

Ministry of Higher Education
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***Synthesis of new polyethylene based copolymer
and study their adhesion, solubility and
photostabilization properties***

A Thesis

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Chapter One
Introduction and
Previous Studies

Introduction

1.1 Definition of polymers

A polymer is a long-chain molecule made up of many chemically bonded repeating units called monomers. The word polymer is of Greek origin, “poly” meaning many and “mer” meaning part. In other words, “many” of the same “part” are connected to form a long chain known as a polymer [1]. The reaction by which the monomers combine to form polymer is known as polymerization [2]. Polymer molecule consists of tens, hundreds, or even thousands of monomer units. The most important features of polymer composites are that they are easy to form, have low density compared to metals, have superior surface quality, and increase corrosion resistance. In addition to many advantages such as high strength, size and thermal stability, adhesion, hardness, and photo stabilization, polymer composites can compete with metals in terms of durability and hardness [3], and to adjust the thermal and mechanical characteristics, it is necessary to control the structure and intermolecular interaction by introducing various functional groups into the main chain and the side chains of the polymers [4].

1.2 Historical development of polymer

Natural polymers, such as wool, cotton, and natural rubber, have been utilized in the past, dating back to before 1800 [5]. The birth of synthetic polymers may be traced back to the mid-nineteenth century. In the 1830s, Charles Goodyear invented the vulcanization technique, which turned natural rubber's sticky latex into a viable elastomer for tire manufacturing [6], Christian F. Schönbein reacted nitric acid with cellulose to produce cellulose nitrate. This was used in the 1860s as the first man-made

thermoplastic, celluloid. In 1907, Leo Hendrik Baekeland [7] produced Bakelite (phenol–formaldehyde resin). Glyptal (unsaturated-polyester resin) was prepared a protective coating resin by General Electric in 1912. By the 1930s, researchers at DuPont in the United States had produced a variety of new polymers including synthetic rubber and more “exotic” materials such as nylon and Teflon. By 1938, Dow had produced polystyrene in commercial scale for the first time and, in 1939, polyethylene (low-density) was made by scientists at ICI in England. In the 1950s, Karl Ziegler and Giulio Natta independently developed a family of stereospecific transition-metal catalysts that made possible the commercialization of polypropylene as a major commodity plastic [8]. The 1960s and 1970s witnessed the development of a number of high-performance engineering plastics polymers that could compete favorably with more traditional materials, such as metals, for automotive and aerospace applications. These include polycarbonates, poly (phenylene oxide), polysulfones, polyimides, aromatic polyamides such as Kevlar, and other high-temperature rigid-chain polymers. specialty polymers with electrically conducting, photoconducting, and liquid-crystalline properties have appeared for a variety of applications [9].

1.3 Classification of polymers

There are thousands of synthetic polymers known today, and with the rapid improvements in the science of polymer synthesis, there is little doubt that more will be discovered in the future. Polymers divide into two groups depending on the type of polymerization process used in their synthesis, a more specific classification system based on polymer structure, polymerization method, and intermolecular forces assists in understanding

polymer characteristics the following below are some basic ways of polymers [10], and are abbreviated as shown classified in Table 1-1.

Table (1-1): General classification of polymers.

Polymer Classification	Type of Polymer
1- Origin	A-Natural polymer
	B- Semi synthetic polymer
	C- Synthetic polymer
2- Thermal Response	A- Thermoplastic polymer
	B-Thermosetting polymers
3- Mode of Polymerization	A-Addition polymers
	B- Condensation polymers
4- Structure	A- Linear polymer
	B- Branched polymer
	C- Cross-linked polymers
5- Mechanical Behavior	A- Elastomers
	B- Plastics
	C- Fibers
6- Tactility	A- Isotactic polymer
	B- Syndotactic polymer
	C- Atactic polymer

1.3.1 Thermal Response

Polymers can be divided into two groups depending on their thermal response [11].

A. **Thermoplastic polymers:** Thermoplastic polymers are long-chain polymers that are held together by intermolecular interactions (Van der Waal's forces). When heated, these polymers soften (like a thick fluid) then harden when allowed to cool, forming a hard mass. They don't have any cross bonds and may be simply molded using heat and molds. Polystyrene, sometimes known as PVC, is a popular example (which is used in making pipes).

B. **Thermosetting polymers:** Thermosetting plastics are polymers with low molecular weights that are semi-fluid in nature. They initiate cross-linking between polymer chains when heated, making them rigid and infusible. When heat is applied, they create a three-dimensional structure. In nature, this reaction is irreversible. Bakelite, which is used to make electrical insulation, is the most frequent example of a thermosetting polymer.

1.3.2 Origin

Polymers have been classified into three types based on their natural occurrence.

A. **Natural polymer:** a polymer that is the results of a polymerization process that occurs naturally in plants and animals also known as biopolymers [12]. Examples of natural polymers are proteins, starch, cellulosic, methyl cellulose, natural rubber.

B. **Semi synthetic polymer:** they are derived from naturally occurring polymers and undergo further chemical modification [13]. For example, Vulcanized Rubber, cellulose nitrate, cellulose acetate.

C. **Synthetic polymer:** the man-made polymers or polymers that humans can synthesize/create artificially in a lab [14,15]. Examples of such polymers are polyvinyl alcohol (PVA), polyethylene (PE), polystyrene (PS), etc.

1.3.3 Line Structure

Polymers made from same compounds can have different properties depending on how they are made, Figure (1-1) shows the three main types of structures: linear, branched and cross linked [16].

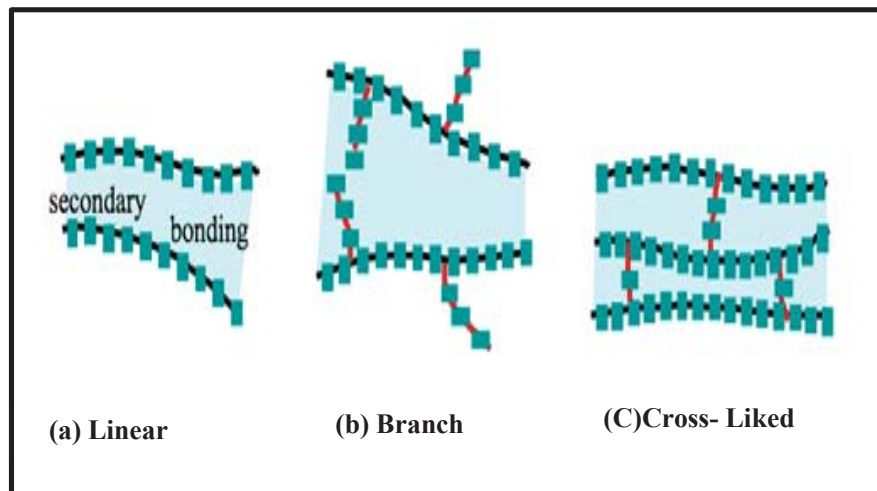


Figure (1-1): polymers types based on structures

A. **Linear polymers:** Linear (Figure (1-1- a) polymer is made up of a series of repeating units that are connected together; Polymer is referred to as a linear polymer if the monomer units are linked in a straight line.

B. **Branched polymer:** A branching polymer (Figure 1-2- b) is formed when monomer units are linked together in a branched configuration.

C. **Cross-linked or network polymers:** (Figure 1-1-c) are joined to one another by linking units, which may be long or short and made of the same repeating units as the main chain or other repeating units.

1.3.4 Mode of Formation

Basis on the mode of their formation, the polymers can be classified as [17].

A. addition polymers: are a polymer formed by chain addition

A. reactions between monomers that contain a double bond through chain polymerization, when the monomers are the same, it's called homo polymer, while the monomers are different, the polymer is a copolymer.

B. Condensation polymers: are a polymer formed by condensation reactions prepared by reactions between bi- or poly functional monomers which involve elimination of some small groups such as $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{NCO}$.

1.3.5 Mechanical behavior

Another important classification is the mechanical behavior of polymers, which can be classified as follows [18]:

A. **Elastomers (rubber):** These are polymers that can be deformed to at least twice their original length at room temperature and then quickly recover to their original length again when the stress is removed. The most common example is vulcanized rubber, which is a generic word that refers to any elastomer or combination of elastomers that has been cross-linked after being formed (vulcanization). Automotive tires, which are the most common use of vulcanized rubber, have these features.

B. **Plastics:** These are solid polymer compounds, high molecular weight compounds that may be molded with or without heat. These are often much stronger than rubbers. at or near room temperature.

C. The initial industrial development of major plastics polystyrene, the polyolefin, poly (vinyl chloride) (PVC), and poly (methyl methacrylate).

D. **Fibers:** are long, thin thread-like particles of material with high tensile Fiber composites having significantly improved stiffness and strength, but they are more complex to produce than other materials. Furthermore, and most essential, the strength of the fiber lies, ultimately, in the strength of the chemical bonds of the polymer chains resulting from by lining them up in the same direction. Some of the most common synthetic fibers are polyamides (nylon) and polyester. Polyacrylonitrile, which is also called acrylic fiber [19].

1.3.6 Tacticity

The “tacticity” term refers the configuration of these asymmetric centers along the chain of polymer. The tactic polymers are, however important consideration because it has effects on the physical and chemical properties of the polymer; tacticity is seen in vinyl polymers that include mono- or disubstituted groups. There are three different types of tacticity in polymers [20].

A. **Isotactic polymer:** is a polymer in which all of the pendant groups are situated on the same it side of the hydrocarbon backbone chain. An example of an isotactic polymer is a popular type of polypropylene. shown in the figure (1-2).

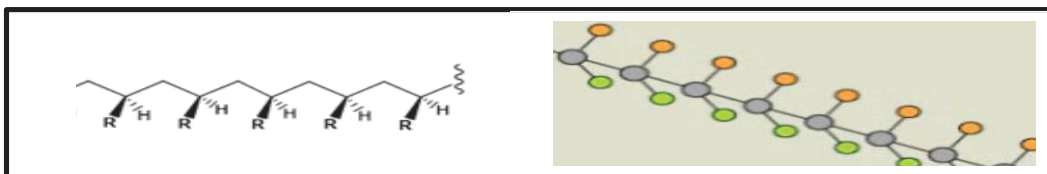


Figure (1-2): configuration of isotactic polymers

B. Syndiotactic: means that the pending groups have a regular, alternating pattern along the hydrocarbon backbone in the polymer chain.

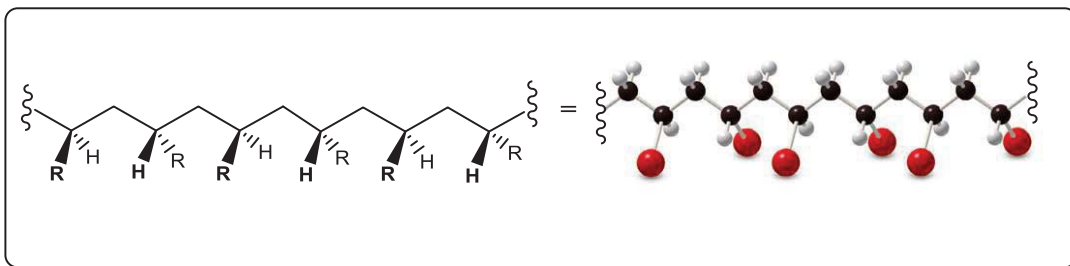


Figure (1-3): configuration of syndiotactic polymers

Atactic: A polymer with a random or irregular arrangement orientation of groups along the hydrocarbon backbone in the polymer chain [21].

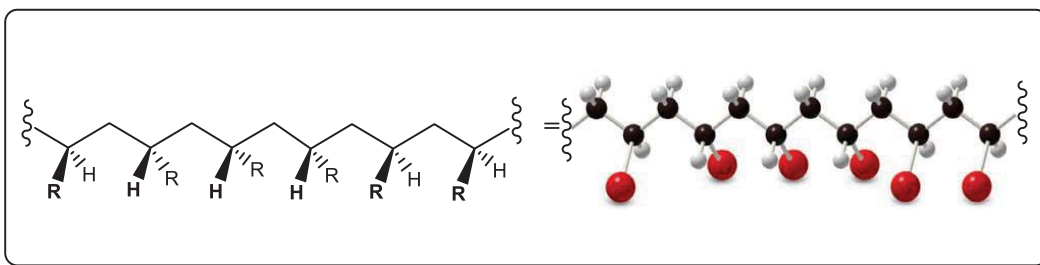


Figure (1-4): configuration of tactic polymers

1.4 Degree of Polymerization (DP)

The degree of polymerization (D_P) of a polymer is defined as the number of monomer units in the polymer chain. It is calculated as the ratio of the polymer's molecular weight to the molecular weight of the repeat unit. The relationship between the degree of polymerization (D_P) and the molecular weight (M_w) of a macromolecule is given by :

$$\text{Degree of polymerization} = \frac{M_w}{M^\circ}$$

Where M_w represents the polymer's average molecular weight and M° is the molecular weight of the repeating unit or monomer [22].

1.5 Polymerization Mechanisms

Polymerization is also known as polymer synthesis, and the small molecules that are chemically bound together to create a polymer are referred to as repeating units. Different polymerization processes are used to make polymers that have different properties and can be used for various applications. There are two main processes of polymerization. addition polymerization and condensation polymerization [23].

1.5.1 Condensation Polymerization or Step-growth Polymerization

Polymerization through step-growth occurs when the monomers have two or more functional groups at the ends. Polymer molecular weight determined by the degree of polymerization (D_p), which increases with increasing conversion of monomers in step-grow polymerizations. Polyamides (PA) and polyurethanes are two polymers that are often generated by the step-growth method (PU) [24].

1.5.2 Addition Polymerization or Chain Growth Polymerization

Chain polymerization occurs when a simple, low molecular weight molecule containing a double bond, referred to as a monomer. In this process, the monomers have been added to the site of the growing polymer, as well as reaction proceeds by the formation of the growth centre. Polypropylene (PP), polyvinyl chloride (PVC), polyethylene (PE), teflon, and polymethyl methacrylate (PMMA) are some of the polymers synthesized by the chain growth metho. which involve the unsaturated monomers as precursors. Chain growth polymerization has four main mechanisms: free radical, anionic, cationic, and coordination polymerization [25].

1.6 Free-Radical polymerization

Free-Radical polymerization is the most convenient method of polymer synthesis due to its versatility to a wide variety of monomers and the high molecular weight of the resulting polymers [26]. Chain-growth free radical polymerization is a major importance in the polymer industry. For example, more than 45% of polymer production is through free radical polymerizations processes [27]. Polymer synthetic conditions lead to outstandingly broad range of applications, including in coatings, inks, paints, adhesives, composites, latex production, packing industry, biomaterials, etc. free radical polymerization takes place in three distinct steps:

1.6.1 Initiation

Initiation is defined as a series of reactions that begins with the formation of primary radicals and culminates in addition to the carbon-carbon double bond of the monomer so as to form initiating radicals Scheme (1-5).

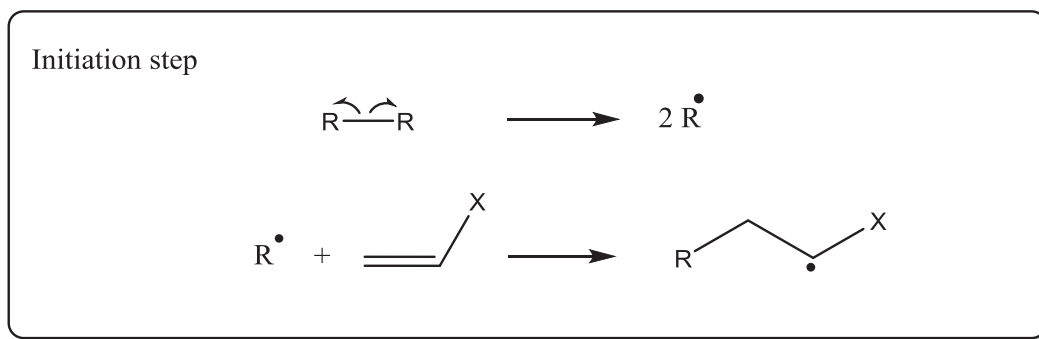


Figure (1-5): General mechanism for Initiation step

The most Important Initiator Classes for free radical polymerization reactions [28]:

1.6.1.1 Thermal decomposition (Peroxy Compounds)

The initiator is heated to the point where a free radical form, benzoyl peroxide and azo compounds are common initiators of free radicals and may generate free radicals by thermal decomposition [29].

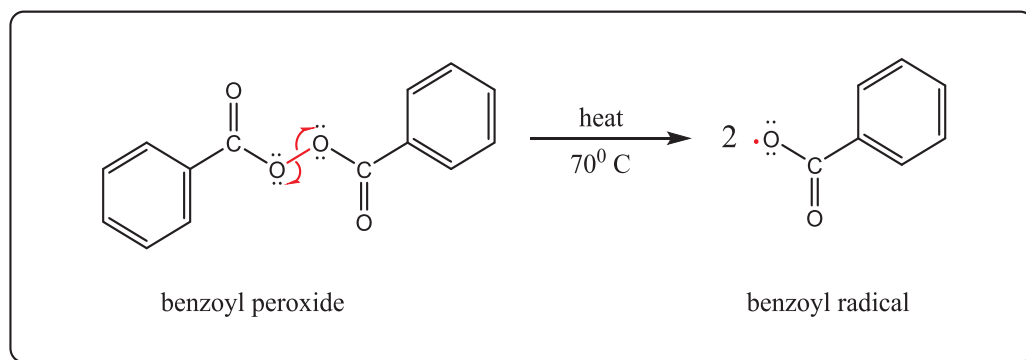


Figure (1-6): Thermal decomposition for benzoyl peroxide

For example, Marian Szkudlarek, and coworkers used benzoyl peroxide [30]. The copolymer modified with both iodides was best effect against *S. aureus*. Moreover, it shows (limited) selectivity to differentiate between mammalian cells and bacterial cell walls as shown in figure (1-7).

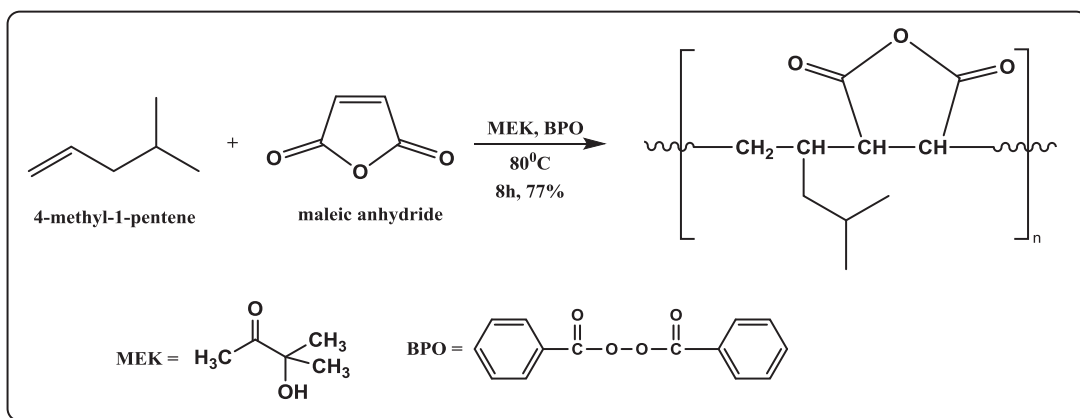


figure (1-7): Copolymerization of maleic anhydride with 4-methyl-1-pentene.

1.6.1. 2 Photolysis

Photo initiators absorb light in the ultraviolet-visible range, typically between 250 and 450 nm, and convert it to chemical energy in the form of reactive intermediates such as free radicals and reactive cations, which then initiate polymerization [31,32].

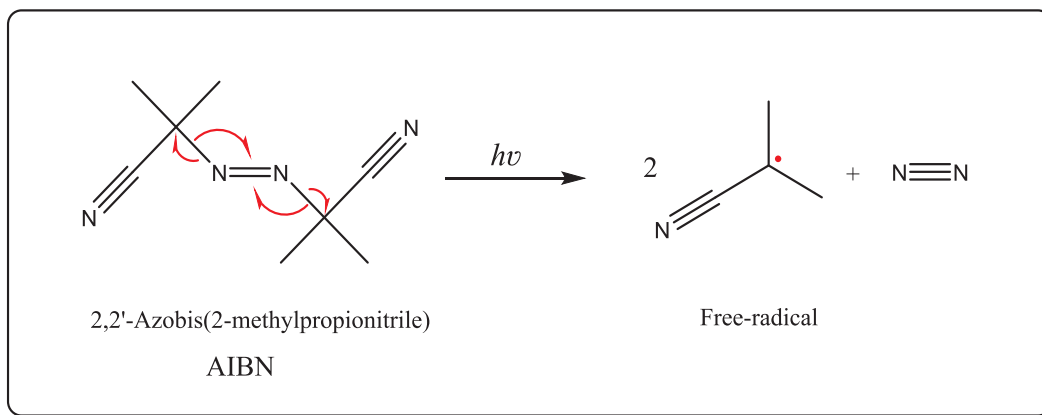


Figure (1-8): Photoinitiation for AIBN

Kirane and co-workers used AIBN as initiator. In the synthesis of the β -Cyclodextrin Based Stimuli-Responsive Star Copolymer, a polymer that can be used for environmental remediation in biodegradable materials and wastewater treatment [33] (Figure 1-8).

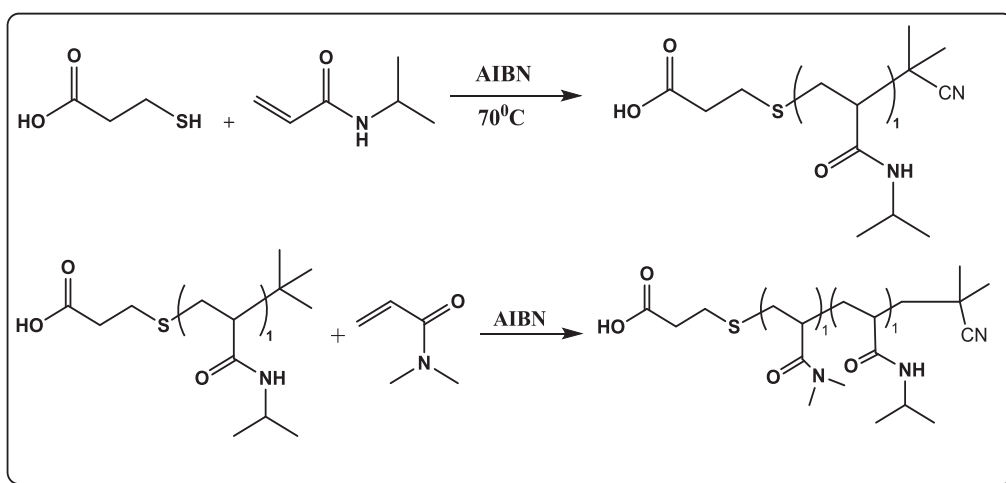


Figure (1-9): Synthesis of β -Cyclodextrin

1.6.1.3 Redox Systems

Reduction peroxides are one of the easiest redox processes to generate free radicals (without light). For example, Fenton's reagent is quite efficient to generate hydroxyl radical figure (1-10). Precisely, an electron is transferred from Iron (II) to the peroxide leading to a dissociation of the peroxide and the formation of iron (III) [34].

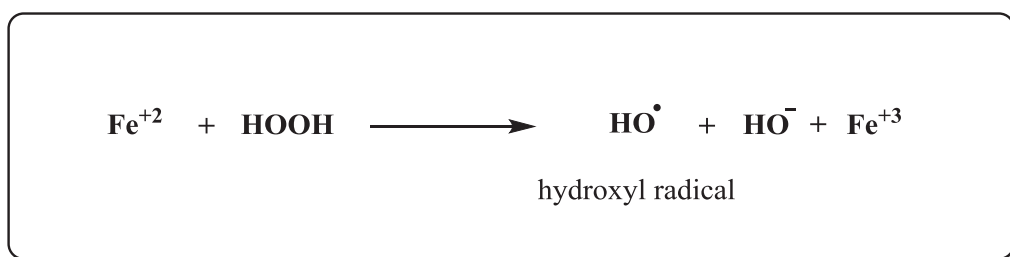


Figure (1-10): Example of interactions between metals (Fe^{2+}) and peroxides (H_2O_2) generate free radicals.

Other metallic reducing agents to generate free radicals are Ag(I), Cu(I), Rh(I), Mn (II), Co(II), V(V). More recently, Chunhong Zhang et al [35].conducted a study using a Rh(I) to Synthesis Helical Poly (phenylacetylene)s with Amide Linkage Bearing L-Phenylalanine and L-Phenylglycine Ethyl Ester Pendants and Their Applications as Chiral

Stationary Phases for HPLC. As shown in figure (1-11).

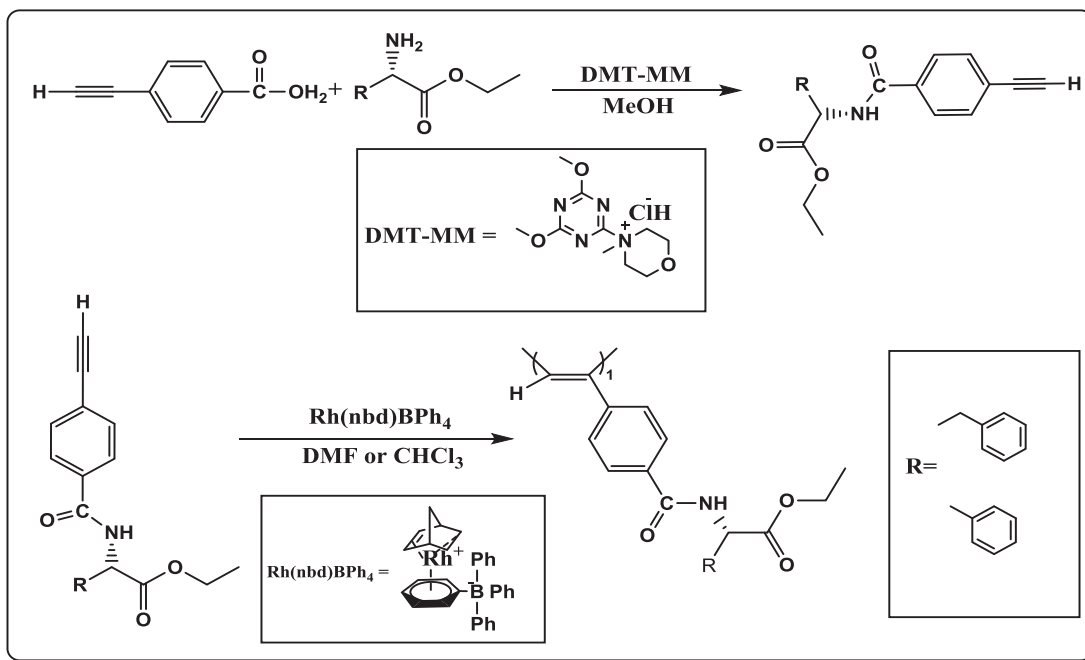


Figure (1-11) synthesis Helical poly (phenylacetylene)s with amide linkage bearing L-phenylalanine and L-Phenylglycine Ethyl Ester Pendants.

1.6.1.4 Disulfides, persulfates compounds

Compounds bearing a weak bond as persulfates, disulfides, disulfides or dihalogens can readily produce radicals when these latter are mixed with efficient reducing agents persulfate is particularly interesting initiating systems are widely used in industry for biomedical applications [36].

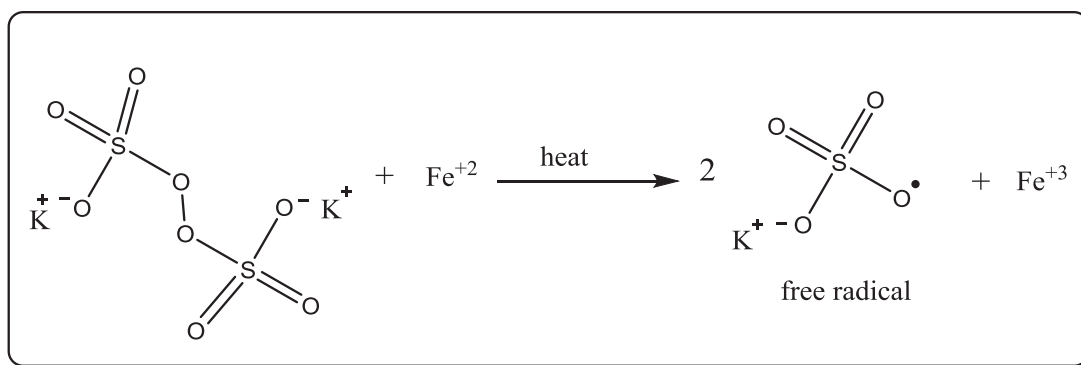


Figure (1-12): Example of persulfates initiating reactions are reduced by Fe(II).

Szczepan Bednarz et al. initiate free radical polymerization of itaconic acid in an un buffered aqueous solution using persulfate figure (1-13). The process results in the formation of poly (itaconic acid) and ammonium sulfate as a product of ammonium persulfate decomposition [37].

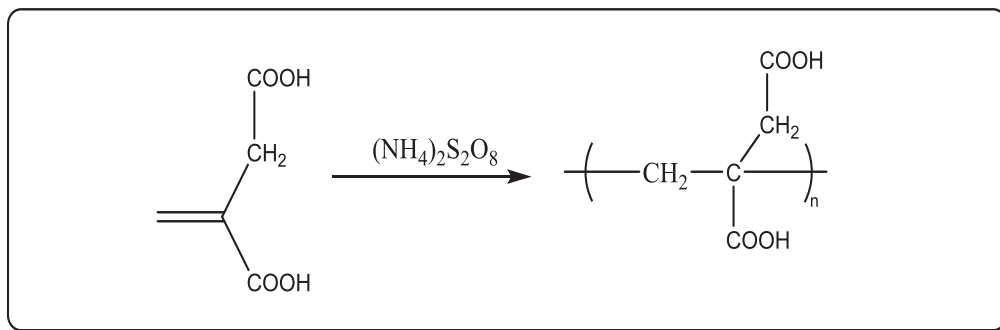


Figure (1-13): Synthesis of poly (itaconic acid) via persulfate as initiator.

1.6.2 Propagation

Propagation is the step that is most closely associated with the polymerization process itself, since it involves the addition of a monomer unit to the propagating macroradical. The chain grows during propagation when the active center is transferred from one monomer to another. The average molecular weight of the addition polymer is controlled by the number of times the propagation steps occur before the chain is terminated [38].

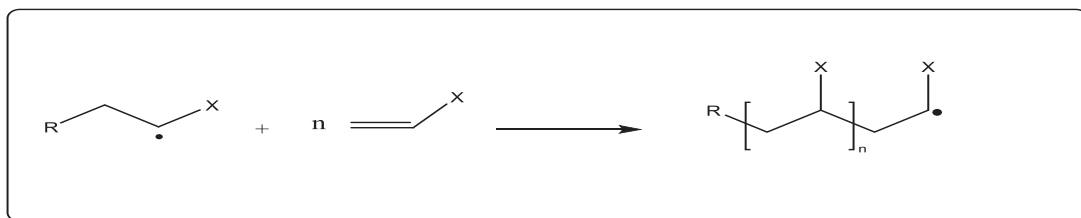


Figure (1-14): General step of propagation.

1.6.3 Termination

The propagation process would theoretically continue indefinitely. However, pairs of radicals have a tendency to react with one another, annihilating their activities in the process. Combination or propagation may be used to terminate. Combination or coupling occurs when two developing polymer chains react to generate a single nonreactive polymer chain [39]. as shown in Figure (1-15).

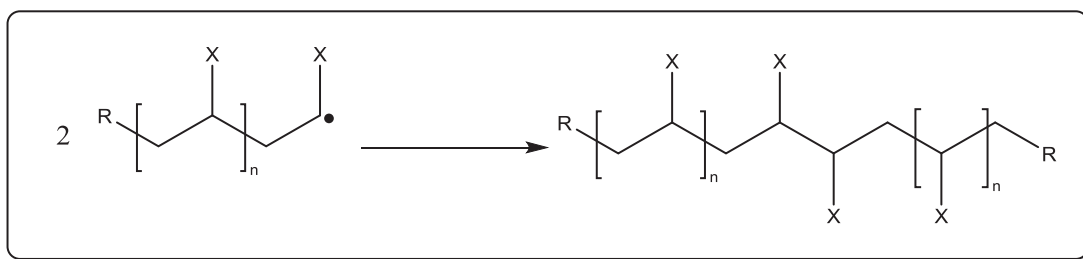


Figure (1-15): General step of termination.

1.7 Polymerization Techniques

The properties of the polymer depend on the method of polymerization techniques for example, its molecular weight distribution which influences its mechanical properties and process ability [40]. there are four industrial techniques for radical polymerization [41].

1.7.1 Bulk Polymerization

The only components of a bulk polymerization mixture consist mainly of liquid monomers and an initiator. The bulk polymerization is carried out with intense agitation [42]. The main advantage of bulk polymerization is the generation of a highly pure polymer. Furthermore, as the polymer is not diluted, the volume yield of the polymer is high. However, the high increase of viscosity during the polymerization makes the stirring and removal of the heat of polymerization difficult.

Xiping Ma and coworkers by bulk polymerization technique synthesized ternary hydrophobic association polymer [41] as shown in figure (1-16), the results of performance evaluation showed that the polymer obtained had excellent temperature and salt resistance.

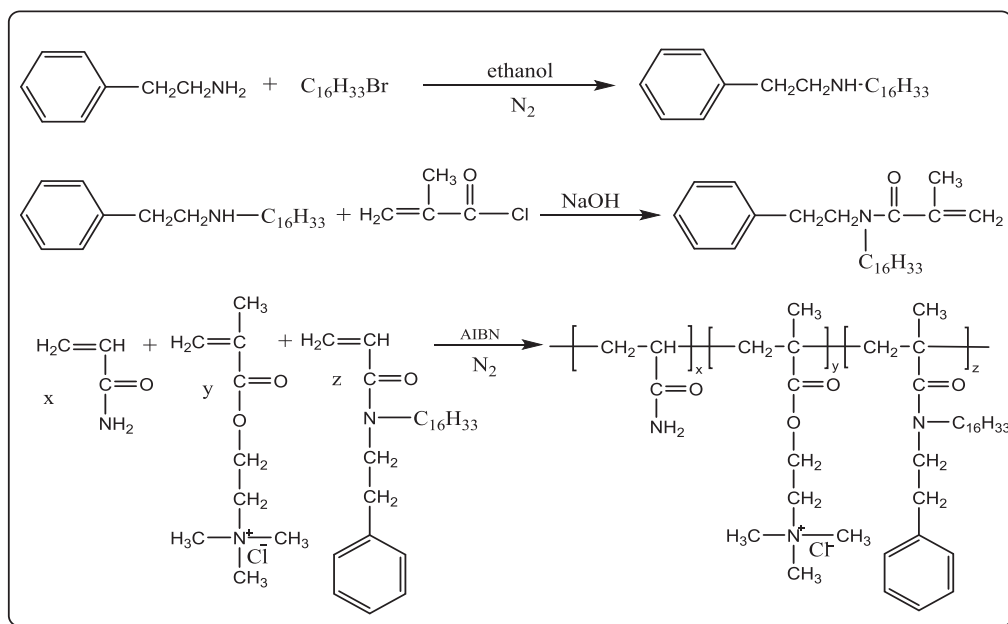


Figure (1-16): Synthesis of ternary hydrophobic association polymer.

1.7.2 Solution Polymerization

Solution polymerization meaning the polymerization occurs in a solution. The presence of a solvent prevents the viscosity of the reaction mixture from becoming too high, which is beneficial for fluid flow and heat transfer. While solvent evaporation and reflux may assist in the removal of heat from a reaction solution, they also result in a larger reactor volume. Additionally, it may result in the transfer of an active chain to the solvent, lowering the average molecular weight of the products and narrowing their molecular weight dispersion [44].

The most advanced work concerning polymer via Solution polymerization has been completed by Rikarani R. Choudhury and coworkers [43].

this group has been synthesized poly (styrene sulfonyl chloride) and characterization thereof for membrane applications for fuel cell and water purification as shown in figure (1-17).

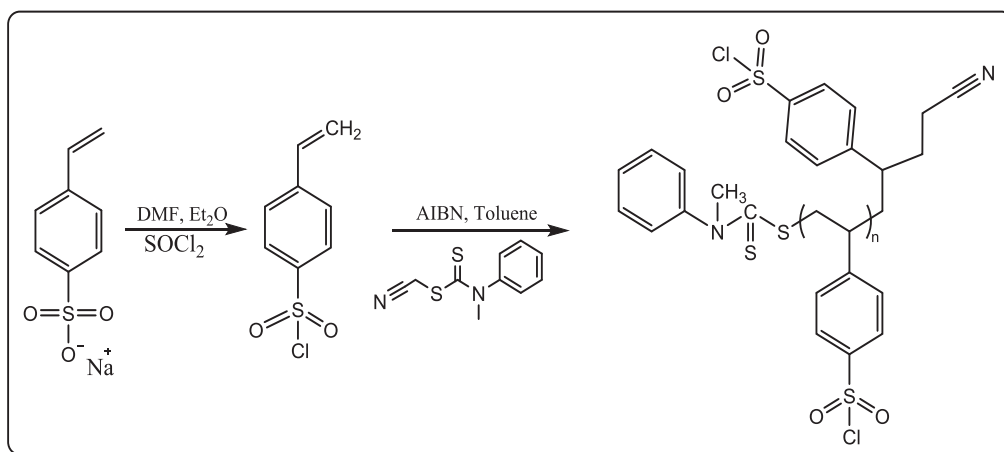


Figure (1-17): Synthesis of poly (styrene sulfonyl chloride).

1.7.3 Suspension Polymerization

During suspension polymerization, the monomer disperses in water as small oil-droplets, which is a specific form of bulk polymerization. This method is used to synthesize a wide variety of commercial resins, including polyvinyl chloride (PVC), polystyrene, and polyethylene (methyl methacrylate). When a small amounts of suspending agent is added and the temperature reaches the decomposition temperature of the free radical initiator, the reaction begins within the droplets and the produced polymer precipitates out of the monomer mixture to form polymer particles [45].

Tao Chen et al. [45] through suspension polymerization of 2-pyrrolidone prepared polybutyrolactam. Polybutyrolactam has excellent mechanical resistance, hydrophilicity and dye ability figure (1-18).

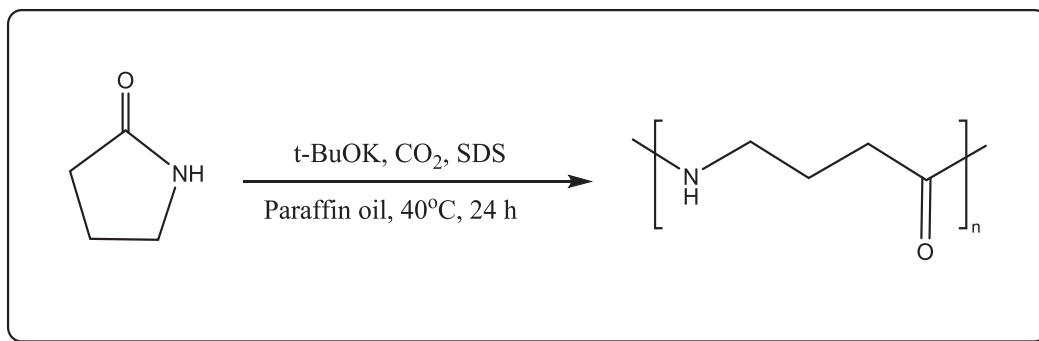


Figure (1-18): Presents the route for synthesizing polybutyrolactam by suspension polymerization.

1.7.4 Emulsion Polymerization

Emulsion polymerization is one of the simplest techniques for polymer formation. Water-soluble initiators are often used in emulsion polymerizations, and polymer chains are initiated in the aqueous phase [46]. Generally, the molecular weight of the polymer produced in an emulsion polymerization is an order of magnitude larger than that produced in a homogeneous homogeneous free-radical polymerization [47].

Nieswandt et al. synthesized thermoresponsive poly ((N,N-dimethyl acrylamide)-co-(N-isopropyl acrylamide)) copolymers via Emulsion Polymerization [48]. Polymers that have been prepared have the potential to be used in filtration membranes and temperature-sensitive coatings see in figure (1-19).

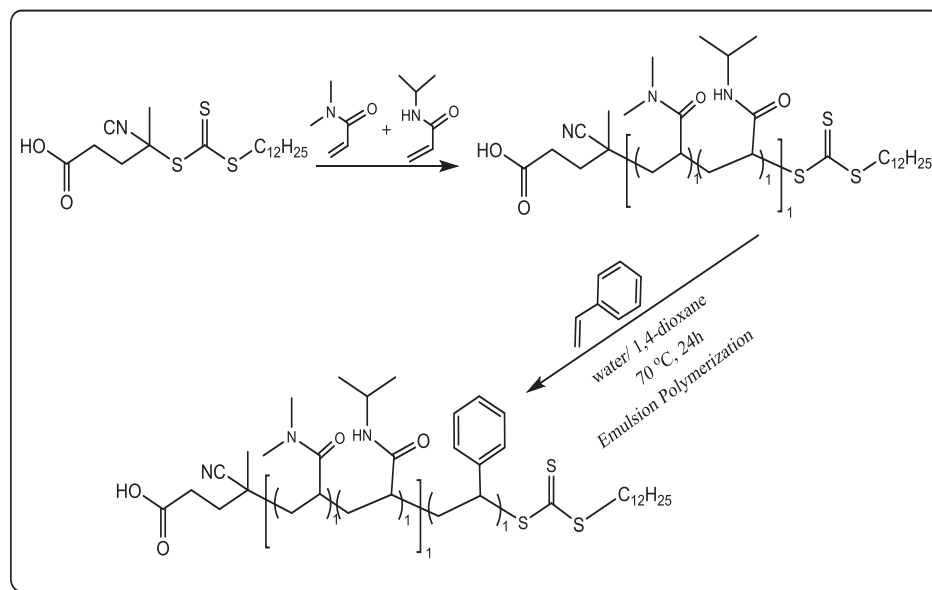


Figure (1-19): synthesis thermoresponsive poly ((N,N-dimethyl acrylamide)-co-(N-isopr acrylamide)) copolymers via Emulsion Polymerization.

1.8 Polymers as Adhesives

An adhesive is a non-metallic material, often in the form of a liquid or semi liquid, which has the ability to bond two surfaces together and withstand separation by transferring applied stresses over the joint region [49]. Adhesives provide a number of advantages over traditional joints, including the ability to join materials with varying geometry and dimensions. Adhesives are widely used in the current daily lives due to their many advantages, including high bonding strength, ease of application to a various surface, and low manufacturing cost [50].

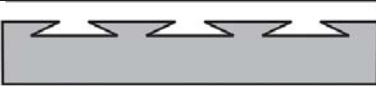
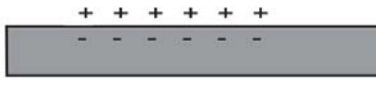
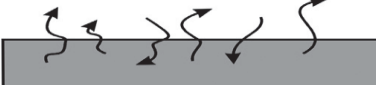
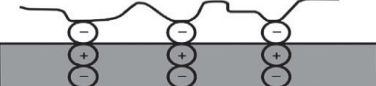
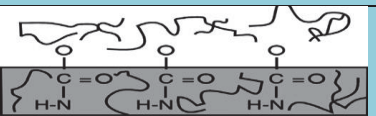
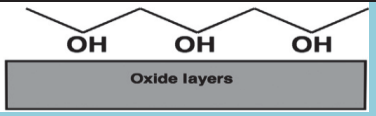
1.8.1 Adhesive classification

classification. The synthetic group has been subdivided into two major classifications: Industrial compounds include acrylics, epoxies, silicones, etc. An example of the specialty group is pressure-sensitive adhesives [51].

1.8.2 Theories of adhesion

Several theories have been developed in order to explain and improve interfacial interaction [52]. Theories have recently been postulated for adhesive bonding mechanisms as mechanical interlocking, electrostatic, diffusion, and adsorption/surface reaction Table (1-2) shows a scale of action for each mechanism, which are intended to aid in the understanding of these mechanisms.

Table (1-2): All six adhesion theories are summarized

No	Theories of adhesion	Scale of action	
1	Mechanical interlocking	Macroscopic	
2	Electrostatic	Macroscopic	
3	Diffusion	Molecular	
4	Wettability	Molecular	
5	Acid-base	Molecular	
6	Weak boundary layer	Molecular	

1.9 Photostabilization of polymers

Sunlight interacts with practically all organic polymers to generate irreversible chemical reactions. Exposure to ultraviolet (UV) light may lead to the significant degradation of many materials. UV light causes photooxidative degradation that results in breaking of the polymer chains, generates free radical and decreases the molecular weight, causing loss of mechanical characteristics and leads to useless materials, during a time. Recently synthesized, UV absorbers as additives to enhance the photostability of polymeric materials and, in particular, polyvinyl chloride and polystyrene [53].

1.9.1 Photo stabilization of poly (vinyl chloride)

PVC is a thermoplastic that is suited for various applications due to its great performance with unique properties. Among synthetic polymers, it is only superseded by polyethylene and polypropylene in terms of production and consumption scales. PVC is non-combustible as 57 % of its weight contains chlorine, and has several characteristics that make it attractive for various outdoor applications. However, sunlight and harsh conditions have a deleterious impact on PVC, resulting to its photo oxidation and photo degradation [54].

The photo stabilization of polymers may be achieved in many ways which depend on the action of stabilizer as light screeners, UV absorbers, excited-state quenchers, peroxide decomposers, and radical scavengers [55]. Olfat Abiad Nief [56], synthesized (5-Amino-1,3,4-thiadiazole-2-yl) phenol and its derivatives that might act as new types of photosensitizers for the photo degradation of poly (vinyl chloride).

1.10 Gel Permeation Chromatography (GPC)

Gel Permeation Chromatography (GPC) is a technique used for characterizing polymers. This technique separates or fractionates a sample based on its size and molecular weight [57]. The basis of gel permeation chromatography separation is based on the difference in permeability of solute molecules of different sized through a gel. According to the size of the pores in the gel, the largest molecules flow out first, followed by the medium-sized molecules, and finally by the smallest ones. GPC can be used in the road material industry to separate and determine the relative molecular weight and distribution of polymer [58]. As illustrated in Figure (1-21), the separation process occurs by connected columns that are filled with stationary phase materials such as silica gel and polystyrene. The stationary phase has been composed of small particles which have a lot of different-sized pores inside of them. When a polymer sample is dissolved in a solvent, it is assumed that the dissolved polymer chains form spherical units of different molecular size. Due to the effect of size exclusion, when these spherical units with larger molecular sizes (marked in red) pass through the columns with mobile phase, they are excluded by pores with smaller sizes in stationary phase. Thus, large molecules are rapidly eluted, resulting in a shorter elution or retention time. In comparison, smaller molecules (marked in blue) flow through a larger network of microscopic pores, resulting in a longer elution or retention time. On this basis, polymer samples can be separated into molecules of different molecular sizes, which are determined by their elution times [59].

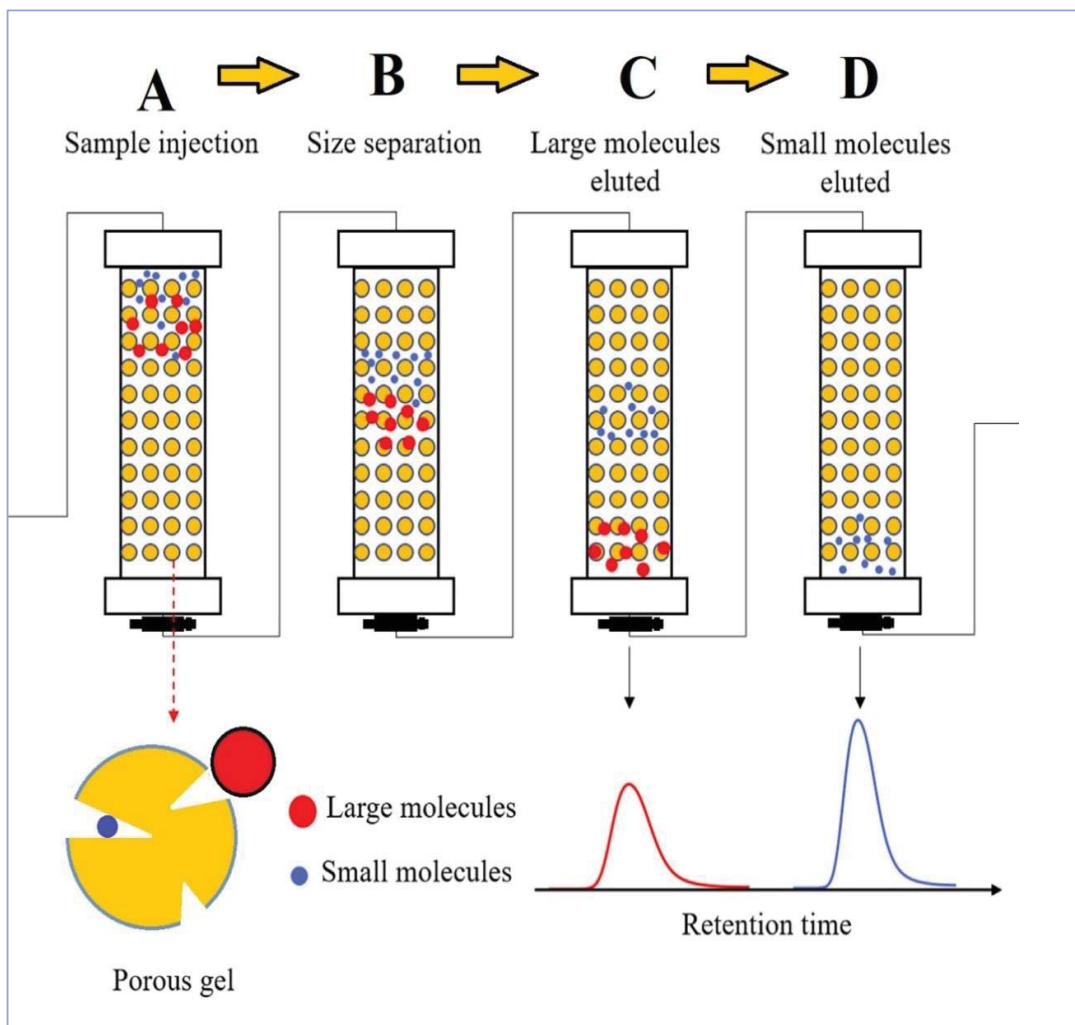


Figure (1-20): Schematic diagram of the gel permeation chromatography (GPC) separation principle.

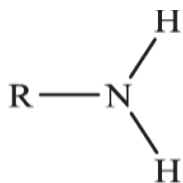
1.11 Aromatic amines

Aromatic amines are one of the organic compounds in chemistry which is found in our life, its functional group is amino group, they have many properties (such as boiling point and solubility) and many reactions (such as acylation, oxidation and alkylation), aromatic amines have a classification and derivatives such as (aniline) like other organic compounds, Aromatic amines are an significant industrial class of organic compounds that are commonly used in the manufacture of chemicals drug-producing industries. They usually contain soluble inorganic salts and even several organic acids. However, they are significantly weaker bases than ammonia or aliphatic amines, on heating with an alkyl halide, Primary aromatic amines undergo N-alkylation to give secondary amines, tertiary amines successively [60].

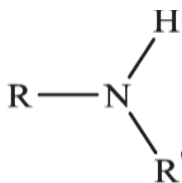
1.11.1 Type of Amines

On the basis of the presence of replaceable hydrogen atoms, it can be classified amines into three types [61]:

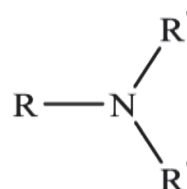
- **Primary Amines:** The amine is primary amine when an alkyl or Aryl group replaces one of three hydrogen atoms
- **Secondary Amines:** It is a secondary amine when the alkyl or aryl group replaces two hydrogen atoms.
- **Tertiary Amines:** The amine is a tertiary amine when total three hydrogen atoms are replaced by alkyl or aryl group.



Primary amine



Secondary amine



Tertiary amine

1.12 Benzothiazole

Benzothiazole is a representative class of sulfur-containing heterocycles and involves a benzene ring fused to a thiazole ring. The benzothiazole ring system was originally found in various marine and terrestrial natural compounds, which is widely used as vulcanization accelerators, antioxidants, plant growth regulators, anti-inflammatory agents, enzyme inhibitors, imaging reagents, fluorescence materials, and electroluminescent devices due to its highly pharmaceutical and biological activity. Especially, benzothiazole plays an important role in the field of medicinal chemistry and renders an extensive range of biological activities including anti-cancer, anti-bacterial, anti-tuberculosis, anti-diabetic, anthelmintic, anti-tumor, anti-viral, anti-oxidant, anti-inflammatory, anti-glutamate and anti-parkinsonism, anticonvulsant, muscle relaxant activities, neuroprotective, inhibitors of several enzymes and so on. Hence, the synthesis of benzothiazoles is of considerable interest due to their potent and significant biological activities and great pharmaceutical value [62]. Different synthetic paths have been developed for the preparation of benzothiazole derivatives (Scheme 1). Among them, the condensation reaction of 2-aminobenzenethiol with a carbonyl or cyano group-containing substance is the most commonly used method (Scheme 1, Method 1) [63]. Riadi and co-workers [64] found that benzothiazoles could be synthesized from the condensation of 2-aminobenzenethiol and aromatic aldehydes in refluxing toluene at 110 °C. Sun and co-workers [65] reported a copper-catalyzed method for the formation of 2-substituted benzothiazoles via condensation of 2-aminobenzenethiols with nitriles. Moreover, many researchers found that benzothiazoles could also be synthesized by the reaction of ortho-halogenated aniline with isothiocyanates, carbon disulfide and piperidine, aldehydes and sulfur, carbon disulfide and thiol, acid chloride and

Lawesson's reagent. (In addition, an alternative method is the intramolecular cyclization of ortho-halogenated analogs (Scheme 1, Method 3) [71]. Sahoo and colleagues indicated that benzothiazoles could be synthesized from ortho-halothioureas using both Cu(I) and Pd(II) transition metal as a catalyst. Unfortunately, these traditional processes have some disadvantages, such as low yield, poor selectivity, harsh reaction conditions, the use of toxic reagents or metal catalysts, etc. However, green chemistry advocates for the use of chemical technologies and methods to reduce or stop the use and production of raw materials, catalysts, solvents and reagents, products or by-products that are harmful to human health, community safety, and the ecological environment. Therefore, an exploration of environmentally friendly synthetic routes to prepare benzothiazoles is highly desirable [72].

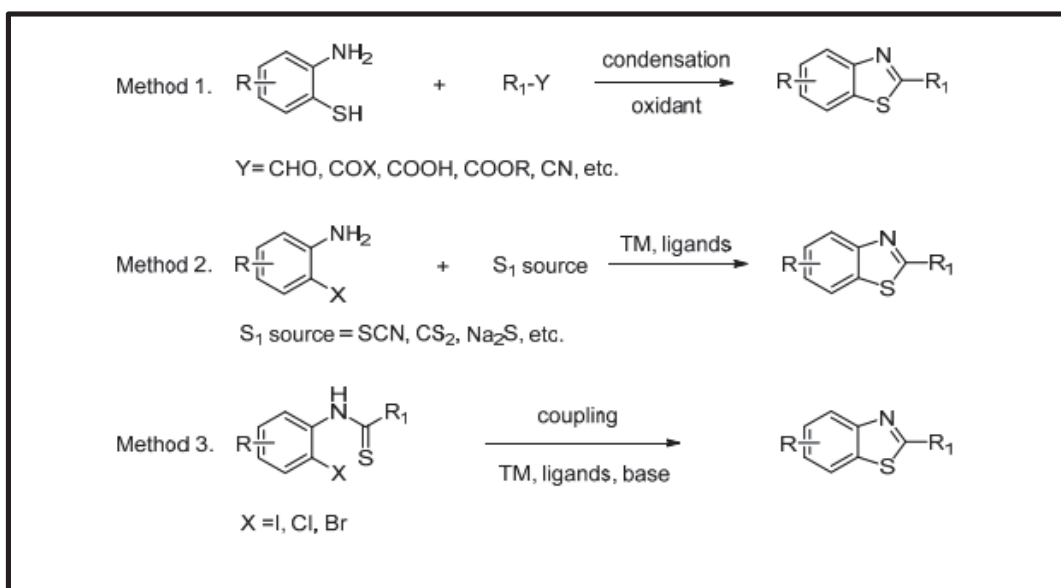


figure (1-21) The common synthetic routes for benzothiazoles.

1.13 Literature Survey

Gorshkov et.al (2020) prepared novel Metal-Polymer Complexes of Gallium/Gallium-68 with Copolymers of N-Vinylpyrrolidone with N-Vinylformamide and N-Vinyliminodiacetic Acid: A Hint for Radiolabeling of Water-Soluble Synthetic Flexible Chain Macromolecules [73], and were used as show in figure (1-23).

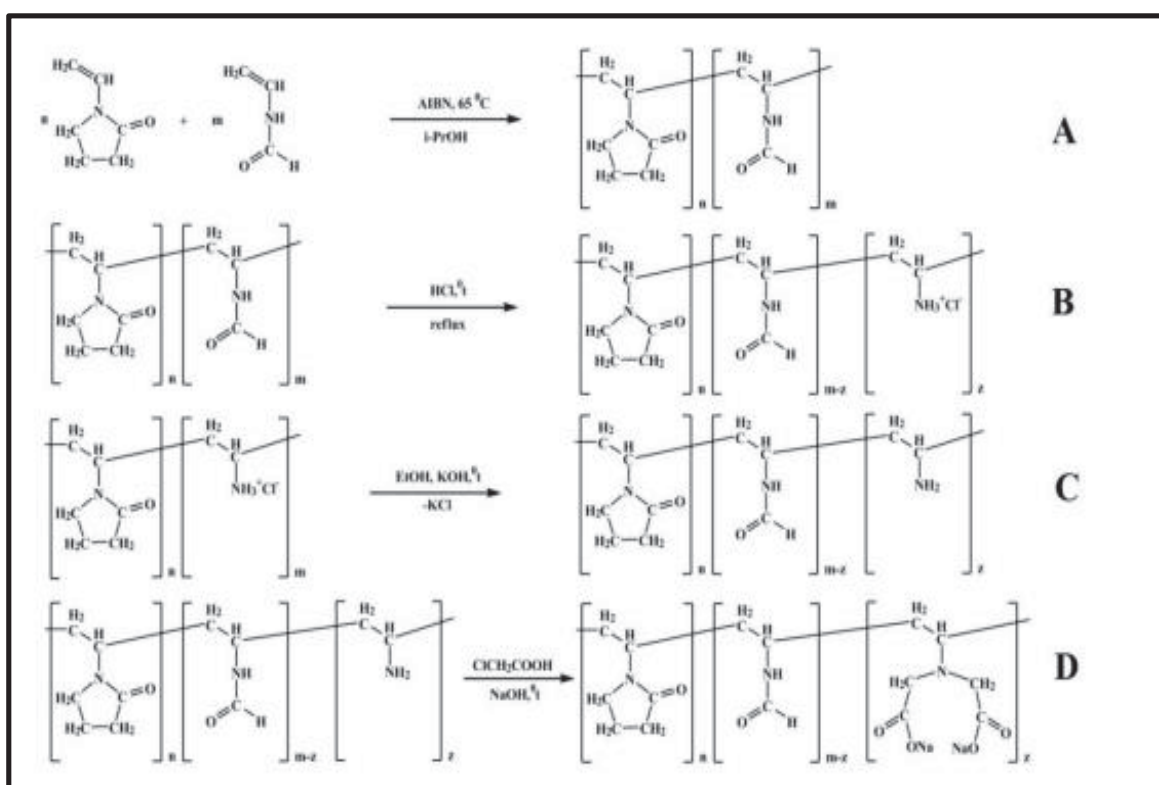


Figure (1-22): Synthesis of ternary copolymer N-vinylpyrrolidone/N-vinylformamide copolymers containing N-vinyliminodiacetic acid (VP-VFA-VIDA).

Jing et.al (2019) synthesized new Biodegradable Poly(acrylic acid-co-acrylamide)/ Poly(vinyl alcohol) Double Network Hydrogels with Tunable Mechanics and High Self-healing Performance [74].

Zhang et.al (2021) studied Preparation and Stabilization of High Molecular Weight Poly (acrylonitrile-co-2-methylenesuccinamic acid) for Carbon Fiber Precursor [75].

Xing et.al (2021) synthesized extremely tough and healable elastomer realized via reducing the crystallinity of its rigid domain [76].

Ai et.al (2021) studied UV-curable hyperbranched poly(ester-co-vinyl) by radical ring-opening copolymerization for antifouling coatings [77].

Shi et.al (2021) studied Physiologically relevant pH- and temperature-responsive polypeptide hydrogels with adhesive properties [78], and were used as shown in figure (1-24).

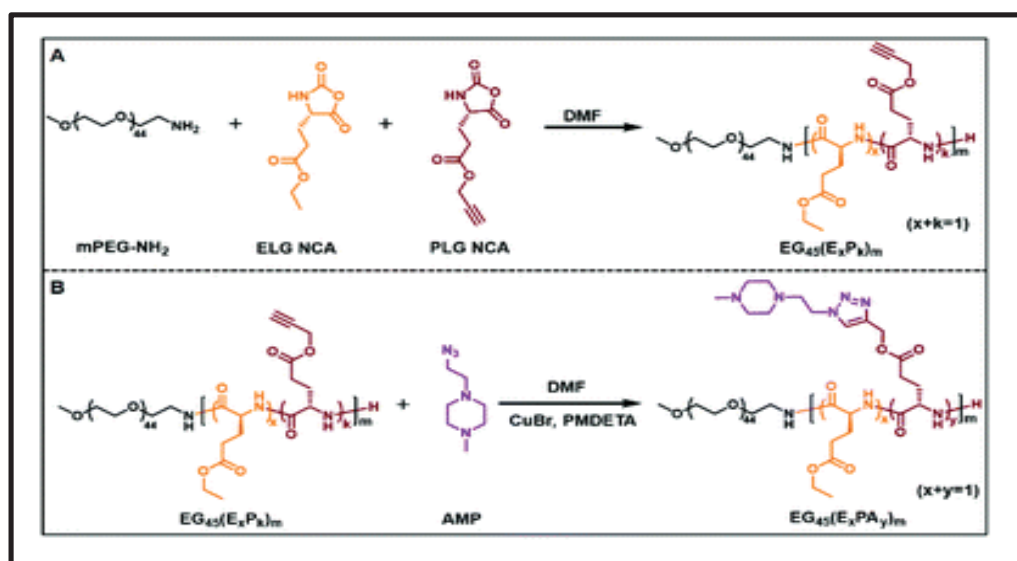


Figure (1-23): Synthesis routes of EG₄₅(E_xP_k)_m (A) and EG₄₅(E_xPA_y)_m (B)

Lee et.al (2021) studied Sequential Post-Polymerization Modification of Aldehyde Polymers to Ketone and Oxime Polymers [79], and were used as shown in figure (1-25).

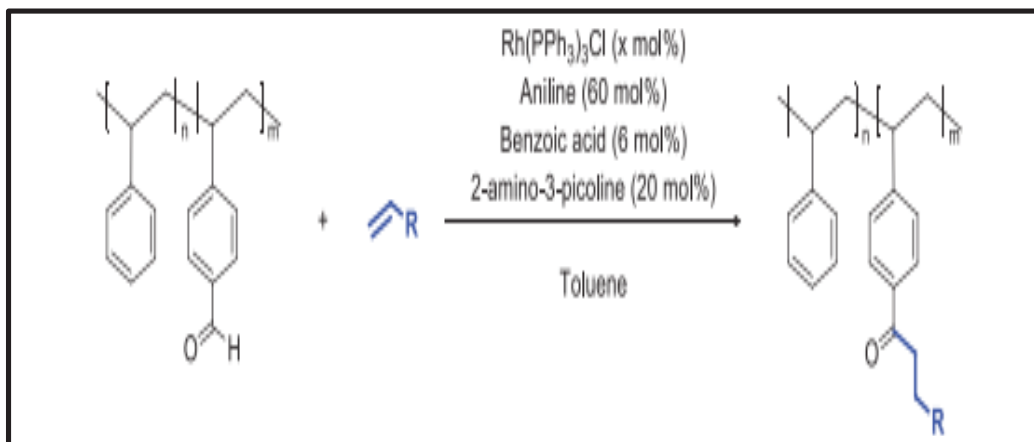


Figure (1-24) Sequential Post-Polymerization Modification of Aldehyde Polymers to Ketone and Oxime Polymers

Zhang et.al (2020) studied a supramolecular polymer with ultra-stretchable, notch-insensitive, rapid self-healing and adhesive [80], and were used us in figure (1-26)

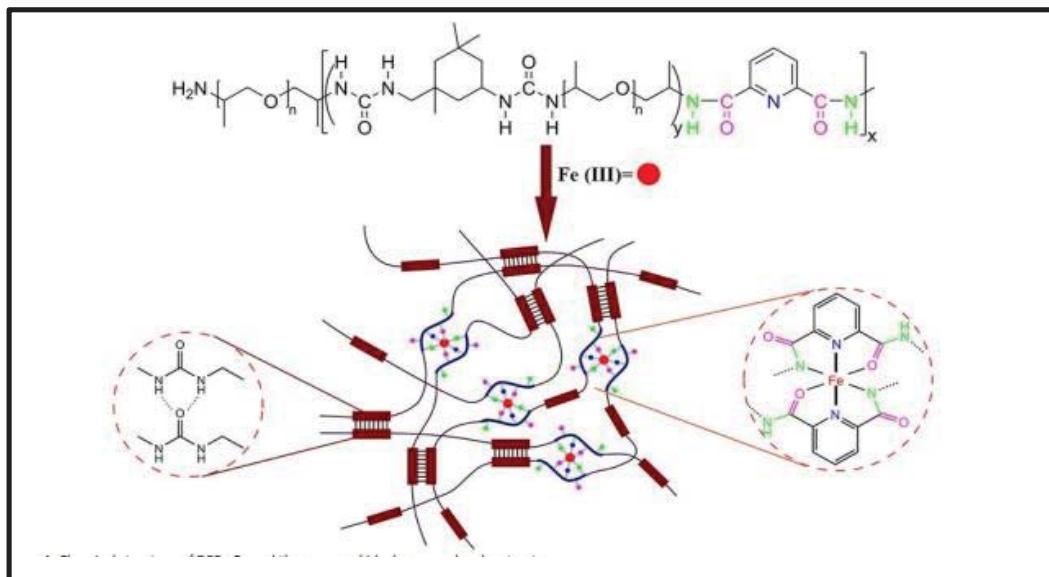


Figure (1- 25): Chemical structure of DPPy-Fe and the proposed ideal 26supramolecular structure

Xing et.al (2021) synthesized new Extremely tough and healable elastomer realized via reducing the crystallinity of its rigid domain [81].

Lin et.al (2020) studied Progress in the Preparation of Functional and (Bio)Degradable Polymers via Living Polymerizations [82]. and were used as shown in figure (1- 29).

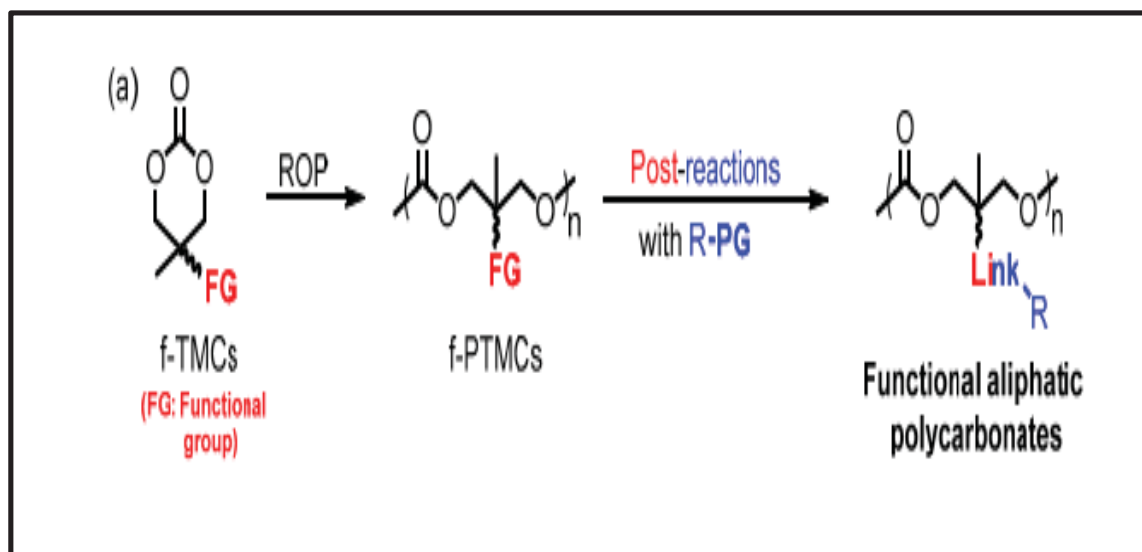
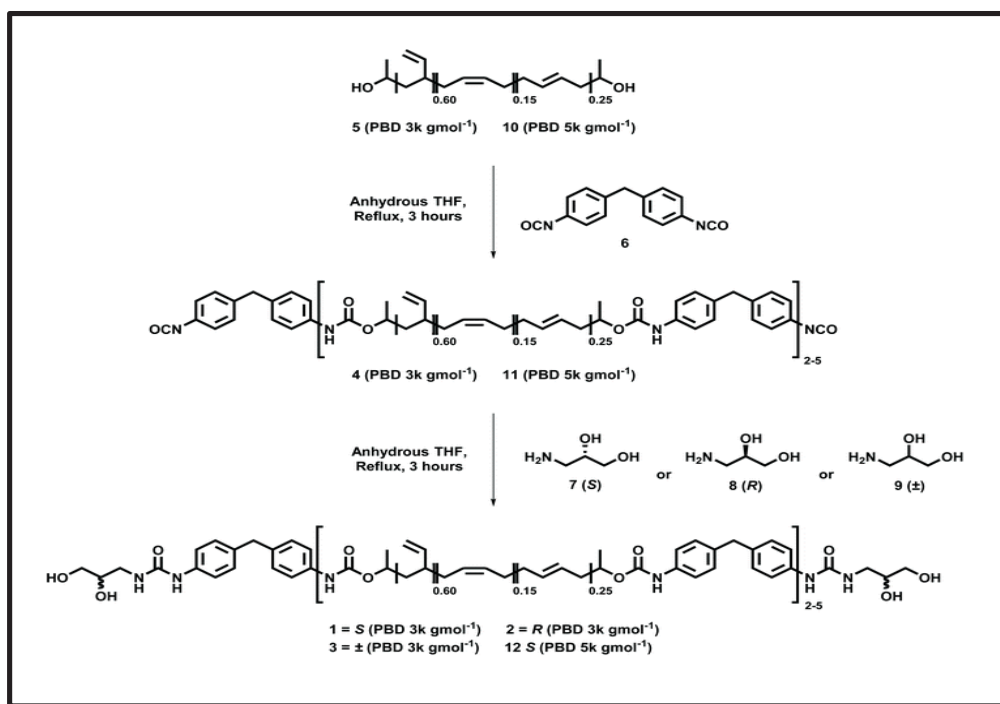


Figure (1-26) Preparation of Functional and (Bio)Degradable Polymers via Living

Merino et.al (2021) studied the effect of chiral end groups on the assembly of supramolecular polyurethanes [83]. and were used as shown in figure (1-30).



Scheme (1-27): Synthesis of supramolecular polyurethanes 1–3 and 12 from a poly(butadiene) (PBD) telechelic polyol of 3000 g mol⁻¹ or 5000 g mol⁻¹ terminated with homochiral (7 and 8) or racemic (9) self-assembly end-groups.

Hadiouch et.al (2021). Studied a versatile and straightforward process to turn plastics into antibacterial materials [84], and were used as shown in figure (1-31).

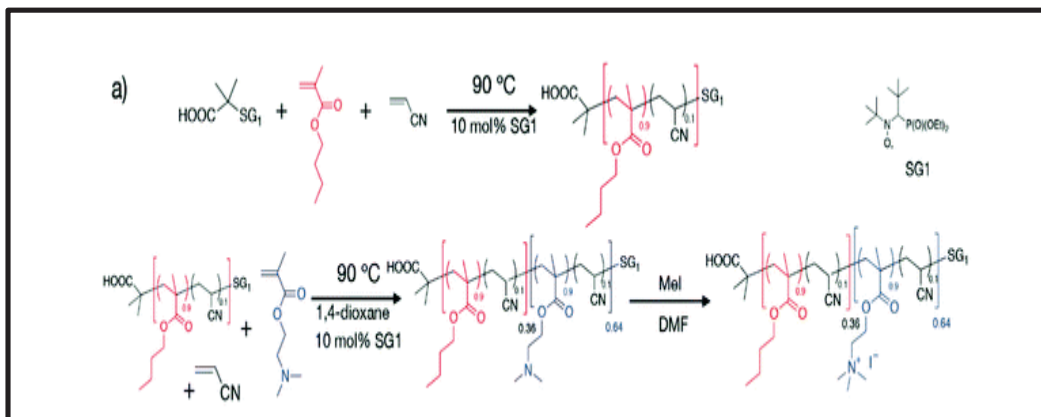


Figure (1-28) a) Synthesis of the antibacterial diblock copolymer B(A10%)Me as previously described (PBMA-*b*-PDMAEMA, $F_{\text{DMAEMA}} = 0.64$, $M_n = 18\,400\text{ g mol}^{-1}$, quaternization with MeI).

Kricheldorf et.al (2021) studied reversible polycondensations outside the Jacobson–Stockmayer theory and a new concept of reversible polycondensations [85], and were us shown in figure (1-32).

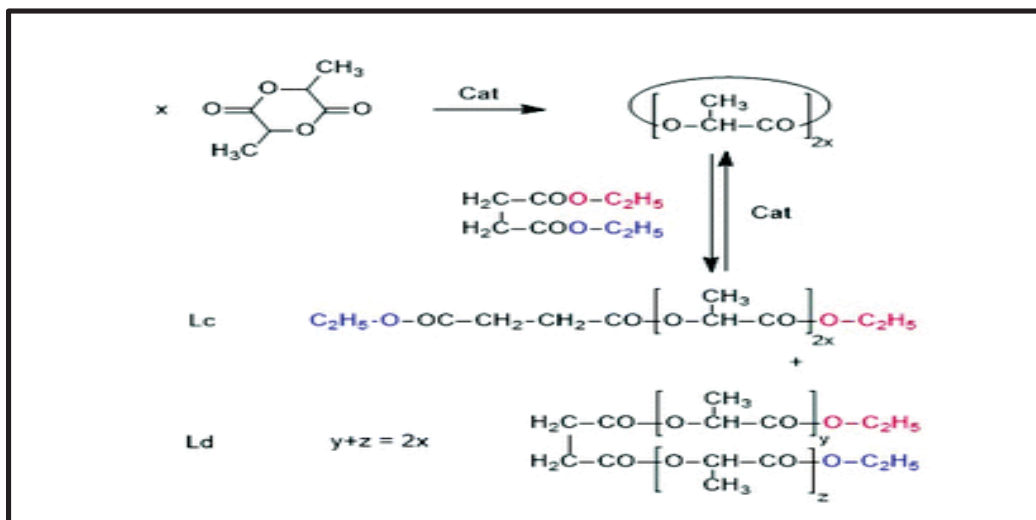


Figure (1-29) Synthesis and transesterification of poly L-lactide with diethyl

Chan et.al (2021) studied RAFT aqueous emulsion polymerization of methyl methacrylate: observation of unexpected constraints when employing a non-ionic steric stabilizer block [86].

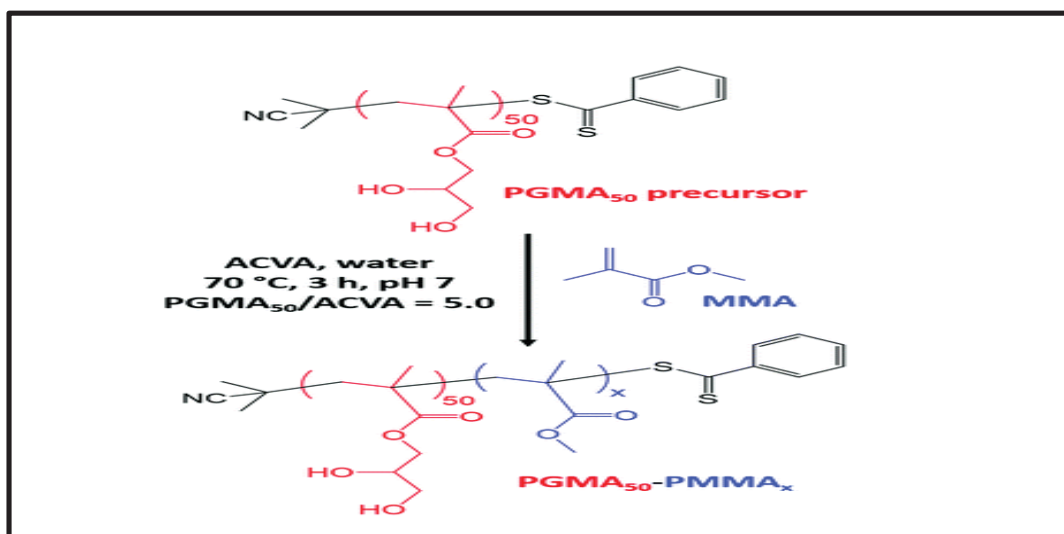


Figure (1-30): Synthesis of PGMA₅₀-PMMA_x diblock copolymer nanoparticles by RAFT aqueous emulsion polymerization of methyl methacrylate MMA at 70 °C using a dithiobenzoate-capped PGMA₅₀ precursor to target $x = 20$ to 130 at pH 7.

Suerkan et.al (2021) studied highly conjugated visible and near-infrared

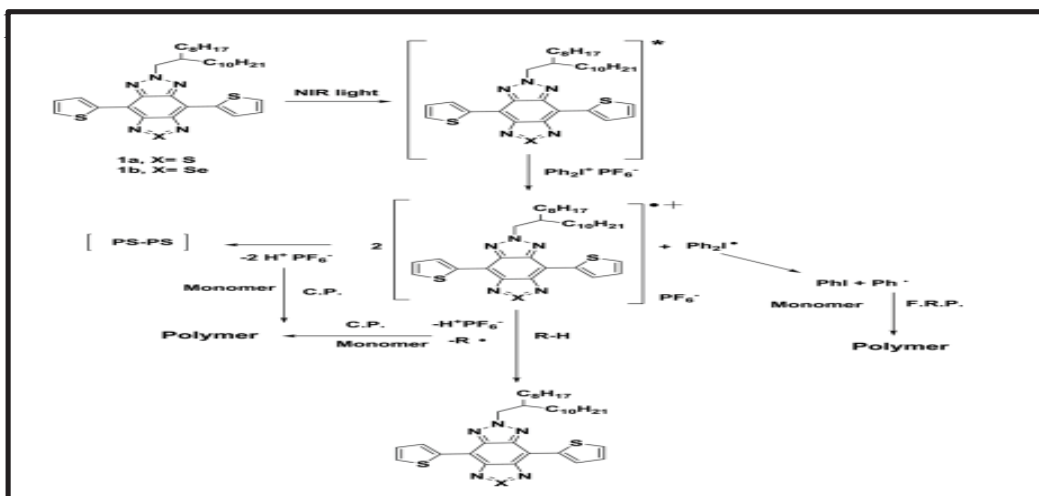


Figure (1-31): Proposed reaction mechanisms with different pathways for NIR-sensitized polymerization.

Pariza et.al (2021) synthesized Novel imino- and aryl-sulfonate based photoacid generators for the cationic ring-opening polymerization of ϵ -caprolactone [87].

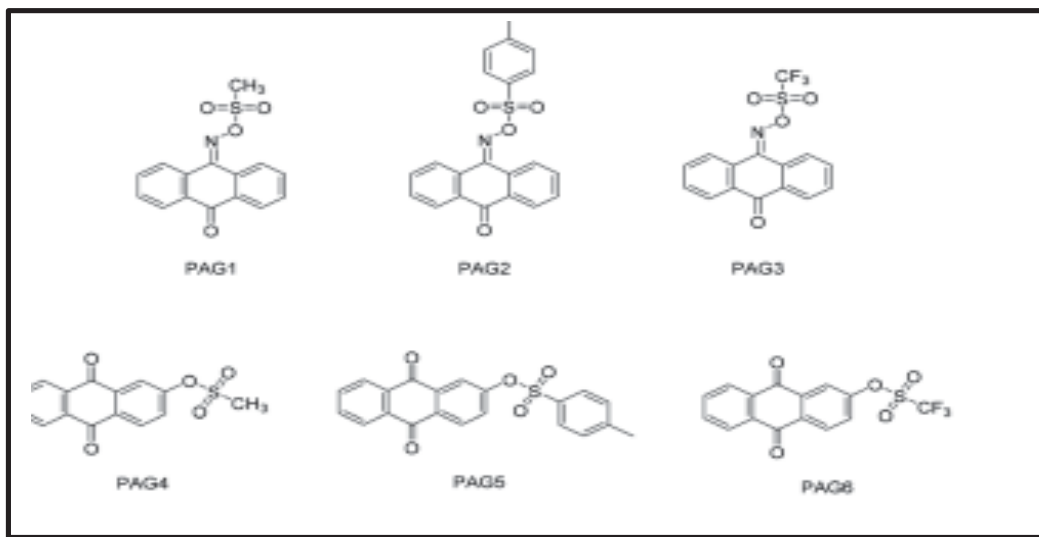


Figure (1-32): Structures of the studied PAGs

1.14 Aim of the Study

Synthesis of new tris-copolymers containing aromatic amines in addition to the acrylic acid and acrylamide and/or acrylonitrile groups and characterizing them using spectral and analytical means such as Infrared Spectroscopy (F.T.IR). Nuclear Magnetic Resonance Spectroscopy (¹H-NMR). Gel Permeation Chromatography Analysis (GPC). Thermal gravimetric analysis (TGA). The polymers will be tested and applied as follows: Adhesion strength using (Single-lap shear). The solubility in different solvents. Photo stabilization for PVC films after irradiation with 254nm.