01M) solution. the measurements were carried out at a temperature of 25°C.

VII.1.Determination of pk_a of the pTPAF resine (5%KOH):

The pTPAF is an polyacid compound , to determine its pk_a, It consists of putting 25 mg of the resin in an beaker containing 50 ml of $NaNO_3$ solution (0.01M) with stirring for 24 hours, dosed with a (0.01M) HNO_3 solution then with (0.01M) NaOH solution. We will have the following graph .



FigureII.20:pH of p TPA/F as a function of volume NaOH

Calculation of pk_aresine :

To determine the pKa of the polymer solution we trace the dpH/dv curve as a function of the volume of NaOH added, relying to the derivate method, we will have the following graph :

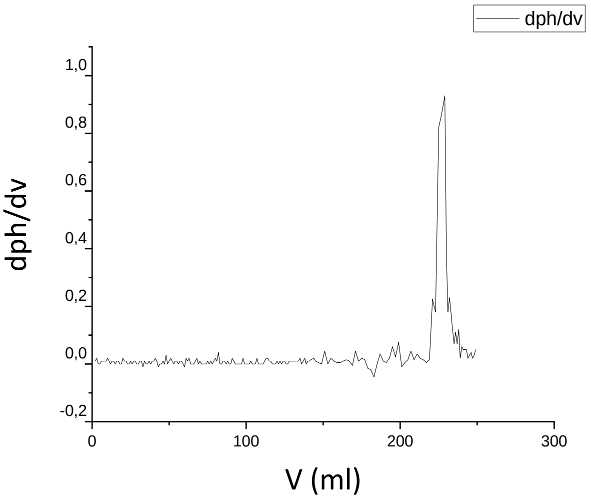


Figure II.21: Variation of dpH/dv depending on the volume of NaOH added

Top of the curve represents the equivalence point the pKa corresponds to the half-equivalent volume lance is 120ml.

Volume of NaOH added at the equivalence point:240ml

The number of moles of H+ ions in the solution

The number of moles of the protonated (-COO) groups

The initial number of moles of HNO_3=moles

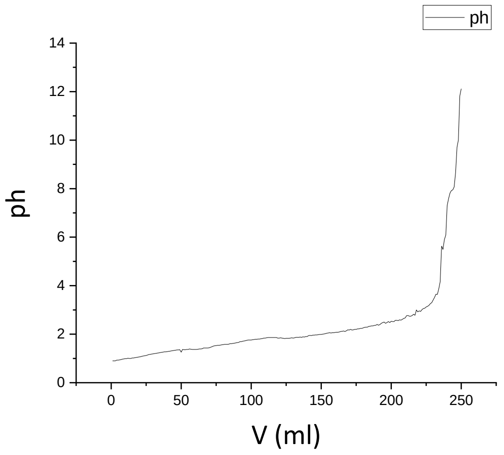
Exchange capacity of AF resin :

For a given quantity of resin, there is a determined number of groups, which constitutes what we call "the exchange capacity" of the resin. This capacity can be expressed in the form of a concentration, number of equivalents. ionic per unit quantity of resin, each group counting for a number of equivalents equal to the charge it carries in the ionized state .

The exchange capacity of the AF resin in the form H*: meq/g

VII.2.determination of TPA/Dg:

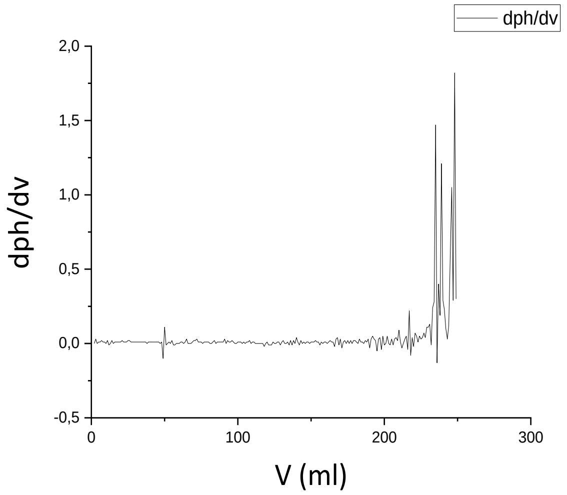
The TPA-Dg is an polyacid compound , to determine its pk_a, It consists of putting 25 mg of the resin in an beaker containing 50 ml of $NaNO_3$ solution (0.01M) with stirring for 24 hours, dosed with a (0.01M) HNO_3 solution then with (0.01M) NaOH solution. We will have the following graph .



FigureII.22 :pH of P TPA/D-gas a function of volume NaOH

Calculation of pk_aresine :

To determine the pKa of the resin solution we trace the dpH/dv curve as a function of the volume of NaOH added, relying to the derivate method, we will have the following graph :



FigureII.22 : Variation of dpH/dv depending on the volume of NaOH added

We cannot determine Pk_a of this polymer .

VIII. IR analyzes of some product :

VIII.1. Infrared spectroscopy[117]:

Infrared spectroscopy is one of the most widely used spectroscopic techniques, measuring the wavelength and intensity of infrared light absorbed by a sample. This method relies on the vibrations of atoms within a molecule. The infrared spectrum of a sample is generated by passing infrared light through it and observing which parts of the incident radiation are absorbed at specific energies. The energy at which peaks appear in the absorption spectrum corresponds to the vibrational frequencies of molecules in the sample. This technique is valuable for identifying functional groups within a molecule because each group has a unique vibrational frequency. Infrared spectroscopy is divided into three spectral regions: near-infrared (NIR) (~14,000–4,000 cm−1), mid-infrared (MIR) (~4,000–400 cm−1), and far-infrared (~400–10 cm−1), named relative to their position in the electromagnetic spectrum.

VII.2.Results of IR analyzes :

VII.2.1.IR spectrum of p TPA/F with KOH :

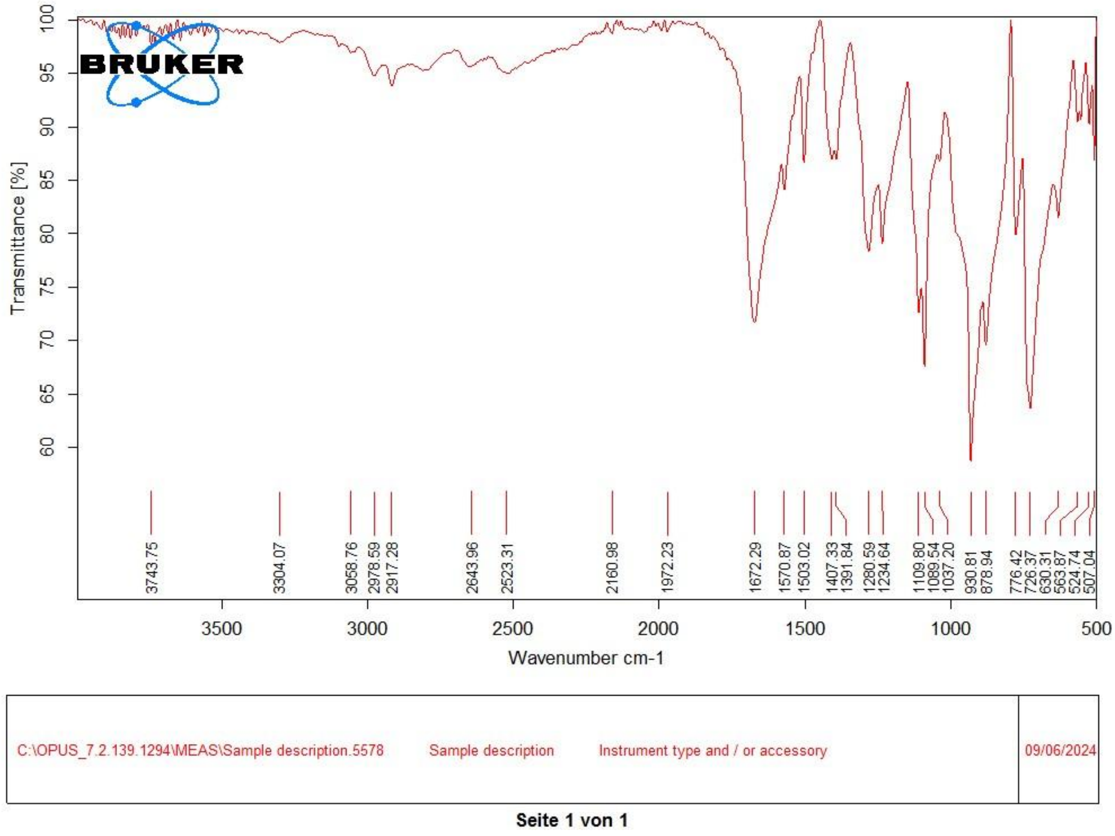


Figure II.23: spectrum IR of p TPA/F with KOH

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[117]- Mohammad Kamal. Romdhane Karoui, Trends in Food Science &Technology,Vol 46,1, pp 27-48, 2015.

Table II.14: Principal characteristic absorption bonds of p TPA/F with KOH

Absorption bonds (cm^{-1})	Attribution
2523.31-3304.07	O-H carboxylic acid elongation
1672.29	C=C
930.81	C-H aromatics
1109.80	C-O alcohol

Interpretation:

The wide bond between 2523.31-3304.07cm^{-1} which corresponds to the (-OH) function is attributable to the presence of carboxylic acid .

The presence of the absorption bond around 1672.29cm^{-1} corresponds to the double liaison between carbon carbon(C=C)

The presence of the absorption bond around 930.81cm^{-1} corresponds the liaison (C-H) of aromatic cycle

The presence of the absorption bond around 1109.80cm^{-1} corresponds to the (C-O) bond is attributable to the presence of alcohol which confirms the formation of polymer

VII.2.2. IR spectrum of p TPA/F with $NaAlO_2$ (5%):

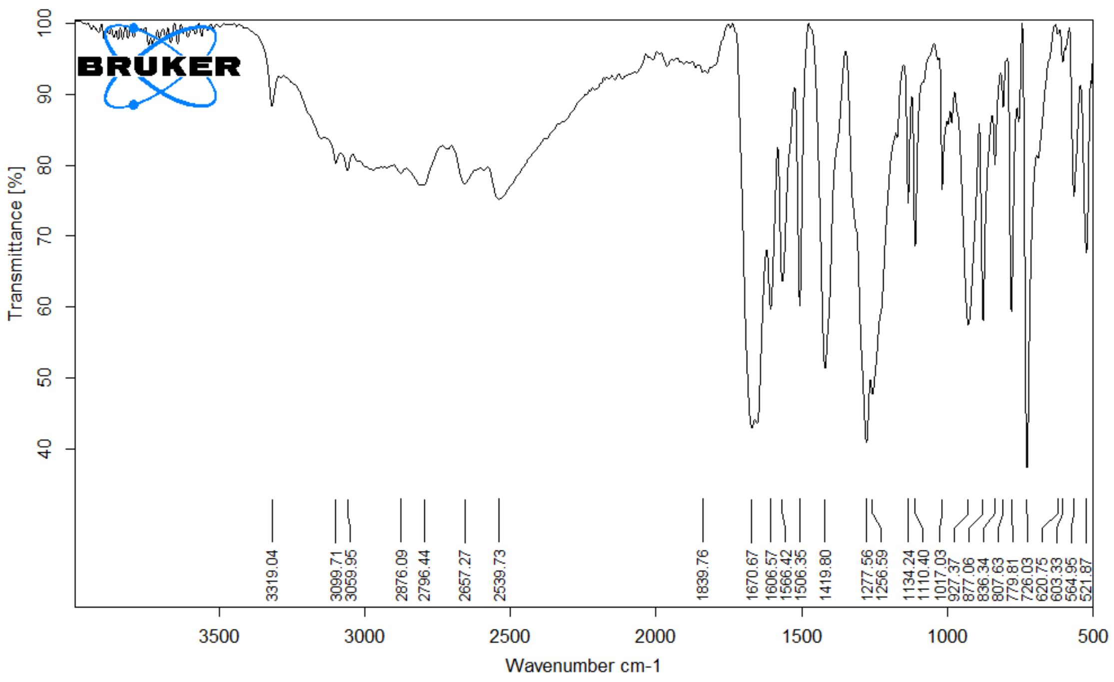

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Figure II.24: spectrum IR of p TPA/F with $NaAlO_2$(5%)

Table II.15: Principal characteristic absorption bonds of p TPA/F with NaAlO2(5%)

Absorption bonds (cm^{-1})	Attribution
2539.73-3319.04	O-H carboxylic acid elongation
1670.67	C=C
1419.80	C-C aromatic
1256.59-1277.56	C-O carboxylic acid
726.03	C-H aromatics
1277.56	C-O alcohol

Interpretation:

The wide bond between 2539.73-3319.04 cm^{-1} which corresponds to the (-OH) function is attributable to the presence of carboxylic acid .

The presence of the absorption bond around 1670.67cm^{-1} corresponds to the double liaison between carbon carbon(C=C)

The presence of the absorption bond around 1419.80 cm^{-1} corresponds to the double liaison between carbon carbon (C-C) in aromatic cycle

The presence of the absorption bond around 726.03 cm^{-1} corresponds the liaison (C-H) of aromatic cycle

The presence of the absorption bond around 1277.56 cm^{-1} corresponds to the (-OH) function is attributable to the presence of alcohol which confirms the formation of polymer .

VII.2.3. IR spectrum of p TPA/D-g with $NaAlO_2$ (5%):

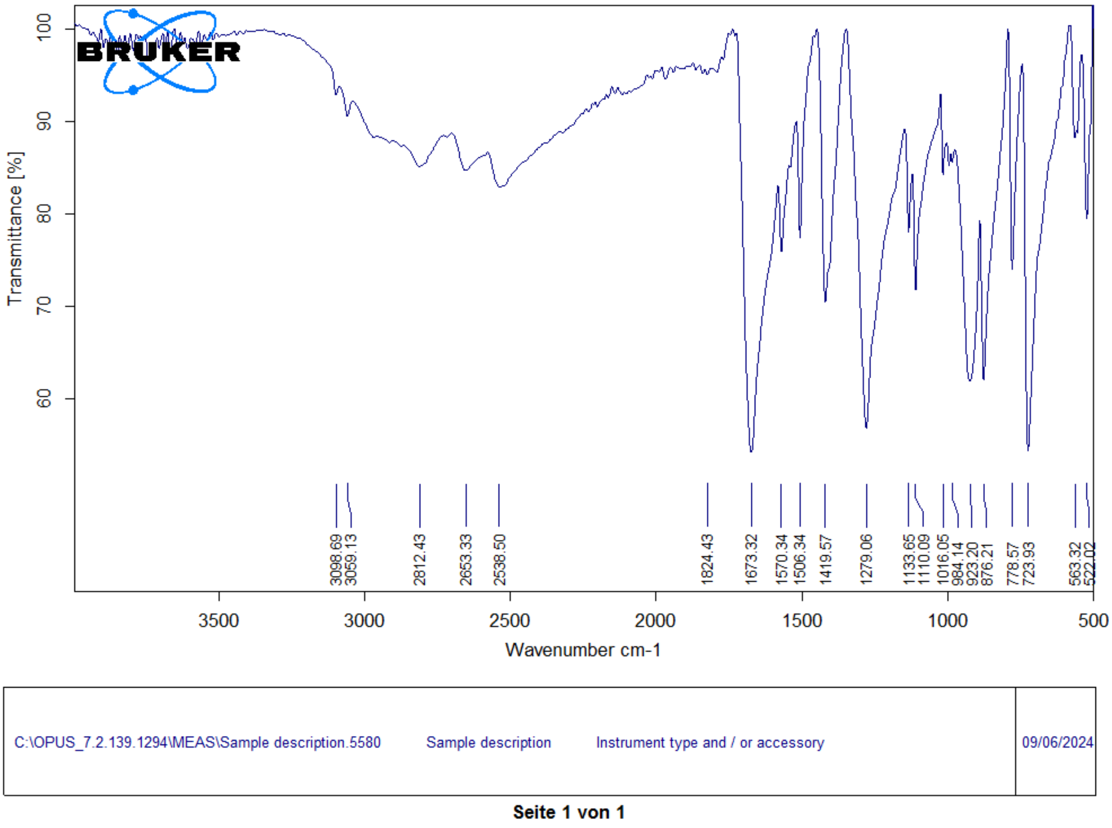

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Figure II.25: spectrum IR of p TPA/D-g with $NaAlO_2$(5%)

Table II.16: Principal characteristic absorption bands of p TPA/D-g with $NaAlO_2$(5%)

Absorption bonds (cm^{-1})	Attribution
1673.32	C=C
1279.06	C-O Alcohol
923.2	
723.93	C-H aromatics
2538.5-3098.69	O-H carboxylic acid elongation
1419.57	C-C aromatics

Interpretation :

The wide band between 2538.5-3098.69 cm^{-1} which corresponds to the (-OH) function is attributable to the presence of carboxylic acid .

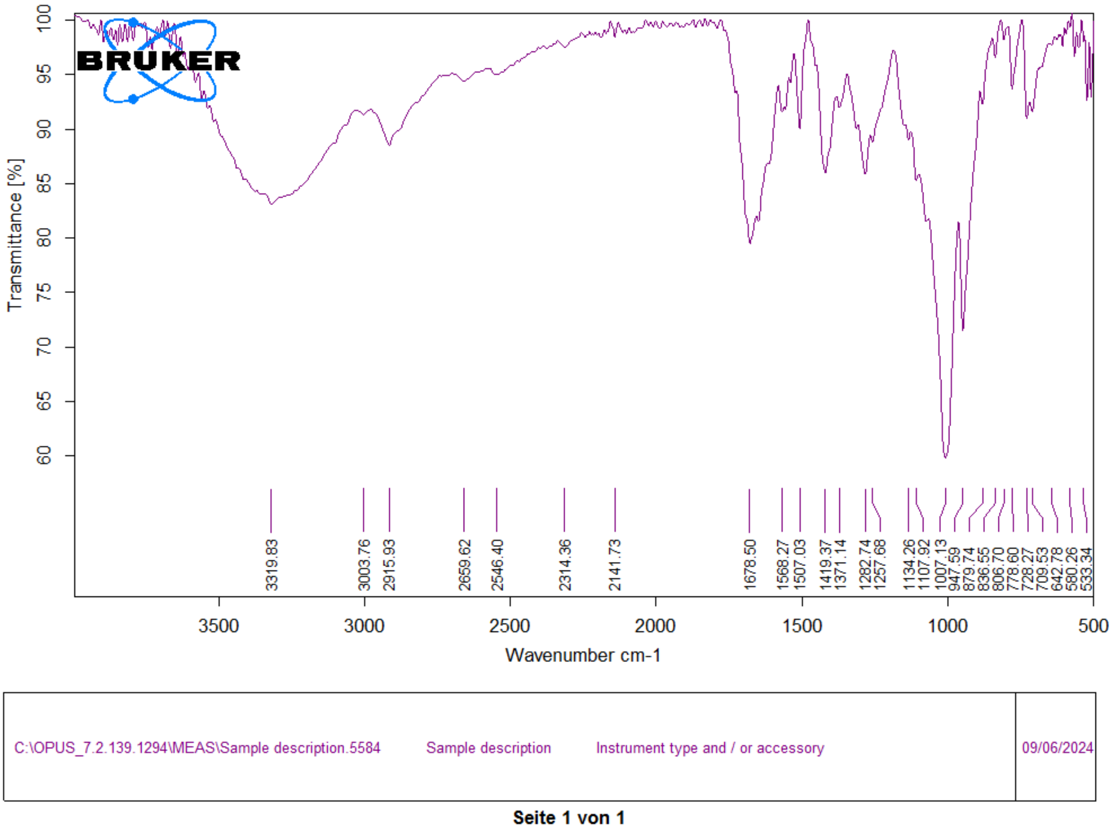
The presence of the absorption band around 1673.32cm^{-1} corresponds to the double liaison between carbon carbon(C=C)

The presence of the absorption band around 1419.57 cm^{-1} corresponds to the double liaison between carbon carbon (C-C) in aromatic cycle

The presence of the absorption band around 723.93 cm^{-1} corresponds the liaison (C-H) of aromatic cycle

The presence of the absorption band around 1279.06 cm^{-1} corresponds to the (-OH) function is attributable to the presence of alcohol which confirms the formation of polymer .

VII.2.4. IR spectrum of p TPA/D-g with HCl :



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Seite 1 von 1

Figure II.26: spectrum IR of p TPA/F with $NaAlO_2$(5%)

Table II.17: Principal characteristic absorption bands of p TPA/F with $NaAlO_2$(5%)

Absorption bonds (cm^{-1})	Attribution
2915.62-3319.83	O-H carboxylic acid elongation
1678.5	C=C
1007.13	C-O alcohol
879.74	C-H aromatic

Interpretation :

The wide band between 2915.62-3319.83 cm^{-1} which corresponds to the (-OH) function is attributable to the presence of carboxylic acid .

The presence of the absorption band around 1678.5cm^{-1} corresponds to the double liaison between carbon carbon(C=C)

The presence of the absorption band around 879.74 cm^{-1} corresponds the liaison (C-H) of aromatic cycle

The presence of the absorption band around 1007.13 cm^{-1} corresponds to the (-OH) function is attributable to the presence of alcohol which confirms the formation of polymer .

IX. Application of the synthetised polymer TPA/D-g 5%:

IX.1. Bacteria used :

A.*Klebsiella pneumonia*:are bacteria widely distributed in nature (water, soil, plants, faecal flora or animals), on the skin , mucous membranes and especially the respiratory tract , superior cells of man thus causing fatal pneumonia 118 . Klebsiella is an opportunistic pathogen frequently involved in serve infections including urinary tract infections, pneumonia and bacteremia 119 . it is responsible for more than 10% of nosocamial infections, is mainly involved in intensive care units[120].

B.*Listeria monocytogene*[121] : is one of the pathogens , it is a Gram-positive bacterium that is is responsible for listeriosis , a sporadic disease that can effect most animal species, including humans and mammals, birds and even cold blooded animals . This ubiquitos pathogenic power demonstrates relatively universal virulence mechanisms. The severity of listeriosis is linked to the ability of bacteria to penetrate the central nervous system and the placenta .

IX.2.Antibacterial activity:

IX.2.1.Operational procedure:

The antibacterial activity of the synthesized product was evaluated using the agar diffusion method. Mueller Hinton agar served as the culture medium for the microorganisms. Young cultures (18 hours) of Klebsiellapneumoniae (ATCC 13883) and Listeria monocytogenes (ATCC 19114) were inoculated into 20 ml of sterile nutrient broth and incubated for 4 hours to

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[118]-Leon Le Minor. Michel Veron, Bacteriologie Médicale, Ed 3, pp 396-795,1989.

[119]-Berrazeg.M, and Al Biotyping of multiduring resistant *Klebsiellapneumoniae*clinical isolates from france and Algeria using MALDI-TOF MS ,2013.

[120]-Hennequin.C ,Forestier.C, Research in Microbiology, pp339-347,2007.

[121]-Bull. Acad. Natle Med, 189, N°3, pp 507-521,2005.

achieve a standardized culture concentration of 10 CFU/ml. Bacterial inocula were then spread onto Mueller Hinton agar plates using sterile swabs, with two replicates prepared for each synthesized product against the test microorganisms. Wells of 6 mm diameter were evenly punched into the agar plates and filled with the synthesized products. After 2 hours of diffusion at room temperature, the plates were incubated at 37°C for 24 hours. The antibacterial activity was determined by measuring the zone of inhibition around each well using a ruler (in mm).

IX.2.2.Results:

Analysis of the data in Figure (II.26) reveals satisfactory results in the activity of the tested product against two bacterial strains: the Gram-negative bacterium *Klebsiella pneumoniae* and the Gram-positive bacterium *Listeria monocytogenes*. The antibacterial activity against K. pneumoniae exhibited the highest inhibition zones, indicating significant activity of 22.90±2.82 mm. Similarly, the synthesized product also demonstrated substantial activity against L. monocytogenes, with an antibacterial activity of 19.49±0.42 mm. These findings suggest that the product is generally effective against the majority of tested bacterial strains.

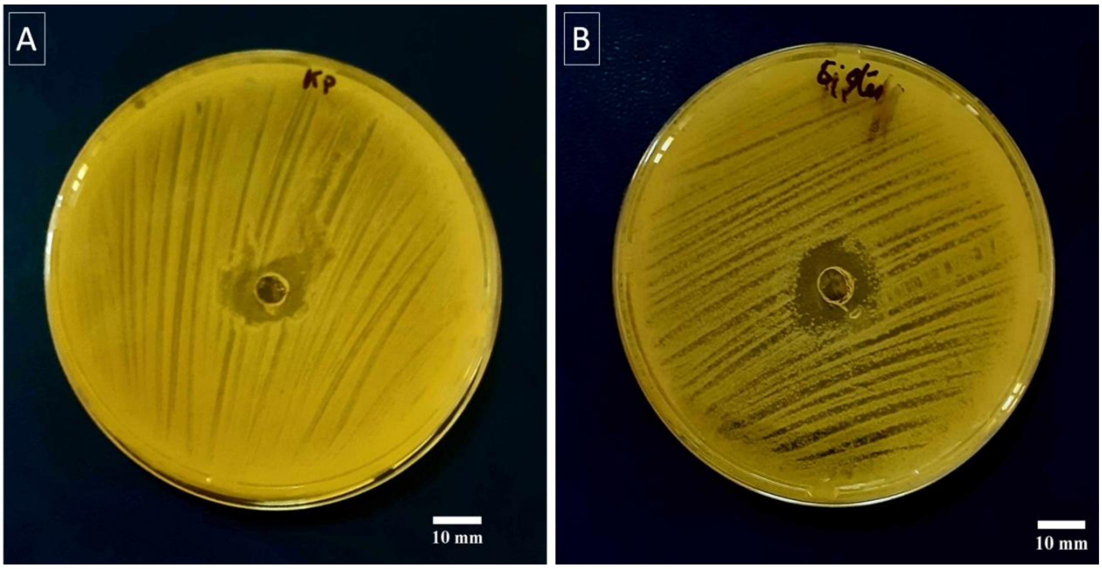


Figure II.27: The antibacterial activity of the synthesized product against (A) *Klebsiellapneumoniae* ATCC 13883, (B) *Listeria monocytogenes* ATCC 19114

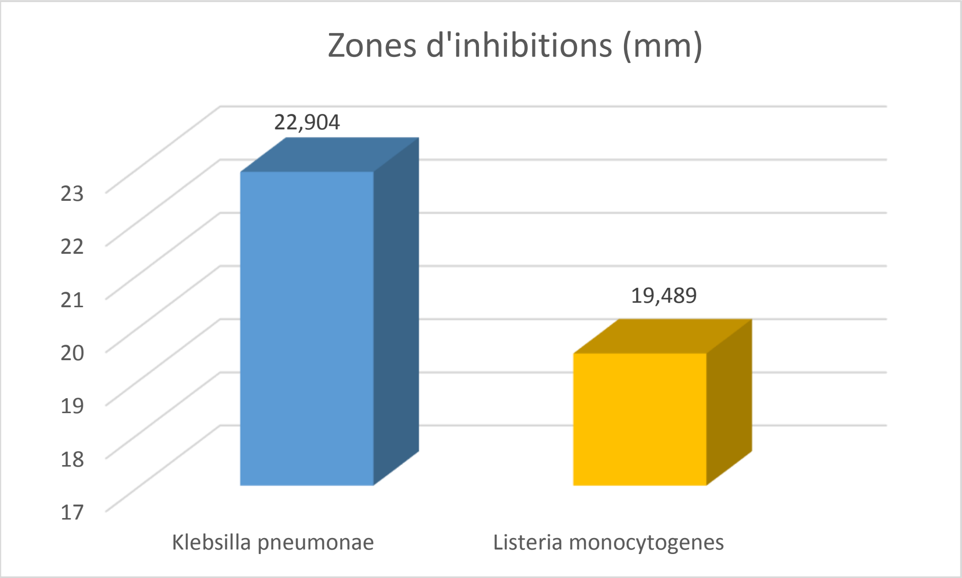


Figure II.28: Comparative analysis of product inhibition zones (mm) synthesized against *(A) Klebsiella pneumoniae* ATTC 13883, *(B) Listeria monocytogenes* ATTC 19114

X.3.Water treatement :

Source water quality :

Chlorine test : in a tube contains witness (source water) add DPD, we observe the apparence of a very light color , therefore there is chlorine in this water but it is still polluted (not drinkable) .

TableII.18: results of analyzes of witness

T°	24.7°C	NH_4^+	0.053
Ph	7.21	NO_2^-	0.016
Cond	2330	SO_4^-	359.06
TDS	1398	NO_3^-	16.9
OD	15.79	Ph	0.037
Turb	0.348	M.O	0.192
Th (mg/l)	610	Fe^{2+}	0.005
Ca^{2+} (mg/l)	140.28	K^+	7.6
Mg^{2+} (mg/l)	63.18	Na^+	140.3
Cl^-	142	Mn^{2+}	0.003
HCO_3^-	405.2	M.E.S	0.033

Operational procedure:

Add 0.007g of p TPA/D-g in becker contains 200ml of witness and leave it under stirring foor30min .put it in a sterile bottle after filtering it .

TableII.19 : results analyzes of water treated by p TPA/D-g

Coliforms totals	0
Reducing sulphates	0
E.C	0
Coliforms	0

Conclusion :

This part , is about the study of evolution of yeild by change in operating condition to determine the right one, syntheses of our product using a toxic reagents and changing it by step for obtaining a non-toxic product with all condition which corresponds to the principales of green chemistry, then synthesis of this product with extracting principal monomer from nature . the characterization of this product confirms that is a polymer which corresponds to the probability of mechanism reaction so we used the right conditions of this synthesis. In application results this biopolymer is satistfactory product for antibacterial activity and also for water treatement .

General conclusion

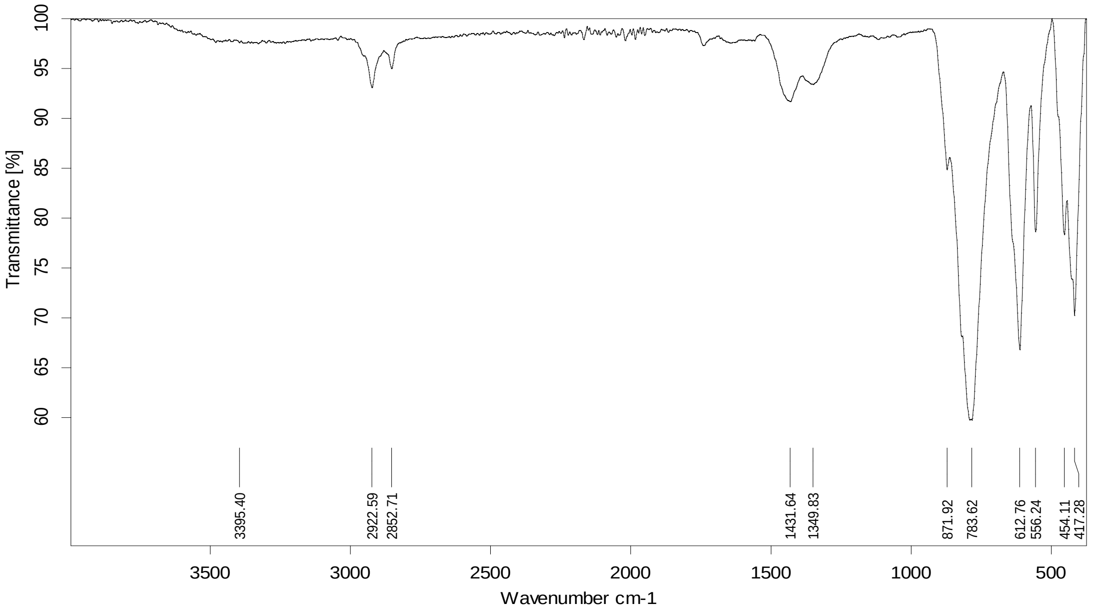
During this research , we focused on the green chemistry, biopolymers and the syntheses for toxic to bio-product , as well as the polymerization on the latter ; on the substitution of a bio-sourced compound D-glucose with a non-toxic product terephthalic acid , then we processed to the characterization of this product after we carried out antibacterial activity as an application choice .

Our study allowed as to synthesize a polymer product by polymerization reaction in base medium at a well chosen condition comprising functional group in the para position of terephtalic acid .

The infrared spectroscopie comfirms the the formation of product with all function that we have in all mechanism reaction , of which we observed the apparence of absorption band 1279.06 cm^{-1} which corresponds the presence of (C-O) of alcohol function .

Bacteriological analyses confirm that we produce a biopolymer which reduces bacteria with a significant results.

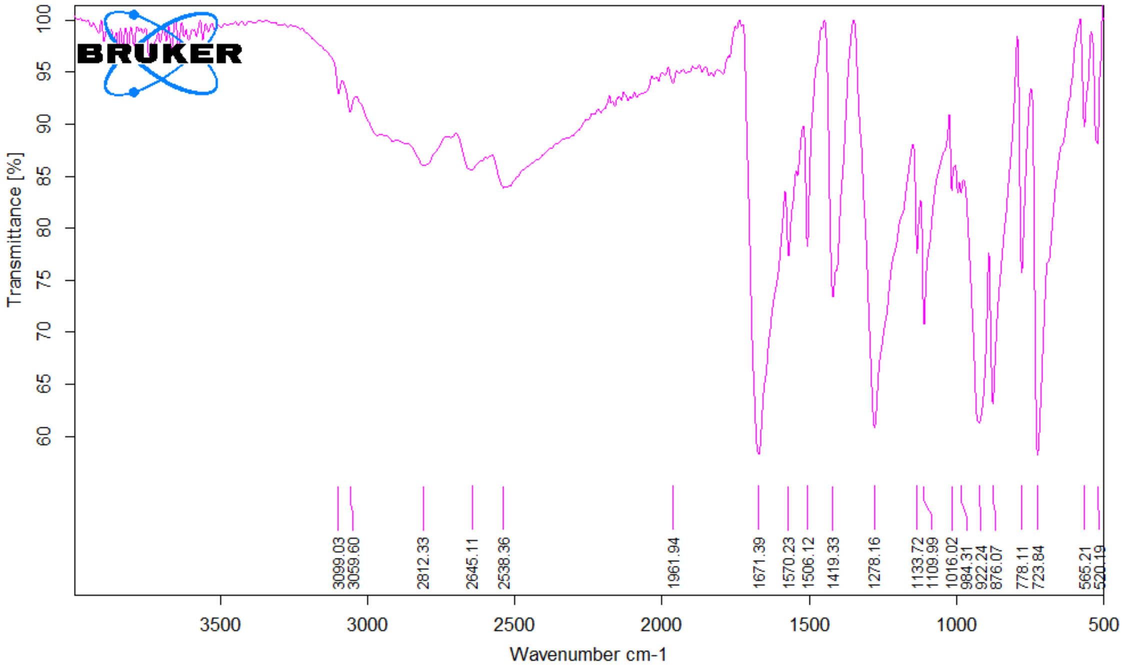
IR spertum of $NaAlO_2$



C:\Program Files\OPUS_65\MEAS\MEAS\NaAlO2.2 NaAlO2 Instrument type and / or accessory	19/01/2015

Seite 1 von 1

IR Spectrum of terephthalic acid



C:\OPUS_7.2.139.1294\MEAS\Sample description.5579	Sample description	Instrument type and / or accessory	09/06/2024

Values of gran method graph (p TPA/F) :

Ph	V(ml)	dph	Dv	dph/dv
1,24	1			
1,26	2	0,01	1	0,01
1,27	3	0,02	1	0,02
1,29	4	0	1	0
1,29	5	0	1	0
1,29	6	0,01	1	0,01
1,3	7	0,01	1	0,01
1,31	8	0,01	1	0,01
1,32	9	0,01	1	0,01
1,33	10	0,02	1	0,02
1,35	11	0,01	1	0,01
1,36	12	0	1	0
1,36	13	0,01	1	0,01
1,37	14	0,01	1	0,01
1,38	15	0	1	0
1,38	16	0,01	1	0,01
1,39	17	0,01	1	0,01
1,4	18	0	1	0
1,4	19	0	1	0
1,4	20	0,02	1	0,02
1,42	21	0,01	1	0,01
1,43	22	0,01	1	0,01
1,44	23	0	1	0
1,44	24	0	1	0
1,44	25	0,01	1	0,01
1,45	26	0	1	0
1,45	27	0,01	1	0,01
1,46	28	0,01	1	0,01
1,47	29	0	1	0
1,47	30	0	1	0
1,47	31	0,01	1	0,01
1,48	32	0,01	1	0,01
1,49	33	-0,01	1	-0,01
1,48	34	0,01	1	0,01
1,49	35	0	1	0
1,49	36	0	1	0
1,49	37	0,01	1	0,01
1,5	38	0	1	0
1,5	39	0,01	1	0,01
1,51	40	0,01	1	0,01
1,52	41	0,02	1	0,02
1,54	42	0,01	1	0,01

1,55	43	-0,01	1	-0,01
1,54	44	0	1	0
1,54	45	0	1	0
1,54	46	0,01	1	0,01
1,55	47	0	1	0
1,55	48	0,03	1	0,03
1,58	49	0	1	0
1,58	50	0,01	1	0,01
1,59	51	0,02	1	0,02
1,61	52	0,01	1	0,01
1,62	53	0	1	0
1,62	54	0,01	1	0,01
1,63	55	0,01	1	0,01
1,64	56	0	1	0
1,64	57	0,01	1	0,01
1,65	58	0,01	1	0,01
1,66	59	0	1	0
1,66	60	-0,01	1	-0,01
1,65	61	0,02	1	0,02
1,67	62	0,01	1	0,01
1,68	63	0,02	1	0,02
1,7	64	0	1	0
1,7	65	0	1	0
1,7	66	0	1	0
1,7	67	0,01	1	0,01
1,71	68	0,02	1	0,02
1,73	69	0	1	0
1,73	70	0,01	1	0,01
1,74	71	0	1	0
1,74	72	0	1	0
1,74	73	0	1	0
1,74	74	0	1	0
1,74	75	0,01	1	0,01
1,75	76	0	1	0
1,75	77	0,01	1	0,01
1,76	78	0	1	0
1,76	79	0,01	1	0,01
1,77	80	0,02	1	0,02
1,79	81	0,01	1	0,01
1,8	82	0,04	1	0,04
1,84	83	0	1	0
1,84	84	0	1	0
1,84	85	0,01	1	0,01
1,85	86	0,01	1	0,01
1,86	87	0	1	0

1,86	88	0,01	1	0,01
1,87	89	0	1	0
1,87	90	0	1	0
1,87	91	0,02	1	0,02
1,89	92	0,01	1	0,01
1,9	93	0	1	0
1,9	94	0	1	0
1,9	95	0	1	0
1,9	96	0	1	0
1,9	97	0	1	0
1,9	98	0,02	1	0,02
1,92	99	0	1	0
1,92	100	0	1	0
1,92	101	0	1	0
1,92	102	0	1	0
1,92	103	0,01	1	0,01
1,93	104	0	1	0
1,93	105	0	1	0
1,93	106	0	1	0
1,93	107	0,02	1	0,02
1,95	108	0	1	0
1,95	109	0	1	0
1,95	110	0	1	0
1,95	111	0	1	0
1,95	112	0,01	1	0,01
1,96	113	0,02	1	0,02
1,98	114	0,02	1	0,02
2	115	0,01	1	0,01
2,01	116	0,01	1	0,01
2,02	117	0	1	0
2,02	118	0	1	0
2,02	119	0	1	0
2,02	120	0,01	1	0,01
2,03	121	0	1	0
2,03	122	0,01	1	0,01
2,04	123	0	1	0
2,04	124	0,01	1	0,01
2,05	125	0,01	1	0,01
2,06	126	0	1	0
2,06	127	0	1	0
2,06	128	0,01	1	0,01
2,07	129	0,01	1	0,01
2,08	130	0,01	1	0,01
2,09	131	0,01	1	0,01
2,1	132	0,01	1	0,01

2,11	133	0,01	1	0,01
2,12	134	0,01	1	0,01
2,13	135	0,02	1	0,02
2,15	136	0	1	0
2,15	137	0,01	1	0,01
2,16	138	0,02	1	0,02
2,18	139	0	1	0
2,18	140	0,01	1	0,01
2,19	141	0,01	1	0,01
2,2	142	0,03	2	0,015
2,23	144	0,02	1	0,02
2,25	145	0,02	2	0,01
2,27	147	0,01	2	0,005
2,28	149	0	2	0
2,28	151	0,09	2	0,045
2,37	153	0	2	0
2,37	155	0,04	2	0,02
2,41	157	0,02	2	0,01
2,43	159	0,01	2	0,005
2,44	161	0,01	2	0,005
2,45	163	0,02	2	0,01
2,47	165	0,03	2	0,015
2,5	167	0,02	2	0,01
2,52	169	-0,01	2	-0,005
2,51	171	0,09	2	0,045
2,6	173	0,02	2	0,01
2,62	175	0,04	2	0,02
2,66	177	0,03	2	0,015
2,69	179	-0,03	2	-0,015
2,66	181	-0,04	2	-0,02
2,62	183	-0,09	2	-0,045
2,53	185	0	2	0
2,53	187	0,07	2	0,035
2,6	189	0,02	2	0,01
2,62	191	0,01	2	0,005
2,63	193	0,04	2	0,02
2,67	195	0,12	2	0,06
2,79	197	0,05	2	0,025
2,84	199	0,15	2	0,075
2,99	201	-0,02	2	-0,01
2,97	203	0,01	2	0,005
2,98	205	0,03	2	0,015
3,01	207	0,09	2	0,045
3,1	209	0,03	2	0,015
3,13	211	0,07	2	0,035

3,2	213	0,04	2	0,02
3,24	215	0,03	2	0,015
3,27	217	0,01	2	0,005
3,28	219	0,03	2	0,015
3,31	221	0,45	2	0,225
3,76	223	0,36	2	0,18
4,12	225	1,64	2	0,82
5,76	227	1,74	2	0,87
7,5	229	0,93	1	0,93
8,43	230	0,38	1	0,38
8,81	231	0,18	1	0,18
8,99	232	0,23	1	0,23
9,22	233	0,18	1	0,18
9,4	234	0,12	1	0,12
9,52	235	0,07	1	0,07
9,59	236	0,11	1	0,11
9,7	237	0,07	1	0,07
9,77	238	0,12	1	0,12
9,89	239	0,02	1	0,02
9,91	240	0,06	1	0,06
9,97	241	0,05	1	0,05
10,02	242	0,05	1	0,05
10,07	243	0,05	1	0,05
10,12	244	0,02	1	0,02
10,14	245	0,03	1	0,03
10,17	246	0,04	1	0,04
10,21	247	0,02	1	0,02
10,23	248	0,03	1	0,03
10,26	249	0,05	1	0,05
10,31	250			

Gran method values graphs (TPA/D-g)

Ph	V(ml)	dph	Dv	dph/dv
0,9	1			
0,9	2	0	1	0
0,9	3	0,03	1	0,03
0,93	4	0	1	0
0,93	5	0,01	1	0,01
0,94	6	0,01	1	0,01
0,95	7	0,02	1	0,02
0,97	8	0,01	1	0,01
0,98	9	0,01	1	0,01
0,99	10	0	1	0
0,99	11	0,02	1	0,02
1,01	12	-0,01	1	-0,01
1	13	0	1	0
1	14	0,02	1	0,02
1,02	15	0	1	0
1,02	16	0,01	1	0,01
1,03	17	0,01	1	0,01
1,04	18	0,02	2	0,01
1,06	20	0,01	1	0,01
1,07	21	0,02	1	0,02
1,09	22	0,01	1	0,01
1,1	23	0,01	1	0,01
1,11	24	0,01	1	0,01
1,12	25	0,02	1	0,02
1,14	26	0,02	1	0,02
1,16	27	0,01	1	0,01
1,17	28	0,01	1	0,01
1,18	29	0,01	1	0,01
1,19	30	0,01	1	0,01
1,2	31	0,01	1	0,01
1,21	32	0,01	1	0,01
1,22	33	0,01	1	0,01
1,23	34	0,01	1	0,01
1,24	35	0,01	1	0,01
1,25	36	0,01	1	0,01
1,26	37	0,01	1	0,01
1,27	38	0	1	0
1,27	39	0,01	1	0,01
1,28	40	0,01	1	0,01
1,29	41	0,01	1	0,01
1,3	42	0,01	1	0,01
1,31	43	0,01	1	0,01

1,32	44	0,01	1	0,01
1,33	45	0,01	1	0,01
1,34	46	0,01	1	0,01
1,35	47	0	1	0
1,35	48	0,01	1	0,01
1,36	49	-0,1	1	-0,1
1,26	50	0,11	1	0,11
1,37	51	-0,01	1	-0,01
1,36	52	0	1	0
1,36	53	0,01	1	0,01
1,37	54	0	1	0
1,37	55	0,02	1	0,02
1,39	56	-0,01	1	-0,01
1,38	57	-0,01	1	-0,01
1,37	58	0	1	0
1,37	59	0	1	0
1,37	60	0	1	0
1,37	61	0,01	1	0,01
1,38	62	0,01	1	0,01
1,39	63	0	1	0
1,39	64	0,01	1	0,01
1,4	65	0,03	1	0,03
1,43	66	0	1	0
1,43	67	0	1	0
1,43	68	0	1	0
1,43	69	0,01	1	0,01
1,44	70	0,02	1	0,02
1,46	71	0,02	1	0,02
1,48	72	0,03	1	0,03
1,51	73	0,01	1	0,01
1,52	74	0,01	1	0,01
1,53	75	0,01	1	0,01
1,54	76	0	1	0
1,54	77	0,01	1	0,01
1,55	78	0,01	1	0,01
1,56	79	0,01	1	0,01
1,57	80	0,01	1	0,01
1,58	81	0	1	0
1,58	82	0	1	0
1,58	83	0,01	1	0,01
1,59	84	0,02	1	0,02
1,61	85	0	1	0
1,61	86	0,01	1	0,01
1,62	87	0,01	1	0,01
1,63	88	0,01	1	0,01

1,64	89	0,01	1	0,01
1,65	90	0,01	1	0,01
1,66	91	0,03	1	0,03
1,69	92	0	1	0
1,69	93	0,02	1	0,02
1,71	94	0,01	1	0,01
1,72	95	0,01	1	0,01
1,73	96	0,02	1	0,02
1,75	97	0,01	1	0,01
1,76	98	0	1	0
1,76	99	0	1	0
1,76	100	0,01	1	0,01
1,77	101	0,01	1	0,01
1,78	102	0,01	1	0,01
1,79	103	0	1	0
1,79	104	0,01	1	0,01
1,8	105	0	1	0
1,8	106	0,01	1	0,01
1,81	107	0,01	1	0,01
1,82	108	0,02	1	0,02
1,84	109	0	1	0
1,84	110	0,01	1	0,01
1,85	111	0,01	1	0,01
1,86	112	0	1	0
1,86	113	0	1	0
1,86	114	0	1	0
1,86	115	0	1	0
1,86	116	0	1	0
1,86	117	0	1	0
1,86	118	-0,02	1	-0,02
1,84	119	0	1	0
1,84	120	0,01	1	0,01
1,85	121	-0,01	1	-0,01
1,84	122	-0,01	1	-0,01
1,83	123	-0,01	1	-0,01
1,82	124	0,01	1	0,01
1,83	125	0	1	0
1,83	126	0	1	0
1,83	127	0,01	1	0,01
1,84	128	0,01	1	0,01
1,85	129	-0,01	1	-0,01
1,84	130	0,01	1	0,01
1,85	131	0,02	1	0,02
1,87	132	0	1	0
1,87	133	0	1	0

1,87	134	0,01	1	0,01
1,88	135	-0,01	1	-0,01
1,87	136	0,02	1	0,02
1,89	137	-0,01	1	-0,01
1,88	138	0,02	1	0,02
1,9	139	0	1	0
1,9	140	0,04	1	0,04
1,94	141	0,01	1	0,01
1,95	142	-0,01	1	-0,01
1,94	143	0,02	1	0,02
1,96	144	0	1	0
1,96	145	0,01	1	0,01
1,97	146	0	1	0
1,97	147	0,01	1	0,01
1,98	148	0,01	1	0,01
1,99	149	0	1	0
1,99	150	0,01	1	0,01
2	151	0,01	1	0,01
2,01	152	0,01	1	0,01
2,02	153	0,02	1	0,02
2,04	154	0,01	1	0,01
2,05	155	0,01	1	0,01
2,06	156	-0,01	1	-0,01
2,05	157	0,01	1	0,01
2,06	158	0	1	0
2,06	159	0,01	1	0,01
2,07	160	0,01	1	0,01
2,08	161	0	1	0
2,08	162	0,01	1	0,01
2,09	163	0,02	1	0,02
2,11	164	0,01	1	0,01
2,12	165	0,01	1	0,01
2,13	166	-0,02	1	-0,02
2,11	167	0,03	1	0,03
2,14	168	0,04	1	0,04
2,18	169	-0,01	1	-0,01
2,17	170	0,03	1	0,03
2,2	171	-0,03	1	-0,03
2,17	172	0,01	1	0,01
2,18	173	0,02	1	0,02
2,2	174	0	1	0
2,2	175	0,02	1	0,02
2,22	176	0	1	0
2,22	177	0,02	1	0,02
2,24	178	0	1	0

2,24	179	0,02	1	0,02
2,26	180	0,02	1	0,02
2,28	181	0,01	1	0,01
2,29	182	0	1	0
2,29	183	0,03	1	0,03
2,32	184	0,01	1	0,01
2,33	185	0,01	1	0,01
2,34	186	0	1	0
2,34	187	0,02	1	0,02
2,36	188	0,01	1	0,01
2,37	189	0,03	1	0,03
2,4	190	-0,03	1	-0,03
2,37	191	0,03	1	0,03
2,4	192	0,05	1	0,05
2,45	193	0,03	1	0,03
2,48	194	0,02	1	0,02
2,5	195	-0,05	1	-0,05
2,45	196	0,03	1	0,03
2,48	197	0,04	1	0,04
2,52	198	-0,04	1	-0,04
2,48	199	0,05	1	0,05
2,53	200	-0,01	1	-0,01
2,52	201	0	1	0
2,52	202	0,05	1	0,05
2,57	203	0	1	0
2,57	204	-0,01	1	-0,01
2,56	205	0,03	1	0,03
2,59	206	-0,01	1	-0,01
2,58	207	0,03	1	0,03
2,61	208	0,04	1	0,04
2,65	209	0,02	1	0,02
2,67	210	0,09	1	0,09
2,76	211	0,01	1	0,01
2,77	212	-0,03	1	-0,03
2,74	213	0	1	0
2,74	214	0,03	1	0,03
2,77	215	0,05	1	0,05
2,82	216	-0,04	1	-0,04
2,78	217	0,22	1	0,22
3	218	-0,08	1	-0,08
2,92	219	0,04	1	0,04
2,96	220	-0,02	1	-0,02
2,94	221	0,07	1	0,07
3,01	222	0,05	1	0,05
3,06	223	0,01	1	0,01

3,07	224	0,05	1	0,05
3,12	225	0,03	1	0,03
3,15	226	0,04	1	0,04
3,19	227	0,07	1	0,07
3,26	228	0,04	1	0,04
3,3	229	0,11	1	0,11
3,41	230	0,11	1	0,11
3,52	231	0,13	1	0,13
3,65	232	-0,01	1	-0,01
3,64	233	0,24	1	0,24
3,88	234	0,28	1	0,28
4,16	235	1,47	1	1,47
5,63	236	-0,13	1	-0,13
5,5	237	0,4	1	0,4
5,9	238	0,19	1	0,19
6,09	239	1,21	1	1,21
7,3	240	0,29	1	0,29
7,59	241	0,23	1	0,23
7,82	242	0,1	1	0,1
7,92	243	0,03	1	0,03
7,95	244	0,12	1	0,12
8,07	245	0,59	1	0,59
8,66	246	1,05	1	1,05
9,71	247	0,29	1	0,29
10	248	1,82	1	1,82
11,82	249	0,3	1	0,3
12,12	250			

Summary

This research focused on green chemistry, bio polymers, and synthesis of bio-product. By replacing D-glucose in terephthalic acid's para position with a polymerization reaction, the study made it possible to synthesize a polymer product with antibacterial activity. The product formed at a high temperature, in an inert medium, and with a favorable yield, as confirmed by the infrared spectroscopy analysis.

In perspective we can perform this synthesis without a temperature or solvent to produce a high-yield biopolymer

Key word: biopolymer, polymerization, terephthalic acid, D-glucose, para position, antibacterial activity.

Résumé

Cette recherche a porté sur la chimie verte, les biopolymères et la synthèse du bio-produit. En remplaçant la D-glucose en position para de l'acide téréphtalique par une réaction de polymérisation, l'étude a permis de synthétiser un produit polymère ayant une activité antibactérienne. Le produit est formé à une température élevée, en milieu inerte et avec un rendement favorable, comme l'a confirmé l'analyse par spectroscopie infrarouge.

En perspective, nous pouvons réaliser cette synthèse sans température ni solvant pour produire un polymère avec un bon rendement.

Mots clés : biopolymère, polymérisation, acide téréphtalique, D-glucose, para position, activité antibactérienne.

ملخص

ركز هذا البحث على الكيمياء الخضراء والبوليمرات الحيوية وتركيب المنتجات الحيوية. من خلال استبدال الجلوكوز في الموضع البارا لحمض التريفثاليك بتفاعل بلمرة، أتاحت الدراسة تصنيع منتج بوليمر ذو نشاط مضاد للبكتيريا. يتكون المنتج عند درجة حرارة عالية، في وسط خامل، وبنتيجة مناسبة، كما أكد ذلك التحليل الطيفي للأشعة تحت الحمراء.

ومن منظور أخر، يمكننا إجراء هذا التوليف بدون درجة حرارة أو مذيب لإنتاج بوليمر حيوي عالي الإنتاجية

الكلمات المفتاحية: البوليمر الحيوي، البلمر، حمض التريفثاليك، الجلوكوز، الموضع البارا، النشاط المضاد للبكتيريا، البلمرة.