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### Original Research Article

## A Review of Frontal Polymerization in the Chemical Industry

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#### ABSTRACT

Frontal polymerization is a relatively old polymerization process that is performed in a limited space and is done with a spontaneously progressive wave mechanism. This process is for quick and easy preparation of all types of polymers, co-polymers, nano composites, large composite parts. In recent years, it has been used to prepare polymer hydrogels. This study is an overview of frontal polymerization in the chemical industry. Hydrogels are a group of lattice polymers with a three-dimensional structure, which, due to their hydrophilic groups, are able to absorb large amounts of water and biofluids without dissolving. SO<sub>3</sub>H- in the structure of hydrogels. These materials can absorb from 10% to thousands of times their initial weight in the dry state of water. The water content of hydrogels plays an important role in determining the overall properties of the polymer network. For this reason, compared to hydrophobic polymer networks, hydrophilic hydrogels show different properties. Also, the preparation conditions of hydrophilic hydrogels are milder due to the formation of gels at room temperature and the rare use of organic solvents.

**Keywords:** Polymerization, Chemical Industry, Water, Hydrogel, Solvent

## Introduction

Due to their special properties, hydrogels can maintain their physical, chemical and mechanical stability in the state of swelling. Due to their high-water content, these materials are more similar to the tissues of the human body than any synthetic biological material. They have different physical shapes such as film, nanoparticles, microparticles and membranes. Due to this diversity in structure, hydrogels can be used in various fields of research such as separation of biomolecules or cells, tissue engineering, biosensors and systems. Medication should be used [1]. On the polymerization of 2-hydroxyethyl methacrylate studied the effect of the type and concentration of initiator, solvent and dilution on the presence of the front, front speed and front temperature. Poly (2-hydroxyethyl methacrylate) was obtained as a gel. Various gels were obtained for water and cyclohexane. They also discussed the porosity and mechanism of gel formation. Among the three diluents used (silica gel,  $\beta$ -cyclo dextrin and silica cell), the highest gel formation was in the presence of silica cell. Which indicates that the combination of starters increases the efficiency of FP [2].

Studied the synthesis of poly (2-hydroxyethyl-co-vinyl versatate) bi-character gels through free radical frontal polymerization. HEA/ VeoVa values 9 = 8: 2 wt / wt and NMP = 20 wt% and APS = 0.12 wt% were used as initiators. These compounds were poured into a human and stirred until a homogeneous mixture was reached, then poured into a 10 ml tube with a diameter of 15 mm. The advance of the front began with a hurricane. In less than  $\text{cm}^2$  the temperature reached above 100 °C. And the maximum temperature indicated by the K-type thermocouple was 132 °C [3].

At APS concentrations less than 0.12% wt, no front was observed, and for concentrations higher than 2 wt%, the front velocity increased slowly and the center of the copolymer turned yellow and the products became heterogeneous. Therefore, APS values were between 0.12% wt and 2% wt. The changes in the front velocity were measured between 0.65 cm / min to 1.15 cm/min. At concentrations of 0.12% wt and 1% wt, the maximum temperature increased from 132 °C to 157 °C.

Prepared temperature-sensitive polymer hydrogels by frontal copolymerization of hydroxypropyl methacrylate (HPMA) with vinyl pyrrolinone (1-vinyl-2-pyrrolinone) in the presence of glycerol by weight: 5 and 1: 9 = NVP: HPMA did not have a porous morphology while hydrogels with a ratio of 3: 7 = NVP: HPMA showed a spongy microporous structure with a relatively uniform

porous size distribution. This ratio can be considered as the optimal ratio of comonomers to obtain the best inflation capability. The swelling (SR) ratio of hydrogels prepared by BP method was 333%, while the SR of samples prepared by FP method was 1059%, which indicates that the SR was tripled using the FP technique [4]

Studied the physicochemical properties of poly (methyl methacrylate) through frontal polymerization. Methyl methacrylate was used as a monomer, the purity of which was controlled by gas-liquid chromatography. Dicyclohexyl peroxycarbonate (DPC) purified through saturated ethanol solution was also used as an initiator [5].

### Classification of hydrogels

Hydrogels can be classified in different ways:

*Segmentation based on hydrogel size:* Hydrogels can be classified into macrogels, microgels and nanogels based on their size [6].

*Homopolymer hydrogels:* crosslinking networks of a hydrophilic monomer

*Copolymer hydrogels:* crosslinking networks of a commune multi-polymer hydrogels: consisting of three or more commons. Interlocking polymeric hydrogels are produced by swelling the primary lattice in a monomer and reacting with them to form an interlocking secondary lattice structure [7].

*Classification based on source of preparation:* Hydrogels are classified into two categories, natural and synthetic, based on their origin [8].

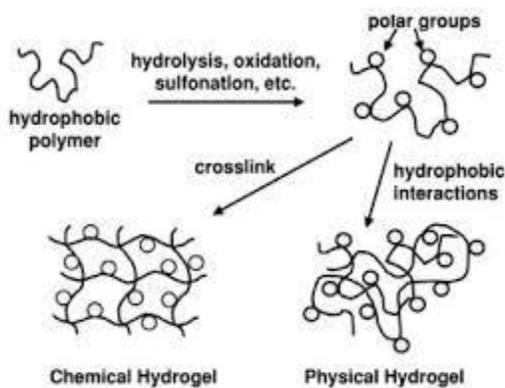
*Division of hydrogels in terms of network structure:* In terms of network structure, hydrogels can be classified into macro-porous, micro-porous and non-porous hydrogels in terms of network structure [9].

*Classification based on stimuli response:* Responsive hydrogels are hydrogels that respond to environmental stimuli. This response causes changes in the size, network structure, mechanical strength and permeability of the hydrogel, hence the name intelligent or environmentally sensitive hydrogels. Physical stimuli such as pressure, light, temperature, electric field, magnetic field, mechanical stress, which change the molecular interaction [10]

Chemical stimuli such as pH, solvent, ionic strength, molecule type, which affect the interaction between polymer chains with solvent or change between polymer chains. Biochemical stimuli include responses to ligands, enzymes, antigens, and other biochemical agents, which affect the

actual function of molecules, such as enzymatic reactions or the detection of molecular receptors. Stimulus-responsive hydrogels are very attractive for pharmaceutical, biomedical and biotechnology applications. The other group is called dual responsive hydrogels, which are obtained by combining two stimulus-responsive mechanisms in the hydrogel [11].

*Classification of hydrogels based on the type of networking:* Hydrogels can be networked both physically and chemically [12]



**Figure 1:** Formation of physical and chemical hydrogels by chemical modification of hydrophobic polymer [3].

## Method of Preparing Hydrogels

There are various methods for preparing hydrogels, the most common method is the use of physical and chemical crosslinking agents, which are described below [13].

### Physical networking

In physically crosslinked gels, there is no covalent bond between the chains and the interactions between the chains are responsible for the connection between them. Typically, through physical processes such as interactions between hydrophobic parts, crystallization, chain aggregation, polymer chain interactions, interactions between opposing charges, and hydrogen bonding between chains are some of the interactions that can occur between polymer chains.

Due to the physical interactions that exist between the polymer chains of these materials, they prevent their dissolution. These gels are of great importance due to their relatively easy fabrication and lack of use of the chemical crosslinking agent during their synthesis protocol [14].

### **Networking on ionic interaction**

Alginate is a well-known example of a polymer that can be crosslinked by lattice ion interactions. Alginate is a polysaccharide with residues of manuronic and glucuronic acid, which can be crosslinked by calcium ion. Networking is done at room temperature and physiological pH. Therefore, alginate gels are used as an abundance matrix for encapsulation of living cells and release of protein [15].

Interestingly, gels can be destabilized by the extraction of calcium ions from the gel by chelating agents. The release of protein from microparticles of alginate is achieved by spraying a solution of sodium alginate in an aqueous solution of calcium chloride. Which can be modulated by coating the particles with cationic polymers such as chitosan and polylysine.

The advantage of ion crosslinking over other non-covalent chemical methods is that ionic bonds are relatively strong, so less crosslinking is required to form functionalized gels [16].

### **Networking through hydrogen bonds**

Gel-like structures can be physically crosslinked through the interaction of hydrogen bonds. The best example of such hydrogels is network formation by hydrogen bonding of carboxymethylcellulose (CMC), which is obtained by the dispersion of carboxymethylcellulose in 0.1 M hydrochloric acid. In this process, sodium ions in carboxymethylcellulose are hydrogenated. They were replaced in acid [17].

### **Networking through crystallization**

*Networking through freezing-thawing process:* Physical crosslinking of hydrogels can take place through freeze-thaw cycles. This mechanism leads to the formation of microcrystals in the structure of the hydrogel due to freezing and thawing. Polyvinyl alcohol is a hydrophilic synthetic polymer that, if kept at room temperature, results in the formation of a gel with low mechanical strength. However, when aqueous solutions of polyvinyl alcohol are exposed to the freezing-thawing process, it shows a stronger, more porous gel with higher elastic and resilient properties than polyvinyl alcohol hydrogels made by other methods [18].

### **Networking through the formation of spatial complex**

In recent years, hydrogels have been developed based on the formation of space complexes, which are used in drug delivery systems. The main advantage of this system is that hydrogels can be easily dissolved by dissolving any substance in Form water and mix with solution. Polylactic acid is a good example to show the properties of the spatial complex [19].

### **Networking through the accumulation of induced heat**

This process leads to the formation of hydrogels with precise molecular dimensions. The best example of this hydrogel system is the gelling of gum arabic through heat induction. Due to accumulation, an increase in molecular weight occurs after the formation of hydrogels by improving the mechanical properties [20].

### **Networking of bonded polymers and two environmentally friendly pieces**

Two environmentally friendly bonded and fragmented polymers have the ability to self-rotate to form polymer hydrogels and micelles in the aqueous medium, where the hydrophobic parts of the polymers are self-assembled. Hydrophilic two-piece polymers form layered phases and micelles. Multi-piece polymers may have hydrophobic chains that are attached to hydrophobic components by having hydrophilic bonds with a water-soluble polymer body [21].

### **Chemical networking**

When a covalent bond is established between polymer chains, crosslinking is of the chemical type. Covalent bonds are stronger than non-covalent bonds and provide good mechanical stability. In physical networking, unlike physical networking, it is necessary for chemical agents to react with other substances [22].

### **Networking through linking**

The formation of hydrogels is achieved by the bonding method, by polymerizing a monomer on the body of a prefabricated polymer. Depending on the initiator activity, grafting can be chemical or radiation. In bonding chemically, macromolecular structures are activated by the reaction of a chemical reagent. An example is the bonding of starch to acrylic acid using N-vinyl-2-

pyrrolidone. Radiation uses high-energy gamma rays or electrons to bond. The bonding of carboxymethylcellulose with acrylic acid by electron beam irradiation in aqueous solution is an example of this system [23].

### **Crosslinking with aldehydes**

Hydrophilic polymers with hydroxyl (OH) groups, such as polyvinyl alcohol, are cross-linked with glutaraldehyde to apply a hard cross-linked bond (low pH, methanol addition as high temperature quenching). Hydrophilic polymers have amine groups using the same lattice to form a lattice under milder conditions in which Schiff base is formed. The Schiff base reaction, which involves the formation of a carbon-nitrogen bond between the amino and aldehyde groups, can be used to achieve in situ crosslinking without the use of chemical crosslinking agents. This method is specially designed for the synthesis of lattice proteins such as albumin, gelatin and amine-containing polysaccharides [24].

### **Networking with chemical reaction of complementary groups**

Water-soluble polymers have solubility properties due to their functional groups (mainly OH COOH, NH<sub>2</sub>), which are used to form hydrogels. Covalent bonds between polymer chains through the reaction of functional groups with complementary reactivity Such as amine-carboxylic acid reaction or isocyanate-NH<sub>2</sub>/OH reaction, or it is formed through Schiff base [25].

### **Networking with radical polymerization**

One of the features of hydrogels is their ability to swell, which is controlled by the amount of crosslinking agent. In addition, stimulus-sensitive materials can be obtained by adding crosslinkers with predetermined properties. In addition to radical polymerization of vinyl monomers, chemically crosslinked hydrogels can also be obtained by radical polymerization of polymerizable groups from hydrophilic polymers. Different hydrophilic polymers (natural, synthetic, semi-synthetic) are used to form hydrogels. This method is very efficient because it leads to the formation of hydrogels even under mild conditions. For example, this method can be used to make hydrogels. He mentioned free radical initiators such as ammonium sulfate and potassium sulfate [26].

### **Networking with density response**

Hydrogels containing hydroxyl, amine, and carboxylic acids and their derivatives are used to form these types of hydrogels. The best examples of these reactions were described by De Nooy through the Passerini and Ugi condensation reactions. In Passerini condensation, hydrogels with ester bonds are obtained in cross-links. In this process, a combination of carboxylic acid and carbonyl (aldehyde or ketone) with an isocyanate are concentrated to form an  $\alpha$  - (acryloxy) amide. In the Ugi condensation method, an amine is added to the reaction mixture, and finally  $\alpha$  - (acryloxy) amide is formed. These types of hydrogels generally have amide bonds in their bonds [27].

### **Networking with incremental reaction**

Two-factor or more crosslinkers are used to react with the functional groups of hydrophilic polymers using additive reactions. Polysaccharides are crosslinked using 1,6-hexamethylene diisocyanate, divinyl sulfonate or 1,6-hexane dicromide.

### **Networking with enzyme**

Sperinde described an interesting method using an enzyme for the synthesis of polyethylene glycol-based hydrogels. In this method, groups of glutamines were used with functionalized polyethylene tetrahydroxy. Polyethylene glycol networks were formed by adding trans-glutamines to an aqueous solution of polyethylene glycol-glutaminy and poly (lysine-CO-phenylalanine).  $\gamma$ -Carboxamide is related to polyethylene glycol-glutaminy and the  $\epsilon$ -amine lysine group is formed [28].

### **Networking by high energy irradiation method**

Unsaturated compounds can be polymerized by high-energy irradiation such as gamma rays or electron beams. By gamma irradiation or electron beam irradiation, polymer aqueous solutions with vinyl groups lead to the formation of radicals on polymer chains.

In addition, irradiation of water molecules leads to the formation of hydroxyl radicals, which can attack the polymer chains and form micro-radicals. The recombination of micro-radicals on different chains forms covalent bonds and ultimately a lattice structure. The advantage of this

method is that, this process can be done in water under mild conditions (ambient temperature and physiological pH) and without the use of toxic crosslinking agent. However, one of the disadvantages of this method is that by forming connections. Carbon-carbon transverse causes the biodegradability of gels. Among the crosslinked polymers, poly (vinyl alcohol), poly (ethylene glycol) and poly (N-isopropyl acrylamide), poly (vinyl methyl ether) can be named [30].

### **Crosslinking of two polymers**

The advantage of using this method is that there is no need to use toxic micromolecules as a crosslinking agent. The only limitation of this method is the requirement to functionalize the polymers before using them in the network. Several types of bonds may be formed between polymer chains. Increasing the density of crosslinking increases the hydrophobicity and decreases the tensile strength of the crosslinked polymer. The amount of water absorbed by the hydrogel is an important property of hydrogels that have therapeutic applications [31].

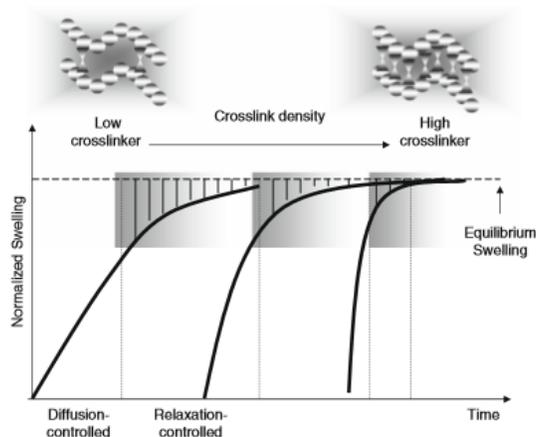
### **Water absorption in hydrogel**

Hydrogels are highly hydrophilic crosslinked polymers that can be multiplied by being in a solvent at their own weight, they absorb water and biological fluids without dissolving and hold them in polymer chains and swell the amount of water in the hydrogel can reach from 10% to thousands of times the weight of the hydrogel. Xerogel refers to a lattice polymer that does not absorb water. Water uptake in hydrogels depends on many factors such as: lattice parameters, nature of solution, hydrogel structures (porous or non-porous) and drying techniques. The most important of these factors is the density of crosslinks that is controlled by the effective concentration of the crosslinking agent used in the crosslinking process. This parameter, in turn, is controlled by the distance (molecular weight) between two crosslinks in a polymer chain. The shorter the distance, the higher the density of the crosslinks.

However, the large order of crosslink density determines the swelling properties of a hydrogel. The process of swelling can be thought of as a process of infiltration followed by a process of relaxation. In other words, the speed at which water can penetrate the network structure spontaneously determines the speed at the beginning of the inflation process. This rate depends

more on the molecular weight of the solvent, the temperature of the solution, and the degree of porosity in the structure of the hydrogel.

Figure 2 shows that the adsorption mechanism in highly crosslinked hydrogels is potentially limited to a diffusion process, and that the movement of the polymer chains is limited due to the high density of crosslinks. In other words, highly crosslinked hydrogels behave like a metal mesh that continuously passes a constant amount of water in a continuous flow [32].



**Figure 2.** Inflation kinetics

## Applications of hydrogels

Hydrogels can have different physical shapes such as sheets, micro particles, nanoparticles, coating structures and films. This variety of structures as well as unique properties have led to the widespread use of hydrogels in various fields. Examples of hydrogels are various fields including drug delivery systems, tissue engineering, biological membranes, artificial skin, artificial muscles, wound dressings, biosensors, food industry and Packaging, separation technology, cosmetics, sanitary ware such as diapers; Adult Disposal Tampons, Liquid Purification and Recovery or Concentration of Dilute Protein Solutions, Biomedicine, Biotechnology, Agriculture (Fertilizer or Pesticide Release Control), Absorbent To remove water contaminants such as heavy metals, oil extraction and soft contact lenses and .... Based on each of these applications, hydrogels can be prepared in various forms such as cubes, hollow tubes, rods, sheets and films.

In recent years, the need for easy methods of rapid and easy preparation of hydrogels and environmental requirements, such as minimizing the residual monomer content in biological applications, has led to the application and modification of some well-known methods and techniques, one of which is the technique is frontal polymerization. 6-1- Biocompatibility of hydrogels, especially those used in pharmacology and bio-skeletal purposes, they must have acceptable biocompatibility and biodegradability. As mentioned, the success of a biomaterial depends on its biocompatibility.

Many factors affect the biocompatibility of a substance, and a review of all available sources shows that hydrogels are biocompatible. This feature depends on several factors:

- The surface tension of hydrogels in the joint with biological tissues is low, and this factor reduces protein absorption and cell adhesion. Due to the high-water content of these materials, the surface of the hydrogel is known as a permeable surface of hydrophilic cloud that has a high biocompatibility. Hydrogels model some of the hydrodynamic properties of the body's biological gels, tissues, and cells, and this makes it easier to study the behavior of natural tissues.
- The soft and elastic nature of some hydrogels reduces the surface friction of these materials with the surrounding tissues. Reducing surface friction causes the mucous membrane to be less damaged, like the inner surfaces of the arteries [33].

## Nanocomposite hydrogels

The advent of hydrogel nanocomposites is to improve and modify the properties of hydrogels and add unique properties to them. The presence of nanoparticles in polymer hydrogels has unique properties such as mechanical, optical, thermal, acoustic, magnetic, and electrical responsiveness. Other improved properties of hydrogels in the presence of nanoparticles are their excellent mechanical properties. These gels are able to withstand a high level of resistance to deformation, bending, tearing, twisting and even twisting.

Hydroxyethyl methacrylate (HEMA) and its polymerization methods:

- Hydroxyethyl methacrylate  $H_2C = C(CH_3)COOCH_2CH_2OH$  is one of the most important hydrophilic monomers obtained from the reaction of methacrylic acid and ethylene oxide. The importance of hydrogels in medical applications in 1950 using this material in the manufacture soft contact lenses started.

The hydrophilicity of PHEMA hydrogels is mainly due to the presence of hydroxyl and carbonyl groups on the monomeric chain, while the hydrophobicity is due to the presence of  $\alpha$ -methyl and carbon groups on the monomer body, which makes the polymer matrix resistant to hydrolysis and mechanical force. PHEMA can show good biocompatibility, so it is very similar to other natural body tissues compared to other synthetic polymers. In addition to being biocompatible with biological fluids, the human body is also compatible. And can be obtained in different forms. It is important in the field of ophthalmic lenses because of its high oxygen permeability, good mechanical properties, and good refractive index. In addition, the swelling behavior of this biopolymer is very important for pharmaceutical and medical applications.

2- Hydroxyethyl methacrylate can be polymerized using free radical, thermal and optical radical initiators. 2- Hydroxyethyl methacrylate is available in colorless and odorless liquid with 98% purity [34]. Some of its properties and characteristics are listed in Table 1.

**Table 1:** Physical properties of 2-hydroxyethyl methacrylate

<b>g/cm<sup>3</sup> 143/ 103</b>	<b>Molecular Weight</b>
<b>205-220 (°C)</b>	Welding temperature at pressure (1013 hPa)
<b>60 (°C)</b>	melting point
<b>55 (°C)</b>	Glass transition temperature
<b>97 (°C)</b>	Ignition temperature
<b>&gt; -60 (°C)</b>	Freezing point
<b>1.073 g/cm</b>	Density 20 (°C)
<b>5 (Against the air)</b>	Vapor density
<b>16.8 Pa</b>	Steam pressure 25 (°C)
<b>Miscible with water in any proportion in 20 °C</b>	Solubility in 20 (°C)
<b>1.453</b>	Refractive index 20 (°C)
<b>0.42</b>	The coefficient of division in 25 (°C)

## **Application of polymers and copolymers of 2-hydroxyethyl methacrylate**

### **Biomedicine**

PHEMA can be easily polymerized into hydrogels due to its hydroxyl groups which are hydrophilic.

In addition, by adding special monomers such as acrylic acid, their swelling behavior can be adjusted. PHEMA is resistant to degradation, also biocompatibility and blood compatibility and can be formed in different forms and forms, so it is very important for medical applications [35].

### **Drug delivery**

PHEMA gels are very resistant to high temperatures and hydrolysis of alkaline and acid. These gels have little interaction with amines. The thermal and chemical stability of these gels makes them suitable for controlled drug delivery applications. Drug release via a PHEMA-based gel network is swollen under the influence of the gel water capacity. Hence, the inflation ratio affects the controlled release systems of the drug due to changes in external conditions such as ionic strength, temperature, pH.

In this system, drug release can be controlled at a suitable level and at a predetermined time [36].

### **Dentistry**

HEMA is a monomer based on methacrylic acid (MMA) that can be used in the dental field such as toothpaste. In restorative dentistry, metals, ceramics and composites are used. To better connect the composite to the tooth tissue, tooth glue is used. Dental adhesives are low-viscosity solutions including solvents, acrylic monomers, and primers. After preparing the tooth surface (enamel or dentin), these adhesives are applied to the surface. Hydrophilic monomers 2-Hydroxyethyl methacrylate (HEMA) in the adhesive solution causes better dentin wettability and penetration of acrylic monomers [37].

### **Tissue Engineering**

2-Hydroxyethyl methacrylate hydrogels are similar to the natural tissue of the body due to their high-water content and high degree of flexibility, and minimize the amount of tenderness and itching in membranes and tissues. HEMA-based macro-porous hydrogels are synthetic

biomaterials commonly used in tissue engineering, which involves the regeneration of the central nervous system. The properties of these hydrogels can be easily manipulated through chemical formulation. In addition, PHEMA scaffolds can be easily connected to neural conduction tubes [38].

### **Contact lenses**

Soft contact lenses are hydrogels made from crosslinked networks of water-soluble monomers. Most contact lenses are PHEMA hydrogels that are transparent and have no porosity and are crosslinked with ethylene glycol dimethacrylate (EGDMA) or silicone-based lenses. High water content, chemical and thermal stability, adjustable mechanical properties and good oxygen permeability are important features of PHEMA, which is very important for daily use of these lenses. 2-Hydroxyethyl methacrylate (HEMA) and its derivatives can also be used to treat eye diseases [39].

### **Wounds**

PHEMA is used in wound dressings, especially for the treatment of burns. In this PHEMA method Combines with a water-soluble mineral solvent, emollient, and antibacterial agent. This compound, which is used for treatment, shows good adhesion to the skin.

### **Implants**

Due to its non-toxicity and high resistance to degradation, sponge PHEMA can be used as implants. Additives can be used to improve the mechanical properties of PHEMA for such applications.

### **Ambulation**

PHEMA hydrogels are used as embolization matrices for various biological enzymes and molecules to increase the use of bioreactors [40].

### **Electro-conducting biosensors and hydrogels**

Electro-conducting hydrogels can be made from poly (2-hydroxyethyl methacrylate) and poly (aniline) -based hydrogels to make a biosensor. Electro-conducting hydrogels fully detect

electrical and optical properties. Isolates, tissues, cells, or any chemical element represent the substance electrically, optically, or thermally. PHEMA hydrogels are very important for biosensor detectors in medical applications. These sensors are commonly used to obtain blood glucose solution concentrations and DNA tests to detect any genetic defects or cancer at birth. 2-Hydroxyethyl methacrylate can be used to make chemical sensors.

These sensors are fabricated through an ink-jet printing process in which the nanoparticles are precipitated and finally the nanoparticles are processed with HEMA polymer. 2-Hydroxyethyl methacrylate is also used for disposable ammeter sensors [41].

### **Transistors**

Other main applications of PHEMA hydrogels include its use in the manufacture of transistors. The main load storage site in PHEMA is the hydroxyl group (OH<sup>-</sup>). PHEMA can improve the memory effect of pentacene based transistor mineral film (OTFT). Electrons are trapped and dielectric polarization is done slowly to form a memory effect.

### **Adsorption of metal ions**

The presence of metal ions from industrial effluents causes environmental pollution. Using hydrogels made of polymers such as poly (2-hydroxyethyl methacrylate) and poly (acrylamide), metal ions such as Cu<sup>2+</sup>, Fe<sup>2+</sup> and Cr<sup>6+</sup> can be adsorbed from industrial effluents.

### **Polymerization methods**

2-Hydroxyethyl methacrylate Polymerization 2-Hydroxyethyl methacrylate can be done by various methods such as radical polymerization of atom transfer, transfer polymerization to reversible addition-separation chain, emulsion, mass, solution, suspension and reverse suspension, which are briefly described below. The method is discussed.

Since 1995, radical polymerization of atom transfer has been used to control the polymerization of various monomers. Monomers including acrylate, methacrylate and styrene. This method is generally used at high temperatures and in bulk or nano-solution environments. This method is also used for hydrophilic monomers in aqueous media under mild conditions.

In polymerization, ATRP method is performed directly on poly-2-hydroxyethyl methacrylate with controlled molecular weight and low dispersion. The reaction conditions for successful

polymerization in this method are consistent with the functional and polarity monomer of methacrylate. In this method, a combined solvent system such as methyl ethyl ketone and 1-propanol can be used, and an alkyl bromide initiator and a copper chloride catalyst can be used at temperatures below 50 °C. The Cu / 2,2-bipyridyl (bpy) complex is a homogeneous non-polar and inorganic mixture that dissolves completely in the high solvent system [42].

### **Polymerization technique of transfer to reversible increment-separation chain (RAFT)**

The advantage of this method is that it has the ability to control the polymerization of many polymerizable monomers such as methacrylates, methacrylamides, styrenes, etc. through radical polymerization. Full adaptation of the reaction conditions to conventional radical polymerization is another advantage of this method. The only difference between them is the presence of RAFT in the reaction medium. The onset and termination of radicals occurs in the same way as normal radical polymerization, but the amount of initiator and consequently the concentration of active ingredients is lower, and this causes the termination reaction to loop.

In this method, with the formation of equilibrium, the polymer chains become potentially active the active state is converted and added to monomeric units, and thus, unlike the conventional free radical mechanism, the chains grow parallel to each other and to the total polymerization time [43].

### **Emulsion technique**

HEMA emulsion polymerization can be performed at 80 ° C, and from starters such as: (2,2-azobis butyl nitrile (AIBN), 2,2-azobis- (2-aminopropane) dihydrochloride (AAP), 4,4-Azobis (4-cyanopentanoic acid) (ACPA) was used. Sodium dodecyl sulfate (SDS) or a combination of sodium dodecyl sulfate (SDS) and poly (vinylpyrrolidone) (PVP) can be used as emulsifiers. Solubility depends on the rate of polymerization.

In this method, there is an aqueous solution phase, repeated particle nucleation, and coagulation during polymerization. As the monomer/water ratio increases, the polymerization rate does not increase in proportion to the particle size. In the polymerization of 2-hydroxyethyl methacrylate using a soluble initiator of azo-bis- isobutyronitrile (AIBN), monomer conversion is increased

and coagulation is reduced. The amount of emulsifier has little effect on the conversion of the monomer. But the coagulation decreases significantly with increasing the amount of emulsifier. Also, the reaction temperature increases from 65 °C to 85 °C, the conversion of the monomer first increases and then decreases. And the coagulation is constantly increasing.

**Mass technique** It is a very simple method that only includes monomers and water-soluble primers. Hydrogels prepared by mass method are prepared with one monomer or more than one monomer. Usually, a small amount of crosslinking agent is added in this method. Polymerization begins with irradiation, ultraviolet or chemical catalyst. The choice of primer depends on the type of monomer and solvent used. Polymerization by mass method to form a homogeneous hydrogel produces a clear, glassy polymer matrix that is very hard. When immersed in water, the glass matrix swells and becomes soft and flexible. The advantage is that high molecular weight and pure polymers are produced in various forms such as films, membranes, particles and emulsions. Implants and lenses made from this monomer can be formed from mass polymerization [44].

### **Solution Technique**

In solution polymerization, ionic or neutral monomers are mixed with multifactorial crosslinking agents. Thermal polymerization begins with UV radiation or an oxidation initiator system. The presence of solvent is the main advantage of this method. If the amount of water during polymerization exceeds the amount of water due to equilibrium swelling, phase separation occurs and heterogeneous polymer hydrogels are formed. Common solvents for solution polymerization include water, ethanol, water-ethanol mixtures, and benzyl alcohol.

The synthetic solvent is removed after the gel is formed by swelling the hydrogel in water. To remove unreacted monomers, oligomers, crosslinkers, primers, soluble and extractable polymers, and other impurities are washed with polymeric hydrogels prepared with distilled water. In previous decades, this method was used to prepare various polymer hydrogels. In the polymerization of 2-hydroxyethyl methacrylate, a transparent glassy material is obtained which has no porosity. On the other hand, in solution polymerization of this monomer, a porous structure can be created, which depends on the type and amount of diluent used [45].

## Suspension and inverted suspension technique

Suspension polymerization is one of the most successful methods for the preparation of spherical hydrogels or microparticles. In this method, the monomer solution is stabilized by the addition of a stabilizer to form fine monomer particles in the dispersed anti-solvent. Polymerization begins with radicals resulting from the thermal decomposition of the initiator. Then, the newly formed microparticles are washed to remove unreacted monomers, crosslinking agent and initiator. The shape of the formed particles is affected by the viscosity of the monomer phase, while the particle size is controlled by adjusting the hydrophilicity-hydrophobicity of the suspension.

Hydrogel beads of 2-hydroxyethyl methacrylate can be formed by this method. The granules are crosslinked by free radical suspension polymerization of 2-hydroxyethyl methacrylate with ethylene glycol dimethacrylate and magnesium hydroxide is used as a stable suspension agent. A good quality is obtained from PHEMA grains when 0.7-1.85% of suspension agent, 20-18% dissolved salt, continuous phase to monomer phase ratio 25.5-5.3, starter -0.4 0.2% and mixing speed should be 80- 120 rpm. In this method, the diameter of PHEMA grains is in the range of 75 and 1000 micrometers, the spherical shape obtained from this method facilitates the entry of particles through the catheter.

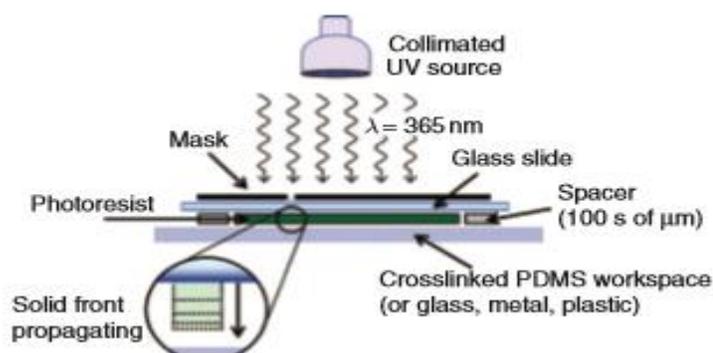
Also, spherical particles of hydrogels for medical use can be formed by reverse suspension polymerization, in which water-soluble monomers are suspended in a mineral phase and polymerized [46].

## Frontal polymerization

Frontal polymerization (FP) is a polymerization process in which polymerization occurs in one direction in a small area. There are three types of FP: The first type is photofrontal polymerization (PFP), in which the driving force is a continuous radiant flux reaction, usually UV. The second type is frontal isothermal polymerization (IFP), the driving force of which is due to the effect of the gel for a local reaction zone that proceeds slowly from a polymer grain in one direction. The third type is thermal frontal polymerization (TFP), which is the result of the combined effect of heat transfer and Arrhenius dependence on the rate of exothermic polymerization reaction. Photofrontal polymerization creates a front whose position is

logarithmically dependent on time if the initiator continues to absorb light, and if the initiator does not continue to absorb light, the position of the polymerization front depends on time.

The application of this method is limited to systems without fillers. The IFP rate is about 1 cm / day and only occurs for 1 cm long bands. Among the three FP methods, the TFP method has the widest range of reaction speed and chemistry. Carbal developed photofrontal polymerization to make microfluidic chips. This was done by irradiating light to a glass plate in contact with a polymerizable resin.



**Figure 3:** Schematic of photofrontal polymerization for the preparation of microfluidic chips [47].

### Isothermal polymerization

IFP is a slow process in which a topical polymerization takes place from a solid polymer piece to a monomer solution and a thermal radical initiator. A typical experiment requires placing a high molecular weight piece of polymethacrylate (PMMA), seeds in methyl methacrylate solution, and azo base isobutyronitrile (AIBN). The monomer solution of the primer produces a highly sticky gel region to dissolve the polymer seeds.

The primer starts throughout the decomposition system, but due to the gelation effect, the polymerization rate in the gel region is higher than in the rest of the solution. The following figure shows a schematic of isothermal polymerization.



**Figure 4:** Schematic of isothermal polymerization.

Refrigeration fronts the adsorption mode of frontal polymerization at a temperature of 77 and below was developed at the Russian Institute of Chemistry and Physics in Chernogolovka. Many systems can be polymerized using this method. Including acetaldehyde, formaldehyde, cyclopentadiol and methyl methacrylate. Filled polymers, such as acetaldehyde and alumina, can also be prepared. The diffusion mechanism is through the non-Arrhenius mechanism. The monomer freezes at 4 to 77 °C and then glows with gamma radiation. A monomer, such as methyl methacrylate, is cooled in liquid nitrogen or even liquid helium.

Fronts begin as the surface warms. The reaction temperature and density gradients are more responsible for layer by layer of the solid sample and create the reaction surface. Since this is the positive feedback between the solid-phase chemical reaction and the cracking of the frozen reactions, the polymerization is carried out in layers and spreads through the whole sample as a front. Epichlorohydrin, for example, can cool rapidly to 77 °C and then glow with a dose of 680 kGy gamma radiation. A polymerization front with a velocity of 1.3 cm/s is released after breaking a small area of the sample. The cations formed by irradiation were released by cracking, resulting in a wave of polymerization.

### **Thermal frontal polymerization**

As mentioned in the previous section, thermal frontal polymerization (TFP) is a process that results from the combined effect of heat transfer and Arrhenius dependence on the rate of exothermic polymerization reaction. Frontal polymerization was discovered at the Institute of Physical Chemistry in Chernogolovka, Russia by Chechilo and Enikolopyan. They studied the polymerization of methyl methacrylate at a pressure of 3500 atm. The studies conducted by this research institute were published in 1984 as a review article [48].

## Conclusion

Present review tried to analyze the literatures on frontal polymerization. The objective of this review was to show not only the advantages of this nonconventional method of polymerization, but also the problems and challenges of researchers and engineers in its technological implementation. The three modes of FP have proven to offer advantages for different applications. Photo frontal polymerization is driven by a continuous flux of energy and has been applied to the preparation of microfluidic chips. It can be applied to any photo polymerization. Isothermal frontal polymerization relies on the gel effect to create a slowly moving localized polymerization through monomers like methyl methacrylate. This method can be used to prepare gradient refractive index materials. Thermal frontal polymerization can be applied to the widest range of materials. Any polymerization that follows Arrhenius kinetics and is highly exothermic can support localized polymerizations that propagate. Frontal polymerization has been studied with many different polymerization mechanisms but free-radical polymerization is the most studied. The main advantages of frontal polymerization are the simplicity of technological equipment's and implementation; high performance and efficiency; ecological safety.

The major applications of frontal polymerization including rapid synthesis of various polymers and copolymers; preparation of hydrogels; gradient materials and nanocomposites; solvent less processing; energy savings; consolidation of stones; autoclave less curing of large composites; cure on-demand repair and adhesives.

At the same time, the problems related to the specificity of frontal polymerization modes are low yields of the product of initiated polymerization and poor molecular weight characteristics. The problems on the regulation of the polymer yield and molecular weight distribution were discussed and the issues related to heat transfer from the reaction zone to the environment and the effect of cooling on the properties of the samples obtained in the frontal mode are reviewed in different publications. Recommendations are given by various authors for regulating the necessary cooling conditions for the synthesis of polymer materials or composites with predetermined properties. These regulated cooling conditions ensure the defectlessness of frontal polymerization products.

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