POLITECNICO DI MILANO

School of Industrial and Information Engineering

Department of Chemistry, Materials and Chemical Engineering "Giulio Natta"

Master of Science in Chemical Engineering

Strategies to develop novel formulations for industrial applications

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*Ai miei genitori, Paola e Giorgio
e ai miei fratelli, Giovanni e Stefano*

*Dal collo in giù, l'uomo vale un paio di dollari al
giorno. Dal collo in su, vale qualunque cosa la
sua mente sia in grado di produrre.*
Thomas Alva Edison

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Abstract

The aim of this work is the development of novel formulations for the production of a solid product after a polymerization reaction. In particular, three different pathways have been properly studied according to the polarity of the systems. The first one involves the free radical polymerization, so a common way to obtain polymers, the second one is based on the frontal polymerization in which a couple of redox initiators is able to propagate the reaction through the front. Both of them have been formulated for hydrophilic purposes. On the contrary, the third pathway is a physical method to create a stable emulsion suitable for the liphophilic fluids. The strategy that have been used to follow up this work is the possibility to have a bicomponent mixture capable to react only under specific conditions and constrains, like temperature, time of reactions, stability over the time, and mechanical properties of the final materials. All the degrees of freedom of these systems have been taken into account to optimize the final formulations in all the cases. In fact, many monomers, crosslinking agents, initiators and solvents have been tried together with different reaction conditions. A possible applications for these solutions can be the oil and gas field. In fact, one of the most expensive issues during the extraction of the oil is the losses of drilling use to ensure the same pressure inside and outside the well. For this reason, the novel formulations that have been developed in this work can be conveniently applied as additives to the common drilling fluid muds. However, further researches are needed to develop a satisfied formulations, coming from all the three pathways examined in this thesis, for the specific purpose in the oil and gas field.

Estratto

Lo scopo di questo lavoro è lo sviluppo di formulazioni innovative per la produzione di materiali solidi grazie a reazioni di polimerizzazione. Nello specifico, sono state esaminate tre differenti possibilità. Le prime due interessano vere e proprie reazioni di polimerizzazione che portano alla formazione di un solido ad elevate proprietà meccaniche per sistemi idrofili, mentre la terza considera la possibilità di sfruttare la formazione di un'emulsione stabile da poter essere utilizzata anche in miscele lipofile. Le tecniche di polimerizzazione utilizzate per la formazione del prodotto finale sono la polimerizzazione radicalica, che sfrutta la classica iniziazione termica per la generazione dei radicali che determinano la crescita della catena polimerica, e la polimerizzazione a fronte, in cui la reazione di ossidoriduzione tra una coppia di iniziatori, un riducente e un ossidante, assicura la propagazione, fornendo il calore necessario, fino alla formazione del prodotto solido voluto. Si è deciso di sviluppare una miscela bicomponente che fosse capace di reagire solo in determinate condizioni, rispettando specifici vincoli operativi, come temperatura, tempo di reazione, stabilità nelle condizioni di stoccaggio e proprietà del materiale finale. E' stato quindi condotto uno studio di ottimizzazione delle tre diverse ricette, esaminando le quantità e i tipi di monomeri, crosslinkanti, iniziatori e solventi coinvolti nei sistemi. Le formulazioni sviluppate durante questo lavoro possono trovare applicazione nel campo petrolifero come additivi reattivi da aggiungere ai tradizionali fluidi di perforazione. Infatti, la perdita dei fluidi usati durante la perforazione di pozzi è un problema ancora irrisolto che determina notevoli costi e addirittura la chiusura e l'abbandono del pozzo stesso. Sicuramente saranno necessari ulteriori studi per adattare le formulazioni qui sviluppate alle esigenze più specifiche, ma senz'altro questo lavoro può essere usato come punto di partenza per successive ottimizzazioni.

Chapter 1: Introduction

In this chapter, the importance of polymers for everyone and every day is presented, together with the available polymerization solutions on the market. In particular, the limitations of the current techniques were highlighted and innovative solutions are proposed.

1.1 Importance and uses of the polymers

The word "polymer", or sometimes "macromolecule", is derived from classical Greek *poly* meaning "many" and *meres* meaning "parts". [1] Polymers are made up of many small molecules, named monomers, that are linked together to form long chains. They are very variety materials, used in a lot of products and goods that all the people use commonly. [2] Nowadays it would be impossible to think of our lives without polymers, but it is only recently, after World War II, that they started to really spread. There were relatively few materials available for the manufacture of the article needed for a civilized life: steel, glass, wood, stone, brick, and concrete for most of the construction and cotton, wood, jute, and a few other agricultural products for clothing. The rapid growth of the needs of new products led to the discovery of novel materials. The solution was the discovery, the study and the way of exploiting polymers. In fact, they are present in clothing, like synthetic fibers, polyethylene cups, fiberglass, nylon bearings, plastic bags, polymer-based paints, epoxy glues, polyurethane foam cushion, silicone heart valves, and teflon-coated cookware. [3]

As mentioned at the beginning, the polymer molecule consists of several structural units usually held together by covalent bonds, so its molecular weight is pretty high (between $10^4 - 10^6$ g mol^{-1}) and. [4] Polymers are obtained through chemical reaction of monomers. Monomers have the ability to react with another molecule of their own or of a different type under the condition suitable for

forming the polymer chain. This process is very common also in nature for the formation of natural polymers, like cellulose, starch, and natural rubber. Over the years, the polymer industry has deeply improved and developed and today its production volumes is larger than the copper, steel, aluminum and some other industries combined together, as shown in Figure 1.[5]
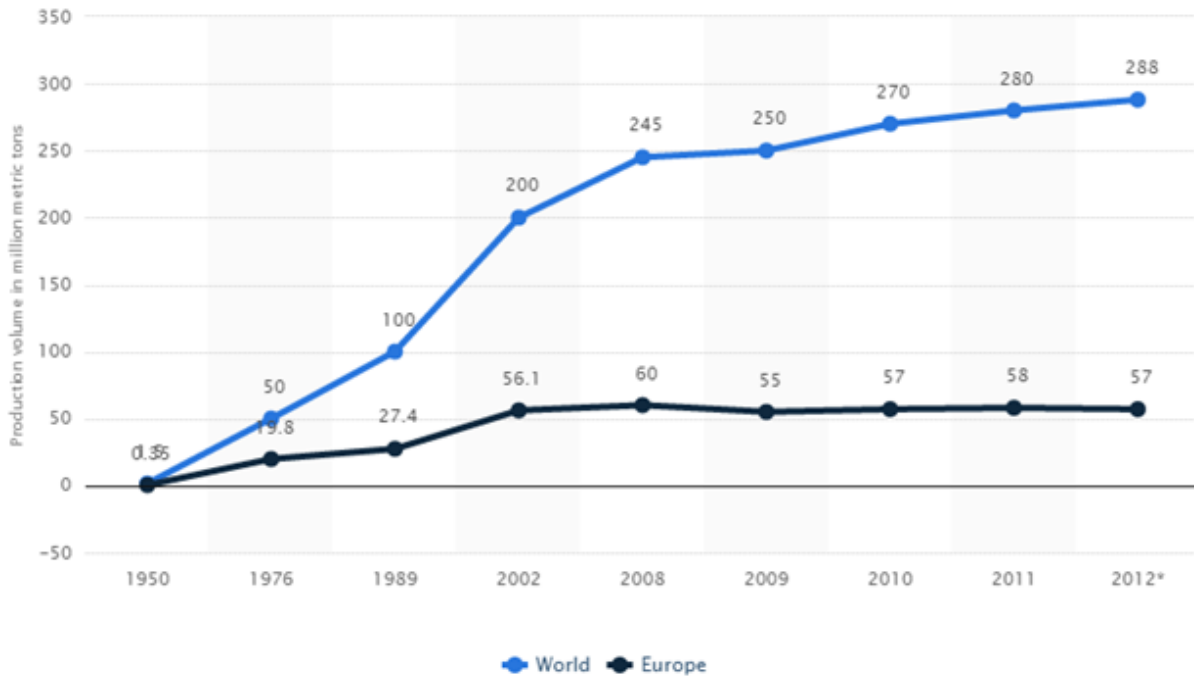
Figure 1: Production of plastics worldwide from 1950 to 2012 (in million metric tons).

Both natural and synthetic polymers are remarkably involved in comfort and facilitation of human life and are involved in the everyday life, such as medication, nutrition, communication, transportation, irrigation, container, clothing, recording history, buildings, highways, and so on. It is clear that it is really difficult to imagine a human society without polymers. Synthetic and natural polymers could be used in the form of organic or inorganic polymers. the first are polymers whose main chains are mainly, if not entirely, made of carbon atoms (proteins, plastics, rubber), while the second don't have carbon atom in the dorsal chain, but in their place have Si, Ge, Sn, P and N atoms (silicones, polysilanes, polygermans, polystannans and polifosfazenes). In general, polymers can be exploited to obtain different types of materials such as: coatings, elastomers, adhesives, blends, plastics, fibers, caulks, ceramics, and composites. It is not surprising that polymer researches

involves material scientists, chemists and chemical engineers, physicists, textile technologists, mechanical engineers, pharmacists and many other scientific groups. [6] The attention on the polymer world has been growing along the past decades due to the significant role of these materials and their chemistry to be applied in important fields like pharmacy, biomedicine, molecular biology, biochemistry, and biophysics. In fact, polymer chemistry can be considered as a specialized, broad and unique discipline that could cover some parts of chemistry and several other scientific aspects as well. Perhaps it is able to cross over and cut the traditional lines of all branches of chemistry, biology, physics, material, engineering, pharmacy, and even medicine.

1.2 Polymers properties

Polymers properties are divided into several classes depending on the scale at which the property is defined as well as upon physical basis. [7] It is very important the identification of the constituent monomers for a polymer. Then, it is necessary to focus on the microstructure that essentially describes the arrangement of these monomers within the polymeric chain. These basic structural properties play a significant role in the definition of the behavior of the polymer. Chemical properties have two different meanings, according to the scale. In particular, at the nano-scale, they describe how the chains interact through various internal physical forces, while at the macro-scale, they are responsible of the interactions among the bulk polymer and other chemicals and solvents.

1.2.1   Monomers and repeating units

As previously mentioned, a polymer is made up of repeating units that determines the final properties of the material. Polymers that contain only a single type of repeat unit are known as homopolymers, while polymers compose by two or more types of repeating units are known as

copolymers. [8] For example, poly(styrene) belongs to the first category as it is synthesized using only styrene monomers. On the other hand, ethylene-vinyl acetate is a copolymer because it contains more than one kind of repeating unit. DNA is also a polymer, because it is composed of several biological chains. In fact, it is made up of four types of nucleotide subunits (adenine, thymine, guanine and cytosine). In addition, a polymer that contains ionizable subunits is known as a polyelectrolyte or ionomer.

1.2.2   Polymer architecture

The architecture and the shape of a polymer are very important microstructural features; they are strictly related to the way branched points lead to a deviation from a simple linear chain. [9] According to the configuration of the polymeric molecule, it is possible to have linear, branched, cross-linked and network polymers, as shown in Figure 2.
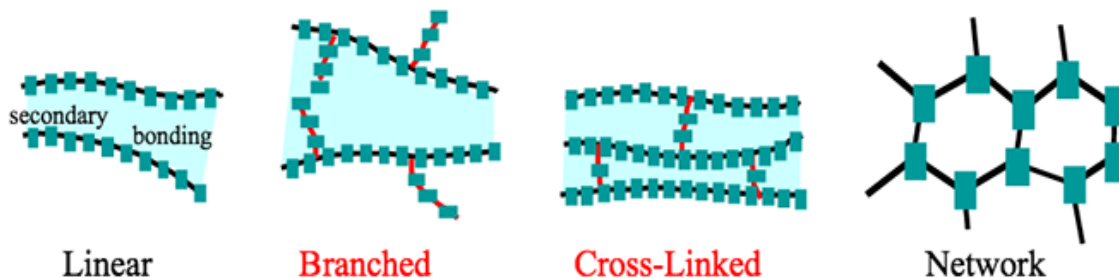
Figure 2: Examples of polymers architectures.

A linear polymer is simply a chain in which all of the C-C bonds exist in a single straight line. An example of a linear polymer is Teflon (Figure 3), which is made of tetrafluoroethylene, so repeating units of $-CF_2-$.
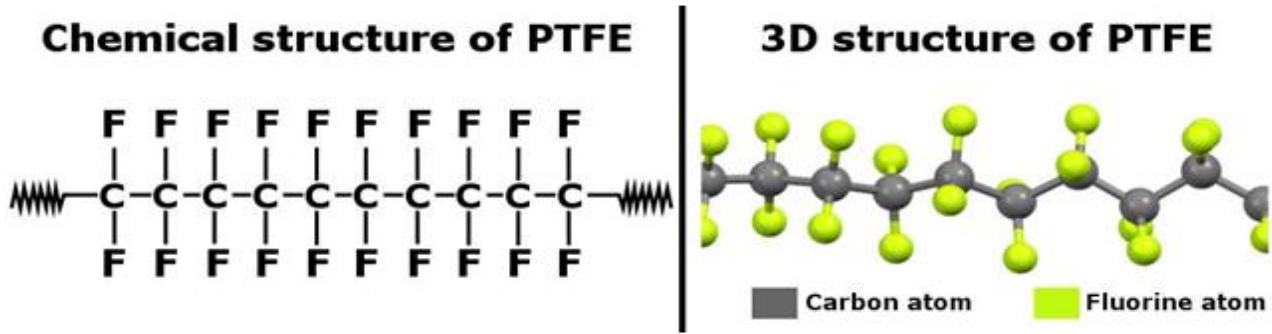
Figure 3: Example of linear polymer: Teflon structure.

A branched polymer molecule is composed of a main chain with one or more substituent side chains. These branches can make the polymer strong in the ideal temperature range. However, when heated, both linear and branched polymers become softer as soon as the temperature vibration overcomes the attractive forces between the molecules. Types of branched polymers include star polymers, comb-like polymers, brush polymers, dendronized polymers, dendrimers, and ladder polymers (Figure 4).
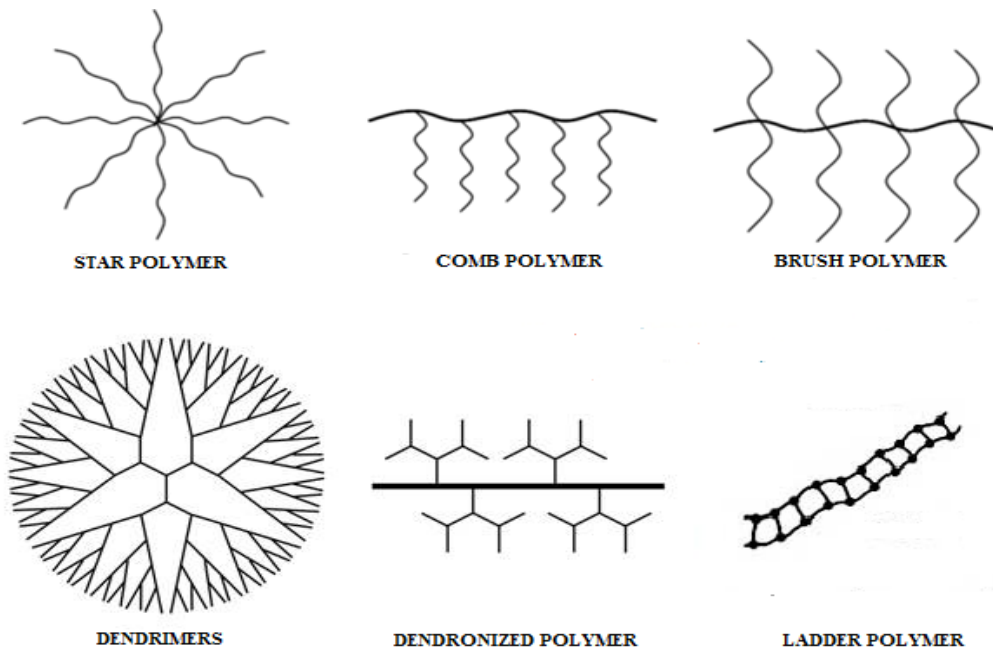
Figure 4: Different branched polymers configurations.

The cross-linked and network polymer forms long chains, either branched or linear, that can create covalent bonds between the polymer molecules. Due to the high strength of covalent bonds, the intermolecular forces that attract other polymer chains are stronger so it is easy to get a more stable materials. An example is the vulcanization of the natural rubber (Polyisoprene). In this process, the rubber is heated so as to the sulfur molecules present in the polymer chains form covalent bonds with each other as shown in Figure 5.
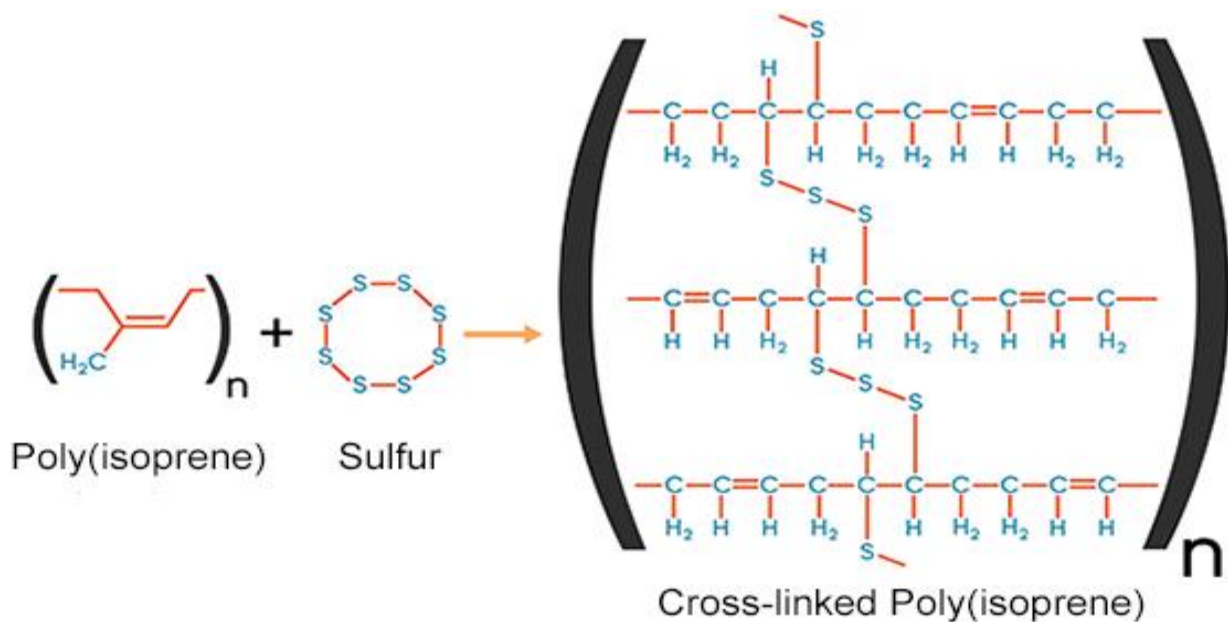
Figure 5: Example of the polymer network: the vulcanization of natural rubber.

This difference in strength is noticeable when you compare the stiffness, rigidity and durability of a car tire with that of a rubber band. [10] It is worth to note that the architecture of a polymer affects many of its physical properties including: melt viscosity, defined as a measure of the rate at which chains can move relative to each other (this will be controlled by the ease of rotation about the backbone bonds); glass transition temperature, that is the gradual and reversible transition in amorphous materials from a hard and relatively brittle "glassy" state into a viscous or rubbery state, due to the increase of temperature; solubility in various solvents, and the size of individual polymer coils in solution. [11]

A proper polymerization reaction allows to synthesize the desired architecture. In this work, the main polymerization techniques adopted were the FRP (Free radical polymerization) and FP (Front polymerization) discussed in the next chapters.

1.2.3   Monomer arrangement in copolymers

In a copolymer, monomers can be organized along the chain in different ways. In particular, if the monomers are arrange in a controlled way, the copolymer is called sequence-controlled polymer, like alternating, periodic and block copolymers, as shown in Figure 6. [12]
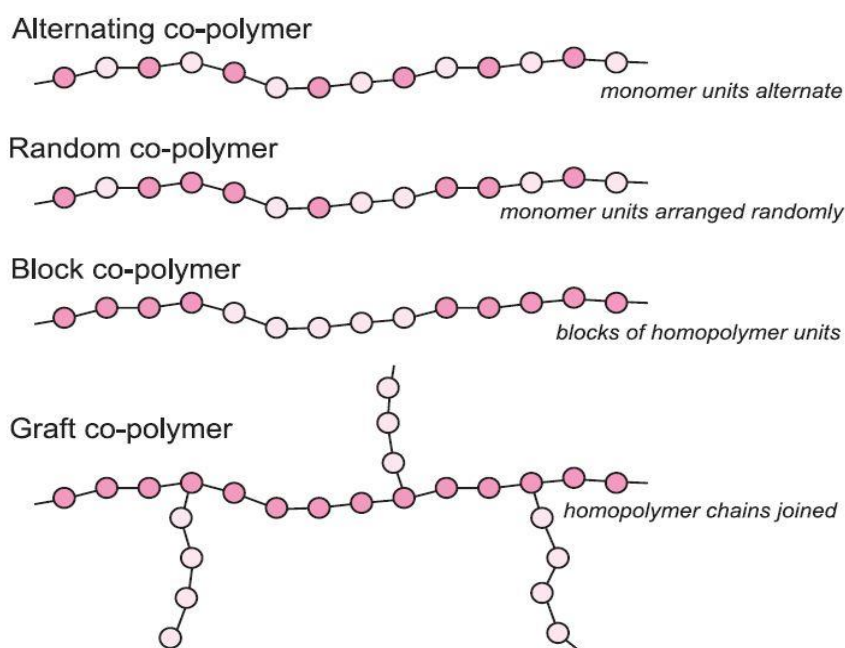
Figure 6: Monomers arrangements in copolymers.

Alternating copolymers possess two regularly alternating monomer residues. [13] An example is the equimolar copolymer of styrene and maleic anhydride formed by free-radical chain-growth polymerization (Figure 7). [14]
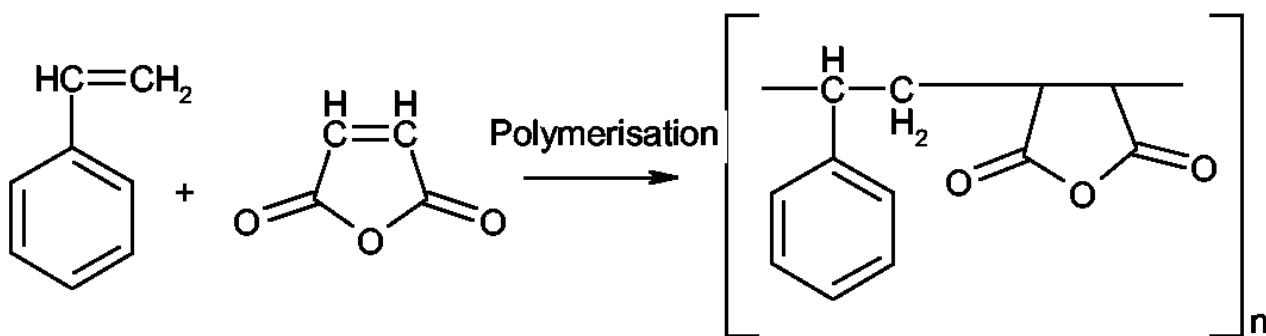
Figure 7: Example of alternating copolymer.

Statistical copolymers have monomer residues arranged according to a statistical rule. A statistical copolymer in which the probability of finding a particular type of monomeric residue at a particular point in the chain is independent of the types of surrounding monomeric residues may be referred to as random copolymer. [16, 17] Figure 8 shows an example of the random chain-growth copolymer involving vinyl chloride and vinyl acetate.
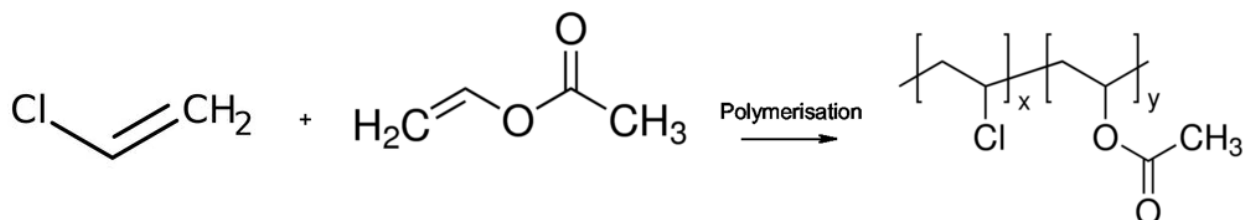
Figure 8: Example of random copolymer.

Block copolymers have long sequences of different monomer units. [14, 15] For example, polystyrene-b-poly(methyl methacrylate) (where b means block) is usually made by first polymerizing styrene, and then subsequently polymerizing methyl methacrylate from the reactive end of the polystyrene chains (Figure 9).
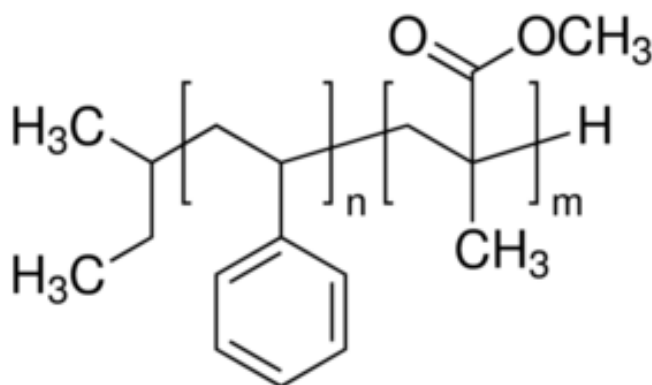
Figure 9: Example of block copolymer.

Polymers with two or three blocks of two distinct chemical species (for example X and Y) are called diblock copolymers and triblock copolymers, respectively. Three-block polymers, each of a different chemical species (e.g. X, Y and Z) are called triblock terpolymers. The graft copolymers contain side chains or branches whose repeating units have a different composition or configuration compared to the main chain. [15] Typically a low molecular weight monomer is radically copolymerized with a methacrylate functionalized macromonomer (Figure 10).
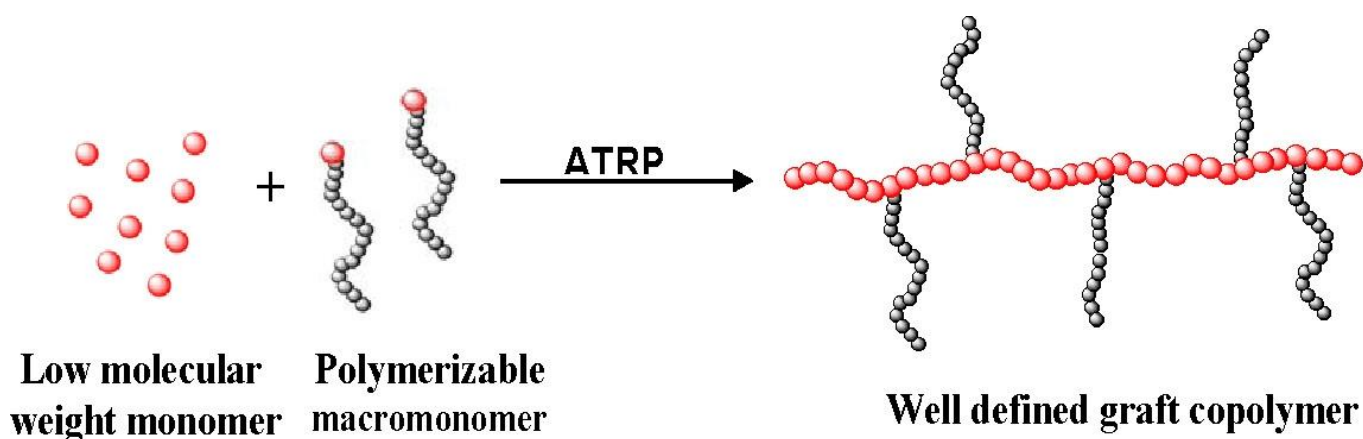
Figure 10: Example of graft copolymer.

Macromonomers such as polyethylene, polyethylene oxide, polysiloxanes, polylactic acid, polycaprolactone can be incorporated into a polystyrene or polymethacrylate backbone.

1.2.4 Physical properties

The physical properties of a polymer are strongly dependent also on the length of the polymer chain. [18] For example, as the chain length increases, melting and boiling temperatures quickly increase. [19] Impact resistance also tends to increase with the chain length, as the viscosity does, as well as the resistance to flow of the polymer in its molten state. [20] Melt viscosity is strongly related to the polymer chain length, for instance a tenfold increase in polymer chain length results in a viscosity increase of over 1000 times. [21] Moreover, the growth of the chain length tends to decrease the chain mobility, increasing the strength, the toughness, and the glass transition temperature). [22] This is a result of the improvement of the chain interactions, such as Van der Waals attractions and entanglements due to the presence of the long chains. These interactions tend to fix the individual chains in a strong and stable position able to resist deformations and matrix breakup, both at higher stresses and higher temperatures. A common way to express the length of a chain is through the degree of polymerization, which quantifies the number of monomers incorporated into the chain. [23, 24] Another way to indentify the polymer size is the molecular weight. Since the synthetic polymerization techniques typically yield a polymer product including a range of molecular weights, it is common to refer to it using a distribution of chain lengths. There are two different molecular weights: the weight molecular weight Mw (1) and the number molecular weight Mn (2). [25, 26] The polydispersity index (PDI) is the ratio between the Mw and the Mn and it gives information about the variance of the distributions (3) (Figure 11).

$$(1) \quad M_w = \frac{\sum_i w_i M_i}{\sum_i w_i} \qquad (2) \quad M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} \qquad (3) \quad PDI = \frac{M_w}{M_n}$$
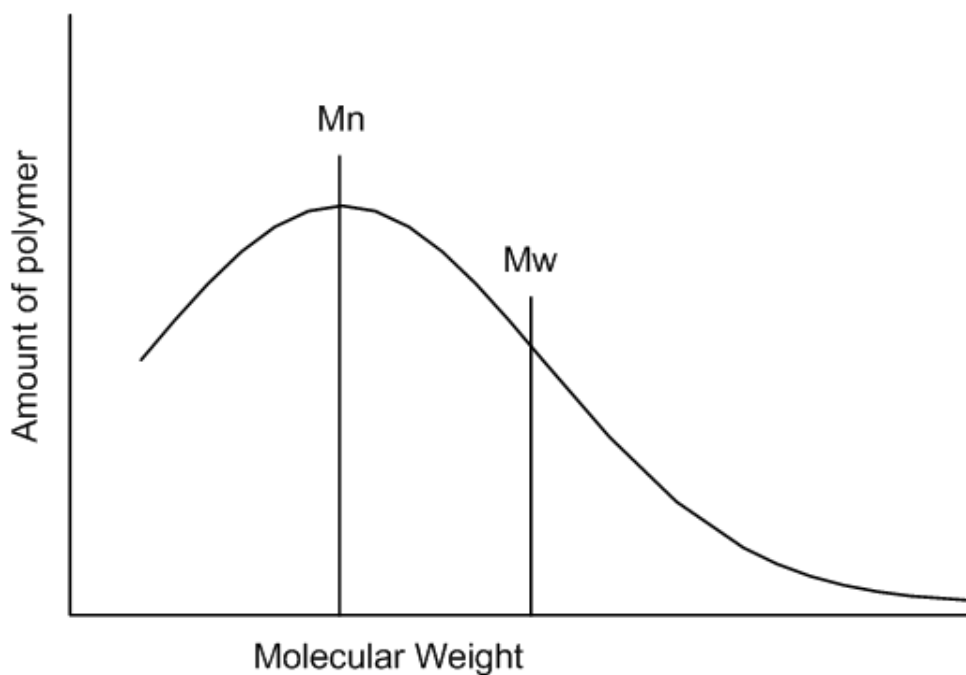
Figure 11*:* Example of molecular weight distribution.

Finally, the length of the contour is a parameter useful to predict the flexibility of an unbranched polymer chain, which can be explained as the length of the main chain in its fully extended state. [27]

1.2.5   Chemical properties

Intermolecular and intramolecular forces are the two types of forces that hold together the individual molecules and atoms. These forces control the movement of molecules and atoms. Both types of forces determine the chemical and physical characteristics of the substances and are summarized in the Figure 12 below.
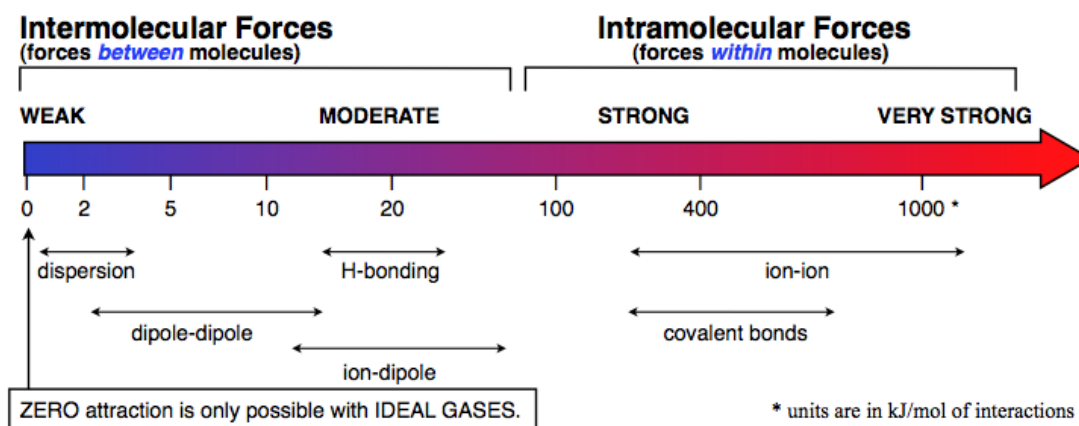
Figure 12: Different inter and intra molecular forces from the weakest to the strongest.

However, as a consequence of the length of the polymer, inter-chain forces are more relevant than the attractions between conventional molecules and determine the properties of the final material. Different side groups on the polymer can allow it to form ionic or hydrogen bonds between its own chains. These stronger forces typically cause greater tensile strength and higher crystalline melting points. A summary can be found in Table 1.

Table 1: List of different inter-chain forces: hydrogen bonds, dipole bonds, and dispersion forces.

Force	Model	Basis of attraction	Energy [KJ mol^{-1}]	Example
H bond	$\delta^-\ \delta^+\quad\ \delta^-$ —A—H········:B—	Polar bond to H– dipole charge (high EN of N, O, F)	10–40	
Dipole-dipole		Dipole charges	5–25	
Dispersion (London)		Polarizable e$^-$ clouds	0.05–40	

The intermolecular forces in polymers can be influenced by the dipoles in the monomeric units. Polymers containing amide or carbonyl groups can form hydrogen bonds (H bond) between adjacent chains. In fact, partially positively charged hydrogen atoms in the N-H groups of a chain are strongly attracted to negatively charged oxygen atoms in the C = O groups of the others. These strong hydrogen bonds, for example, determine the high tensile strength and melting point of polymers containing urethane or urea bonds. The polyesters have a dipole-dipole bond between the oxygen atoms in the C = O groups and the hydrogen atoms in the H-C groups (Dipole- dipole). The dipole bond is not as strong as the hydrogen bond, so the melting point and strength of a polyester are often lower than the polyamide, but the polymer have **a** greater flexibility. However, ethane does not have a permanent dipole. The attractive forces between the polyethylene chains derive from the weak forces of van der Waals (Dispersion London). Molecules can be considered surrounded by a cloud of negative electrons. When two polymeric chains approach, their electron clouds repel each other, leading to a decrease of the electronic density on one side of a polymer chain, creating a slight positive dipole on the same side. This charge is sufficient to attract the second chain of polymers. Van der Waals forces are rather weak and lead to polymers with lower melting temperature. At the end, some of the different chemical properties due to inter-chain forces are summarized in the table below (Table 2)

Table 2: Chemical properties of different polymers due to their inter-chain forces: polyurethane (PU), polyethyleneterephtalate (PET), and Polyethylene (PE).

Properties	PU	PET	PE
Melting point [°C]	280	255	135
Elastic Modulus [MPa]	660	3000	800
Tensile Strength [MPa]	40	85	22
Density [g cm^{-3}]	1.2	1.38	0.94

1.3 Polymerization techniques

As mentioned before, polymeric materials are made up of long chain molecules formed by the chemical combination of small reactive units, called monomers. [28] The reaction that leads to the formation of polymer molecules is called polymerization. Polymerization reactions involve a wide variety of mechanisms according to the complexity of the functional groups present in the system, considering also their steric effects. [29] For instance, alkenes form polymers through relatively simple radical reactions; in contrast, the reactions that involve substitution at the carbonyl group require more complex synthesis due to the way in which reacting molecules are able to polymerize. [29] Alkanes can polymerize in presence of strong acids. [30] Common products obtained from the polymerizations of alkenes are polyethylene and polyvinyl chloride. Both of them are produced in high tonnages each year, due to their usefulness in manufacturing processes of commercial products, such as piping, insulation and packaging. In general, these kind of polymers are called homopolymers, as they consist of repeated long chains or structures of the same monomer unit, whereas polymers that consist of more than one molecule are referred to as copolymers. Other monomer units, such as formaldehyde hydrates or simple aldehydes, are able to polymerize themselves at quite low temperatures to form trimers; molecules consisting of 3 monomer units, which can cyclize to form ring cyclic structures, or undergo further reactions to form tetramers, or 4 monomer-unit compounds. Further compounds either being referred to as oligomers in smaller molecules. [28] Formaldehyde is a very reactive electrophile that easily allows nucleophillic addition of hemiacetal intermediates, which are in general short-lived and relatively unstable "mid-stage" compounds that react with other molecules present to form more stable polymeric compounds. There are several classifications to combine the polymerization techniques. The most common one was introduced by Wallace Hume Carothers in 1929 and it is based on the type of products, like poly condensation and poly addition. [31] Polycondensation is a polymerization in which the growth of polymer chains proceeds by condensation and by addition

reactions between molecules of all degrees of polymerization, respectively. Both of them produce a polymer but in the polycondensation there is also the formation of a low-molar-mass by-product, such as water. A condensation polymer is so defined as a polymer that involves loss of small molecules during its synthesis, or contains heteroatoms as part of its backbone chain, or its repeat unit does not contain all the atoms present in the hypothetical monomer to which it can be degraded. Going deeper into the mechanism of the polymerization reactions, Paul Flory in 1953 highlight the differences between a chain-growth and step-growth polymerization. [32]

- STEP-GROWTH

Step-growth polymers are formed by only one reaction mechanism: the stepwise reaction among functional groups of monomers involves their heteroatoms such as nitrogen or oxygen. Most step-growth polymers are also classified as condensation polymers. An example is reported in Figure 13, which shows two different ways to obtain the same polymer, polydimethylsiloxane, but through the formation of different condensates: H_2O or a generic alcohol (ROH).
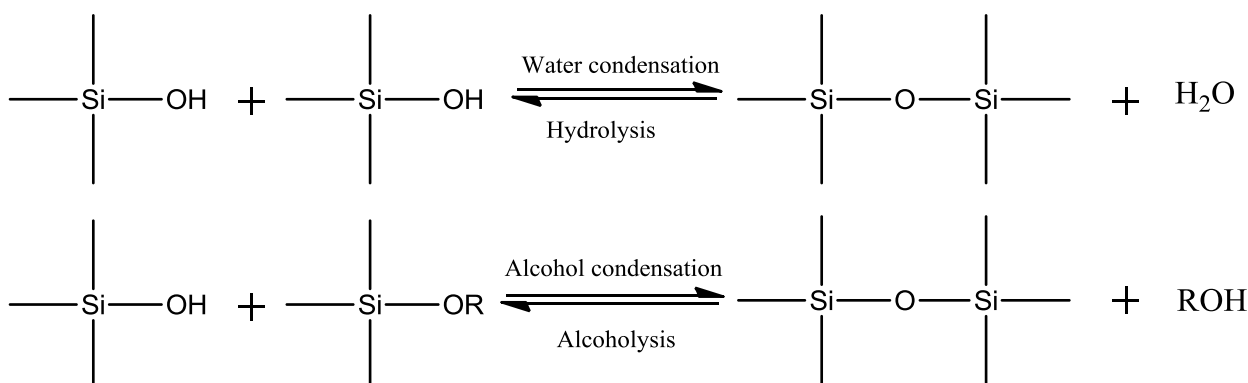
Figure 13: How to get the same material using condensation reaction.

Step-growth polymers increase in molecular weight at a very slow rate at lower conversions and reach moderately high molecular weights only at very high conversion (i.e., >95%). The distinct initiation, propagation, and termination steps of chain-growth polymerization are meaningless in step-growth polymerization. A difunctional monomer or equal molar amounts of two different difunctional monomers are necessary at least to form a linear high molecular weight polymer. The polymerization reaction proceeds by individual reactions of the functional groups on the monomers. Thus, two monomers react to form a dimer. The dimer may now react with another dimer to produce a tetramer, or the dimer may react with more monomer to form a trimer. This process continues, each reaction of the functional groups proceeding essentially at the same reaction rate until over a relatively long period of time and the average molecular weight of the polymer slowly increases. Therefore, it is difficult to control the molecular weight of polymer, and polymer possesses a broad molecular weight distribution.

- CHAIN-GROWTH

The chain-growth polymerization is the reaction in which each polymer chain, after being started by a free radical initiator grows rapidly, producing a high molecular weight polymer since the very beginning of the reaction due to the successive addition of the monomer molecules. Chain-growth polymerization (often called addition polymerization) involves the reaction among molecules with double or triple carbon-carbon bonds. The unreacted monomer in the reaction is slowly decreasing over the time. Chain-growth polymerization is typically involved in the manufacture of polymers such as polyethylene, polypropylene, and polyvinyl chloride. The reaction proceeds with three different steps: the initiation, the propagation and the termination. In the first one, there is the generation of radicals, very reactive atoms or molecules that have unpaired electrons the mechanism. In the propagation step, the radicals attach the unsaturated bond in the monomer structures, generating other longer radicals that continue to react with the monomer unit. The

propagation reaction is over when the termination occurs. It means the addition of two radical species. It is clear that the termination occurs randomly, when two chains collide, so it is not possible to control the length of individual chains and the degree of branching. In this case, it is pretty tough to tune the final molecular weight and its distribution. To solve these issues, it is worth to note that exists the living polymerization, in which the molecular weight of polymer is controlled by the feed ratio of monomer to initiator and the molecular weight distribution is narrow. In addition, the molecular weight increases in proportion to monomer conversion while retaining low polydispersity over the whole conversion range. [33] Other forms of chain growth polymerization include cationic and anionic addition polymerization, very useful to polymerize some monomers that cannot be polymerized by free radical methods. An example can be the isotactic polypropylene that is obtained through a coordinated anionic polyaddition with Ziegler-Natta catalyst. [34] The mechanism can be schematized as follows (Figure 14).
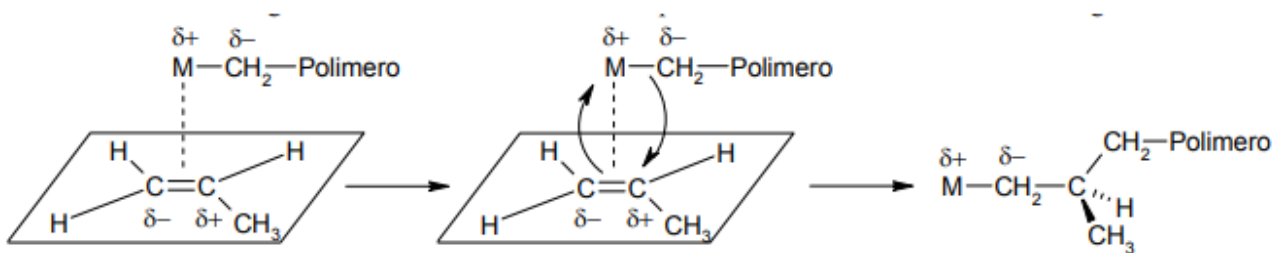
Figure 14: Reaction mechanism of a coordinate anionic polyaddition.

The process involves an anionic mechanism at the beginning. However, the attack on the monomer is not brought directly from the growing polymer, but from the metallic counterion, indicated in Figure 14 with M, which is linked to the carbanion with a strongly polar bond. Metal M initially coordinates and orients the monomer (propane, in this case) and only then, it let the anion of the growing polymer attacks the monomer forming a new anion that remains linked to the counterion. Plotting the molecular weight values and the polydispersity against monomer conversion, the

molecular weight does not increase much in the initial and middle stage and is accelerated in the last stage. Figure 15 shows the evolution of the molecular weight with the conversion.
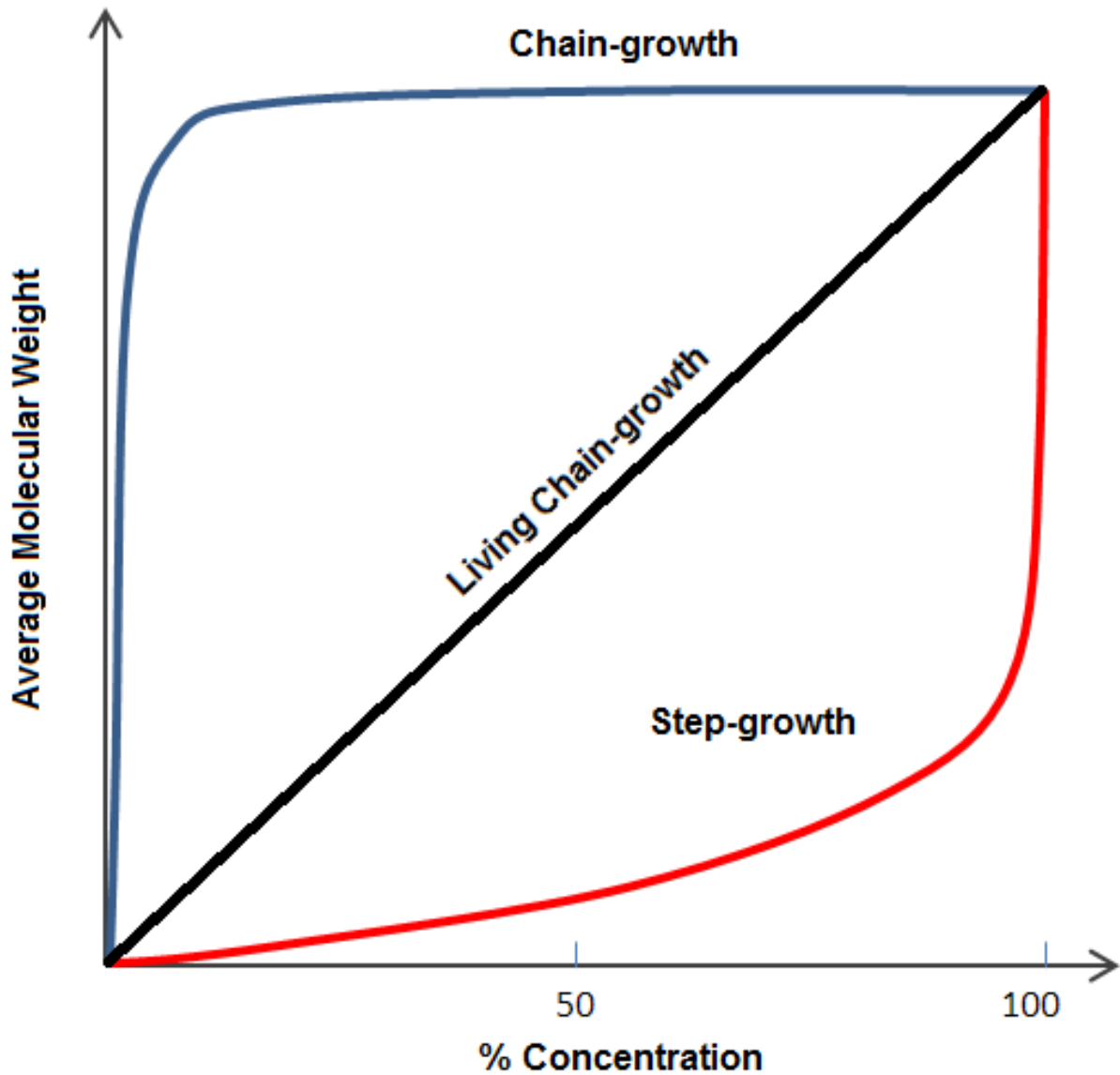
Figure 15: Increase of the molecular weight of the polymer according to its concentration and different mechanisms.

The main differences among these two polymerizations are reported in the Table 3.

Table 3: Differences among step-growth and chain-growth polymerization.

	Step- Growth	**Chain- Growth**
Reaction	One reaction, similar steps	Three steps having different rates and mechanisms
Polymer Growth	Through matrix	By the addition of one monomer at a time to the active end of the polymer chain
Polymer Molecular Weight	Molecular Weight rises steadily throughput the reaction. High conversion is required for high molecular weight polymer	High molecular weight polymer is formed immediately
Monomer Concentration during Polymerization	Monomer disappears in the early stages of the polymerization	Monomer concentration decreases steadily throughput the reaction
Composition of the Polymer reaction	A relatively broad, calculable distribution of molecular species are present throughput the course of the polymerization	Mixture contains only monomer.

Esters of acrylic acid contain a C=C conjugated to an ester group allows the possibility of both types of polymerization mechanism. An acrylic ester by itself can undergo chain-growth polymerization to form a homopolymer with a carbon-carbon backbone, such as poly(methyl methacrylate). At the same time, it can react with diamine monomers, by nucleophilic conjugate addition of amine groups. In this case the polymerization proceeds by step-growth and the products are poly(β-amino ester) copolymers, with backbones containing nitrogen (as amine) and oxygen (as ester as well as carbon. [35] Two different polymerization techniques have been studied and used for these thesis work, such as Free Radical Polymerization (FRP) and Frontal Polymerization.

1.4 Free Radical Polymerization and Frontal Polymerization

In this work, two polymerization processes are used in order to obtain the desired products: Free Radical Polymerization (FRP) and Frontal Polymerization (FP). FRP is a type of chain growth in which there is the addition of the monomer units. [36] The mechanism is well known and it is widely used in industry for many reasons: the relative easiness of implementation, the good batch-to-batch reproducibility of the polymer products, the tolerance of radicals towards functional groups, and the possibility to use water and protic solvents as polymerization media. [37] In contrast, the high reactivity of propagating radicals combined with the existence of concomitant modes of chain deactivation have long been considered a barrier for obtaining polymers with controlled architecture. [38] FRP allows to operate at relatively mild conditions to produce different types of polymers, like poly(acrylic acid), poly(methacrylic acid) and poly(N-vinylpyrrolidone), used for a wide variety of applications, such as cosmetics, antiflocculants, water treatment, textiles and paper processing. [39] Figure 16 shows the kinetic scheme of FRP that includes three steps: initiation, propagation and termination.

1) *Initiation*

$$\text{Initiator} \longrightarrow R^\bullet$$

$$R^\bullet + M \longrightarrow RM^\bullet$$

2) *Propagation*

$$RM^\bullet + M_n \longrightarrow RM_{n+1}^\bullet$$
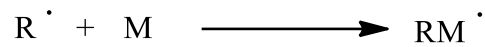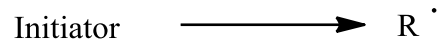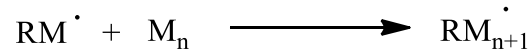
3) *Termination*

combination:

$$RM_n^\bullet + {}^\bullet M_m R \longrightarrow RM_n M_m R$$

disproportionation:

$$RM_n^\bullet + {}^\bullet M_m R \longrightarrow RM_n + M_m R$$
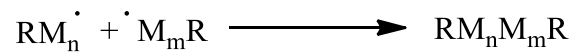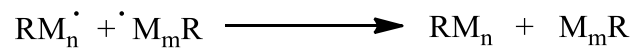
Figure 16: FRP mechanism.

Step 1 allows the formation of free radicals. This usually occurs with the homolytical cleavage of bonds which can be thermal, chemical or by radiation. The generation of the radicals involves a slow reaction due to the unstable nature of the compounds. A proper initiator must be chosen according to the operating conditions of the process. In the propagation (step 2), the radical produced in the initiation step reacts with a monomeric unit, usually on a vinyl group. In this way, a new radical is produced and it can react with another monomeric unit for other additions. The chain transfer reactions stop the growth of a radical chain, transferring its active site on another chemical species, like a monomeric unit or a polymeric one. It is important to underline that the chain transfer affects the molecular weight of the final polymer produced. The length of the chain continues until a chain termination reaction (Step 3) occurs. In the terminations reactions the different radicals form dead chains that are not active anymore. The most common reaction is the combination of two radicals, which form a dead polymer chain whose molecular weight is the sum of the ones of the two reactive radicals. Another possible termination step is the disproportionation reaction, where a

radical chain takes a hydrogen atom from another radical species, leading to the formation of a double bonded species. In this case, the molecular weight of the dead chains remains unaltered. The termination steps are usually very fast and they are often limited by diffusion. In addition, since the global polymerization reaction is an exothermic process and the propagation step has an Arrhenius dependence on temperature, runaway could happen. Such a problem can be avoided by properly diluting the system with an adequate solvent. [40] Due to the high propagation rate, the growing chains experience different conditions at different times. As a consequence, the molecular weight is not the same for every polymeric chain, but it is represented by a distribution (as shown in section 1.3). Virtually all free-radical chain reactions require a separate initiation step in which a radical species is generated in the reaction mixture. Therefore, radical initiation reactions can occur in several ways, according to the manner in which the first radical species is formed: homolytic decomposition of covalent bonds by energy absorption or electron transfer from ions or atoms, containing unpaired electrons followed by bond dissociation in the acceptor molecule. A very effective method of generating free radicals under mild conditions is by one-electron transfer reactions. This method has found wide application for initiating polymerization reactions and has industrial importance, e.g. in low-temperature emulsion polymerizations. For the homolytic cleavage of covalent bonds of most practical thermal initiators, the bond dissociation energy required is in the range of 125–160 kJ mol^{-1}. Compounds that have value above or below this range give either too slow or too rapid rate of generation of radicals at the polymerization temperatures used. Besides the very short induction period (almost negligible), a lower energy of activation (40–80 kJ mol^{-1}) allows the redox polymerization to be carried out under milder conditions than thermal polymerization. This lowers the possibility of side chain reactions giving high molecular weight polymers with a high yield. [41] In this work, together with the generation of the radicals after the homolytic cleavage of a labile bond, a redox initiation has been considered. The starting of the reaction is based on a redox mechanism that generates the heat wave that trigger the decomposition of the initiator which start the free radical polymerization, known as frontal polymerization (FP). FP

is a kind of polymerization in which a localized zone of reaction propagates in an unstirred medium, most often through the coupling of Arrhenius kinetics and thermal diffusion (Figure 17). FP was first studied by Chechilo and Enikolopyan in 1972. [42]
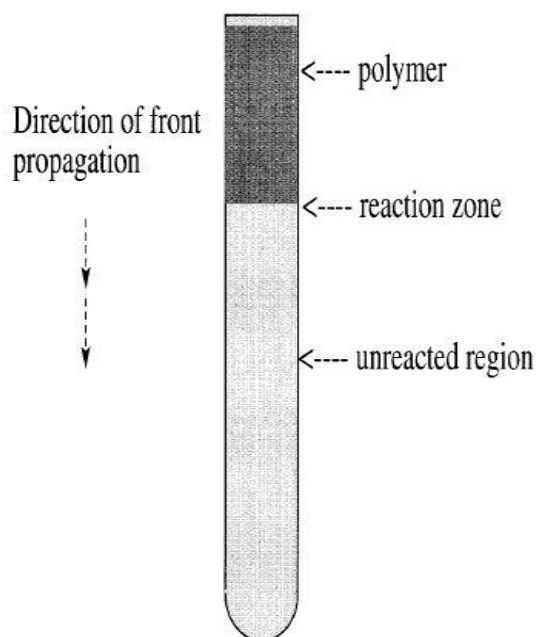
Figure 17: Frontal polymerization.

In order to perform the FP, the reaction must be enough exothermic to sustain the heat wave and reach the decomposition temperature of initiator. [43] The idea is to start the reaction only when the two mixtures (one contains the reductant and one contains the oxidant) are in contact and then, once they intimately mixed due to the high speed, the reaction must be able to propagate in the direction of the front. This increases the stability of the solution, avoiding possible unwanted polymerization in storage and giving the possibility to initiate the reaction at lower temperature. It acts like a FRP, but the radicals are generated by a redox reaction. The propagation of the polymerization involves the different displacement of the front in the direction of the unreacted monomers. (Figure 18).
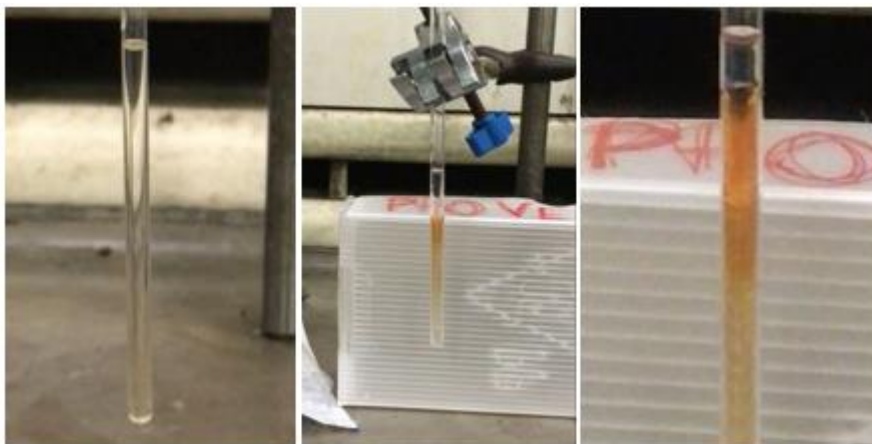
Figure 18: Propagation of the polymerization front over the time.

In this work, one component contains the monomer mixture and initiator for the polymerization, and the other contains the second initiator needed to start the redox polymerization. The two solutions are stable when they are keep isolated but once the two mixtures enter in contact the polymerization starts and the final product is a hard-solid.

1.5 Emulsions

It is known that oil and water are two immiscible fluids, but they can be stabilized in an emulsion, as shown in Figure 19.
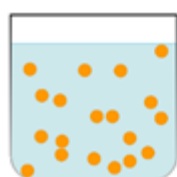
Figure 19: Oil in water: the blue is the water (Phase I) while yellow is the oil (Phase II).

Emulsions are kind of dispersions composed of two immiscible liquids (usually water and organic solvent) and can be classified into two types: oil in water (O/W) and water in oil (W/O). The most common is oil in water and it is called direct emulsion. In this case, the water is the continuous phase, as it is present in large amount, while oil is called dispersed phase. In addition, it is possible to have an inverse emulsion, so water in oil emulsion. The main difference is related to the fact that in the first case the continuous phase is aqueous solution, while in the second one the continuous phase is the oily solution. Research in emulsions has experienced a continuous increase in the last years, as evidenced by the numerous publications. [44–46] The significant interest is triggered by the widespread applications, for example, food, cosmetic, agriculture, pharmacy and also polymers synthesis. However, they are non-equilibrium systems and may undergo the breakdown process of coalescence, sedimentation and Ostwald ripening, the main instability process of nano-emulsions. They are thermodynamically unstable systems that are stabilized kinetically. Consequently, the stability of an emulsion depends both on its composition and on the size of the emulsion droplets. Typically, the droplet size of conventional emulsions is larger than 1 μm making these droplets susceptible to gravity forces. Depending on the preparation method, different droplet size distributions might be achieved, explaining why the route of preparation can have an influence on the emulsion stability. In order to make them kinetically stable, some emulsifiers such as surfactants, polymers and solid particles are always added. The important role of emulsifiers during emulsification is to adsorb at the oil/water interface and lowers the interfacial tension. Emulsions stabilized by surfactants have been known for a long time and the hydrophilic-lipophilic balance (HLB) is one crucial parameter which conventionally determines the type and stability of emulsions. [47-48] Surfactants with high HLB generally tend to stabilize O/W emulsions while those with low HLB tend to stabilize W/O ones. It is well known that a certain mixture of surfactants can provide better performance than the pure surfactant (even if it gives the same HLB of a single surfactant) and so, in the section 2.5.3, the interactions between different surfactants will be studied, together with the evaluation of HLB. The types of emulsion may be dependent on some

factors such as temperature, phase volume ratio, additives (electrolyte) and emulsification process. [49-56] There are two ways of emulsification: high energy and low energy. High-energy emulsification methods require intense mechanical energy inputs and the three main types of devices: high-shear stirrers, high-pressure homogenizers and ultrasound generators are usually used. [57-59] This high-energy input leads to deforming forces that are able to break the droplets into smaller ones, provided the Laplace pressure is overcome (See section 2.5.4). Additionally, an increase of the surfactant content at the interface reduces the Laplace pressure [60]. Therefore, the smaller the droplet size, the more energy and/or surfactant is required, making this preparation route unfavorable for industrial applications, when very small droplets are desired. However, submicron emulsions can also be obtained by employing the physicochemical properties of the system generally referred to as low-energy emulsification methods. These methods, such as emulsion inversion point method (EIP) or process inversion temperature (PIT), making use of internal chemical energy stored in the components by changing the spontaneous curvature of the surfactants, are more energy efficient as only a low quantity of applied energy is needed (Figure 21). [61-64]
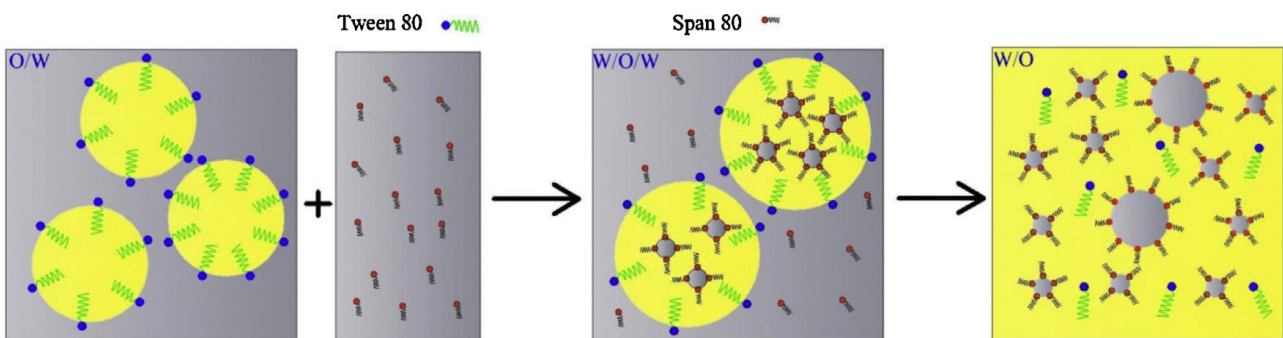
Figure 20: Schematic illustration for the inversion of O/W to W/O, through the formation of an intermediate W/O/W multiple emulsion

1.6 Purpose

One example of the formulations developed in this work can be the oil and gas field. In fact, the continuous increase in the price of fossil fuel and the decreasing in the reserves have asked an optimization in the engineering techniques for the extraction. In particular, the loss of drilling fluids represents one of the most important concerns during the perforation and they determines consistent economic losses and, in some cases, the shutdown of well. The drilling fluids are generally lost when the drill bit passes through fractures in porous formation. There are different conditions of the formation that induce the losses of mud: the soil can be naturally fractured or present cavernous space inside or have high permeability zone (Figure 4).
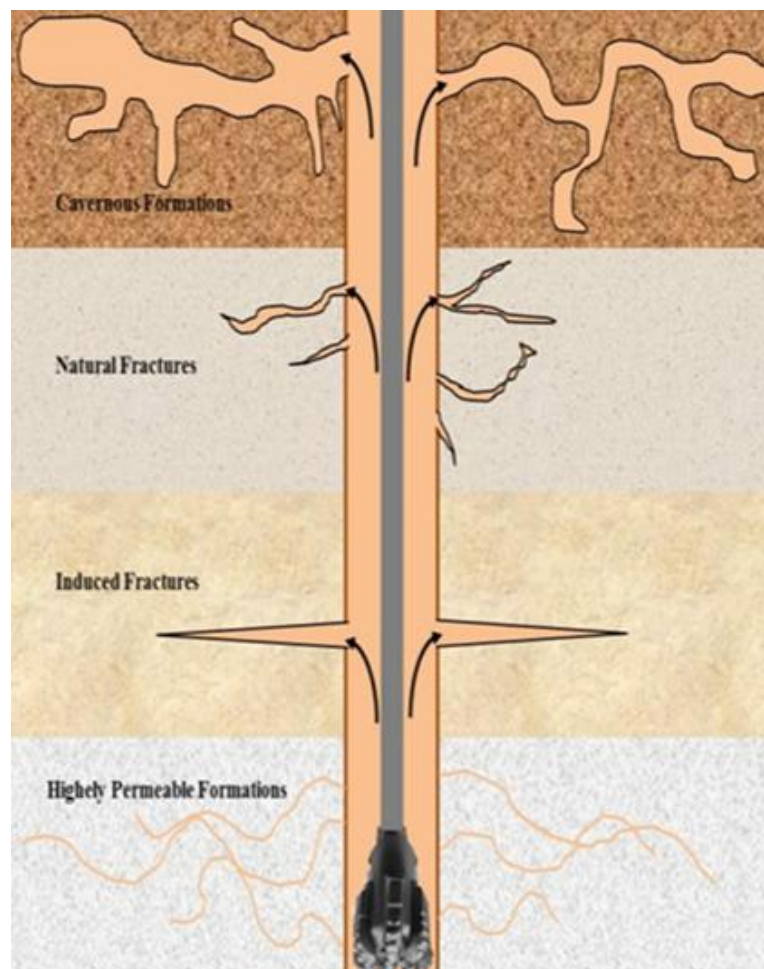
Figure 21: Possible fractures for losses events.

The state of art of drilling fluids offers a great quantity of additives that can be used in the operations but they do not satisfy all the expectations. [65-68] For this reason, the new methods and innovative formulations developed in this work can be considered as additives to avoid the loss of drilling mud. In particular, the bicomponent blend is suitable for this aim. It has been developed focusing on the immiscibility of the reactive mixtures with the mud and it is able to act as a blocker, like concrete, simplifying the occlusion of fractures or caves in the wellbore, producing a solid cover-up that interrupts any losses. Respect to the existing solutions, this novel formulation has different advantages:

- Rapid restart of operations, if concrete is used the drilling operations are stopped typically for 9-12 hours.

- Easy injectability: this formulation has the same viscosity of the drilling fluids and does not affect the mud function, due to its immiscibility. It is also possible to use the same technical equipments for the circulation of mud to inject this formulation.

- Easy destruction of the solid block in the case it affects part of the wellbore, with the injection of specific compounds, like acetic acid or hydrochloric acid: the mechanical resistance of the solid polymer is reduced, and the drill bit can easy remove the occlusion in the well and restart the perforation.

- Better control in the operations, the reaction starts only when the two mixture are in contact, preventing accidental blocking.

- Efficient formation of solid block. The start of the polymerization reaction does not depend on the efficiency of mixing of the two compositions, because the trigger of the reaction is the heating wave generated in the starting of the reaction.

Different type of monomers mixture and initiators couple can be used, depending on the needed time, pH, temperature conditions and the lipophilicity/hydrophilicity of the muds. The two different muds that have been considered are the water-based muds (WBM) and the oil-based muds (OBM).

The first ones are drilling fluids based on water as continuous phase and a solid fraction constituting of clay, natural polymers, weighting agent and other additives like fluidizing and inhibiting substances, in order to control the density, filtration and rheological proprieties. Water could be fresh or salted water, depending on the performances and availability. WBM are widely used in most of the drilling systems in the world due to low cost and low environmental impacts. On the contrary, OBM are used only in about 5-10% of the wells drilled. This type of fluids is based on inverse emulsion in which oil is the continuous phase and water is the dispersed phase. In this case, the continuous phase is non-ionic, so the interaction with the formation is much less. The principal advantages are related to the better stabilization, lubrification power and resistance at high temperature. The principal issues are the higher environmental impact and the higher investment costs compared to WBM. An important need that must be fulfilled is the immiscibility with the mud, to avoid dilution problem regarding the reactive bicomponent mixture. For this reason it will be necessary to develop a hydrophilic formulation for the OBM and a lipophilic formulation for the WBMs. The pathways 1 and 2, presented in the following chapters, will deal with hydrophilic mixtures and initiators using the two different polymerization techniques tested, FRP, with a common thermal initiation, and FP, with the use of a couple of redox initiators. The strategy adopted for the WBM, instead, was the exploitation of a stable emulsion to make happen the polymerization using a hydrophilic initiator in a lipophilic mixture. In this way it will be possible to avoid to use lipophilic initiators such as BPO or DMA that give good results but that have safety issues and toxic concerns.

Chapter 2: Materials and Methods

This chapter shows all the materials used in the development of this work, together with the experimental procedures used to obtain the final formulations.

2.1 Materials

In this section, the main components for each developed formulations are described: monomers, curing agents, initiators and surfactants. After that, the selection of the materials and the procedures used are showed.

2.1.1   Monomers

The monomers are the main constituent of the studied formulations: they are needed to form a complex three-dimensional network with certain specific properties. For this reason, they have been properly chosen in order to obtain high mechanical resistance within one hour. The general classes of chosen monomers are acrylates and methacrylates for their reactive properties. In fact, the acrylates react faster than methacrylates, but the final polymer is really soft. According to the possibility to find out the best formulation capable to react in one hour, forming a hard product, the following monomers   were tested: [2-(methacryloyloxy)ethyl]trimethylammonium chloride (TMAEC), poly(ethylene glycol) methacrylate (PEGMA), lauryl acrylate (LA), hydroxyetyl acrylate (HEA) and dodecyl methacrylate (LMA). (Table 4)

- **Poly(ethylene glycol) methacrylate**

Poly(ethylene glycol) methacrylate (PEGMA) is a linear and monofuctional methacrylate used as a chemical modification agent or as polymerization reactant (Figure 22).
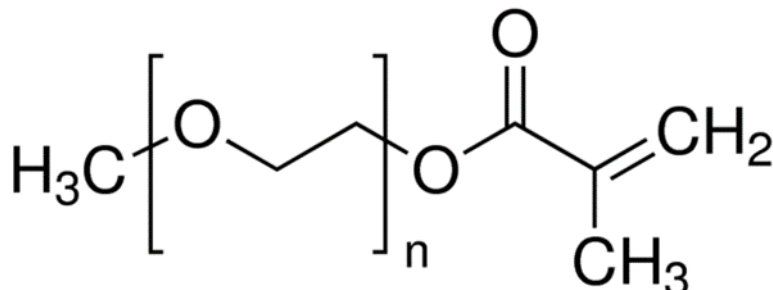
Figure 22: Poly (ethylene glycol) methacrylate.

Under 700 Da, PEGMA appears clear to slightly hazy, colorless, hygroscopic liquids with a slight characteristic odor; over 1000 Da, it is creamy white waxy solids, flakes, or free-flowing powder. For the easier handling and transportation and the safety concern, in this work, two liquid types of PEGMA have been selected and then tested with the molecular weight of 300 and 500 Da respectively.

- **[2-(Methacryloyloxy)ethyl]trimethylammonium chloride**

[2-(methacryloyloxy)ethyl]trimethylammonium chloride (TMAEC) is a bit viscous colourless liquid. It is a weak poly-base that is soluble in aqueous media because of protonation of its tertiary amine group (Figure 23).
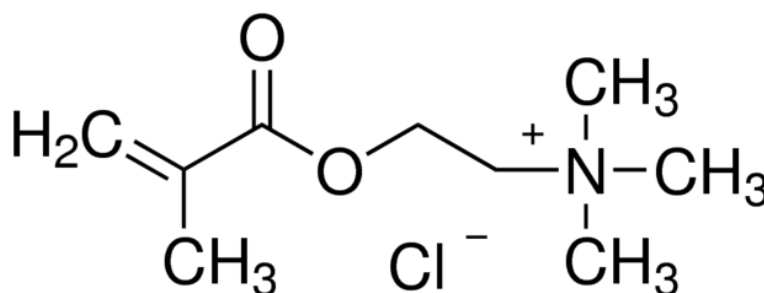
Figure 23: [2-(Methacryloyloxy)ethyl]trimethylammonium chloride.

- **Lauryl acrylate**

Lauryl acrylate, also known as dodecyl acrylate (LA), is a low viscous and low toxic monomer (Figure 24).
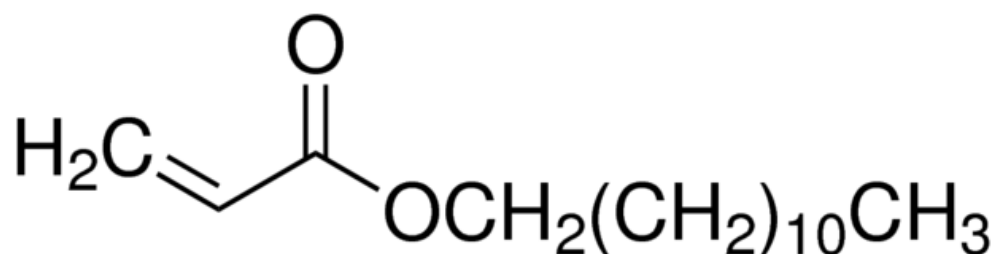
Figure 24: Lauryl acrylate.

In addition, it is also extremely hydrophobic due to the long pendant aliphatic chain and it is a very reactive acrylate. For this reasons, LA can be used to prepare several copolymers with a lot of other monomers such as methacrylic acid and its salts, its amides and its esters, and with methacrylates, acrylonitrile, maleic acid esters, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, butadiene, unsaturated polyesters and drying oils. This information can be found in the technical data sheet supplied by BASF.

- **Hydroxyethyl acrylate**

Hydroxyethyl acrylate, HEA, is a colorless liquid organic compound (Figure 25).
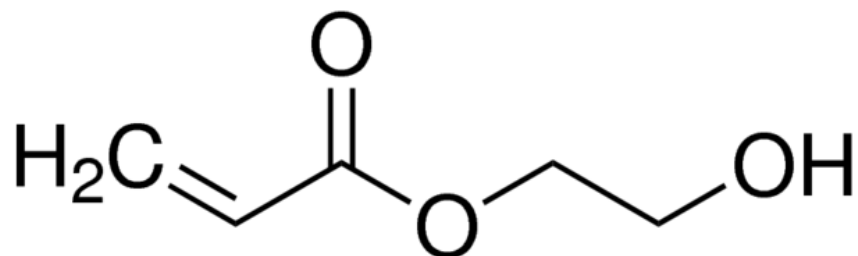
Figure 25: Hydroxyethyl acrylate.

It has a melting point of -60°C and a boiling temperature of 210°C. It is soluble in water and it polymerizes very easily with high exothermicity.

- **Dodecyl methacrylate**

Dodecyl methacrylate, also called Lauryl methacrylate (LMA), is a water insoluble, low volatile, monofunctional methacrylate monomer with a long, hydrophobic side chain that polymerize much less readily than the corresponding ordinary acrylates (Figure 26).
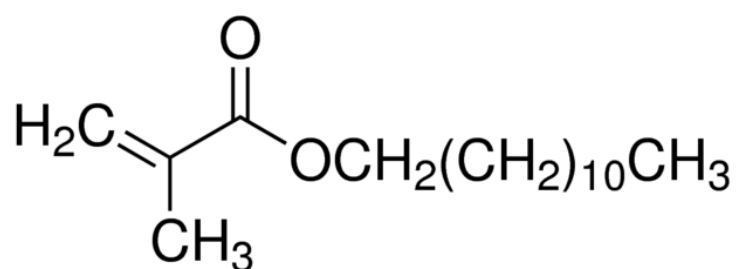
Figure 26: Dodecyl methacrylate.

It can be used to impart many properties to the polymers, like adhesion, low shrinkage, flexibility, water resistance and improved impact strength. Table 4 lists the monomers that have been adopted in this work, specifying the supplier, the purity, the molecular weight and the physical state.

Table 4: Monomers.

Monomers	Producers	Purity	Molecular Weight [Da]	Physical state
LA	BASF	90%	240	Liquid
PEGMA	Aldrich	99%	300-500	Liquid
TMAEC	Aldrich	80%	208	Liquid
HEA	Aldrich	96%	116	Liquid
LMA	Aldrich	96%	254	Liquid

2.1.2   Crosslinking Agents

Crosslinking agents are molecules that have at least two functional groups which permit the crosslinking of two molecular chains. A cross-link is a bond that links one polymer chain to another. They can be covalent or ionic bonds. When polymer chains are linked together by crosslinking, they lose some of their abilities to move as individual polymer chains and they also change their proprieties. When crosslinking agents are added, the flexibility typically decreases while the hardness and the melting point increases. The resulting modification of mechanical properties strongly depends on the cross-link density. The crosslinking agents used in this work are ethylene glycol dimethacrylate (EGDMA) and poly(ethylene glycol) diacrylate (pEGDA). The proprieties of the crosslinking agents are reported in Table 5.

- **Ethylene glycol dimethacrylate**

Ethylene glycol dimethacrylate EGDMA is a diester formed by condensation of two equivalents of methacrylic acid and one equivalent of ethylene glycol (Figure 27).
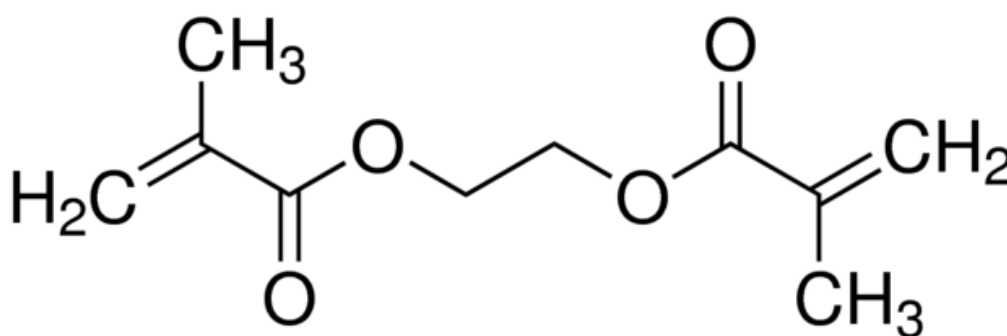
Figure 27: Ethylene Glycol Dimethyl Acrylate.

It has a boiling temperature of 100°C. EGDMA is a reactive resin and can be used as a functional monomer and a crosslinking agent in polymer production (free radical copolymer crosslinking reactions) according to the technical data sheet.

- **Poly(EGDA)**

Poly(ethylene glycol) diacrylate, (pEGDA), is a linear homobifunctional acrylate, used as crosslinking agent in the polymerization reactions (Figure 28).
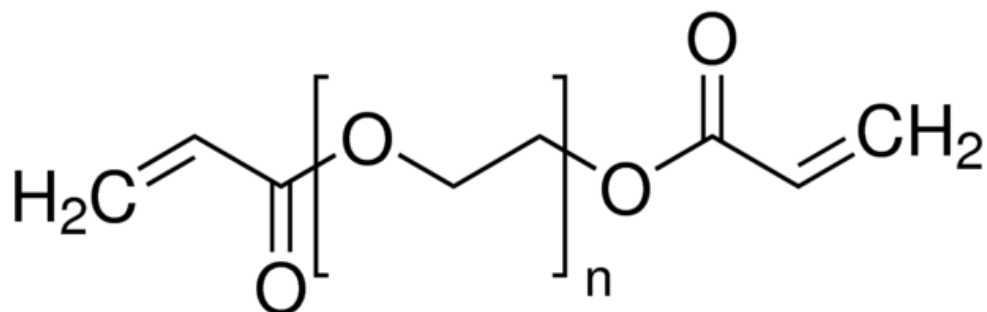
Figure 28: Poly(ethylene glycol) diacrylate.

It affects the chemical resistance, the flexibility, the adhesion, the low shrinkage, the abrasion resistance and the impact strength of the final polymer.

Table 5: Crosslinking agents.

Compounds	Producers	Purity	Molecular Weight [Da]	Physical state
EGDMA	Aldrich	98%	198	Liquid
pEGDA	Aldrich	99%	575	Liquid

2.1.3 Initiators

Initiation is the first step of any polymerization process. During initiation, an active center is generated and then a polymer chain can propagate. Initiation has two steps: in the first one, one or two radicals are produced from one single molecule of initiator, while in the second, radicals are added to the monomer units. There are several ways to generate radicals from the initiator molecules. In fact, it can occur after the thermal decomposition of the initiator or a redox reaction

among two species. In the thermal decomposition, the initiator is heated up until a bond is homolytically cleaved, producing two radicals (Figure 29).
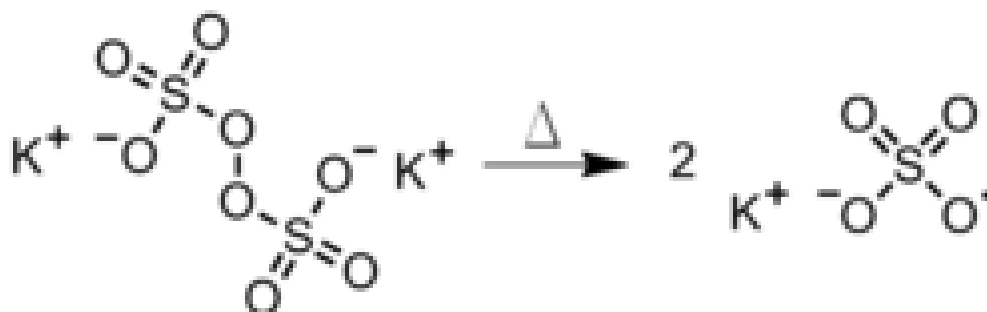
Figure 29: Example of thermal decomposition of potassium persulfate.

This method is most often used with organic peroxides or azo-compounds, for instance benzoyl peroxide or azobisisobutyronitrile. In the redox initiation, there is a couple of compounds that reacts through a redox reaction. In fact, it is necessary to have an oxidant reactant and a reducing agent at the same time. An example is given by the reaction between hydrogen peroxide and iron ion (Figure 30).

Figure 30: Example of redox initiation.

The initiators tested in this work are both hydrophilic and hydrophobic. Hydrogen peroxide (H_2O_2), iron (II) sulfate ($FeSO_4$), ammonium persulfate (APS), potassium persulfate (KPS) and 2,2′-azobis(2-methylpropionamidine) dihydrochloride (AAPH) are the water soluble initiators. Benzoyl peroxide (BPO) is the only one tested as lipophilic initiator.

- **Hydrogen peroxide**

Hydrogen peroxide (H_2O_2) is a colorless liquid, slightly more viscous than water. It is the simplest peroxide, a compound with an oxygen–oxygen single bond (Figure 31).
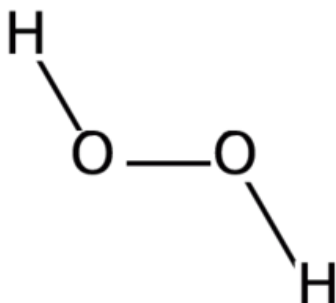
Figure 31: Hydrogen peroxide.

It is used as an oxidizer bleaching agent and disinfectant. H_2O_2 is unstable and slowly decomposes in the presence of base or a catalyst. Because of its instability, H_2O_2 is typically stored with a stabilizer in an aqueous solution. In this work, solutions of 10% and 35% of H_2O_2 in water are used.

- **Ammonium persulfate**

Ammonium persulfate (APS) is a colorless inorganic salt that is highly soluble in water. It is a strong oxidizing agent that is used in polymer chemistry, as an etchant, and as a cleaning and bleaching agent (Figure 32).
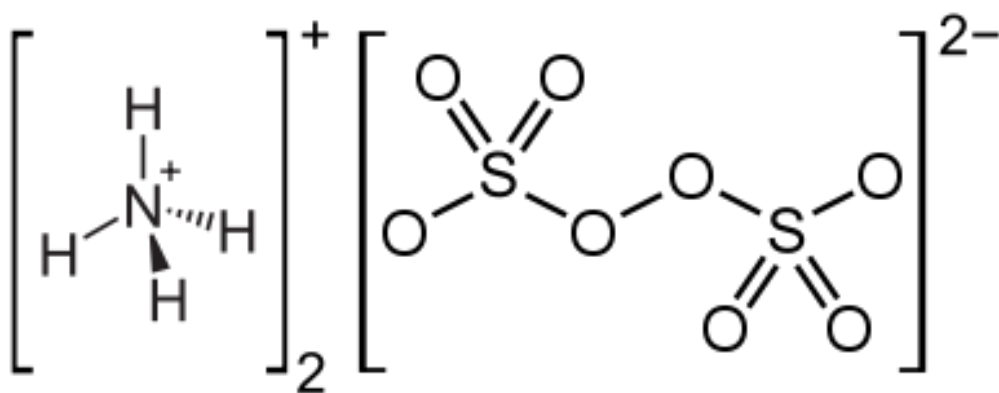
Figure 32: Ammonium persulfate.

- **Potassium persulfate**

Potassium persulfate (KPS) is a white powdered solid sparingly soluble in water, especially at low temperature (Figure 33).
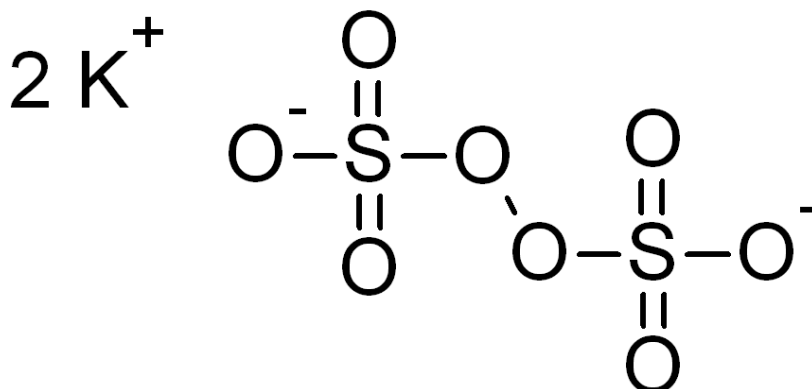
Figure 33: Potassium persulfate.

This salt is a powerful oxidant commonly used to initiate polymerizations.

- **Iron sulfate (II)**

Iron sulfate ($FeSO_4$) denotes a range of salts with the formula $FeSO_4 \cdot x H_2O$ (Figure 34).
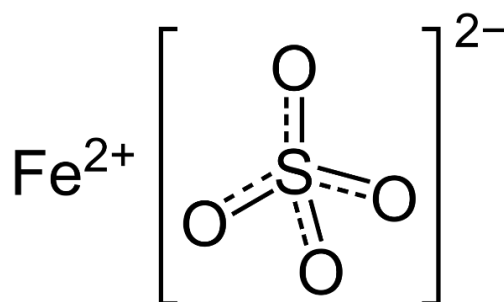
Figure 34: Iron sulfate.

In this work, heptahydrate iron sulfate is used. It is presented in form of solid crystal and it is soluble in water. Ferrous sulfate is mainly used as a precursor to other iron compounds and as reducing agent.

- **2,2′-Azobis(2-methylpropionamidine) dihydrochloride**

2,2′-Azobis(2-methylpropionamidine) dihydrochloride (AAPH) is a free radical-generating azo-compound. It is gaining prominence as a model oxidant for its ability to initiate oxidation reactions via both nucleophilic and free radical mechanisms (Figure 35).
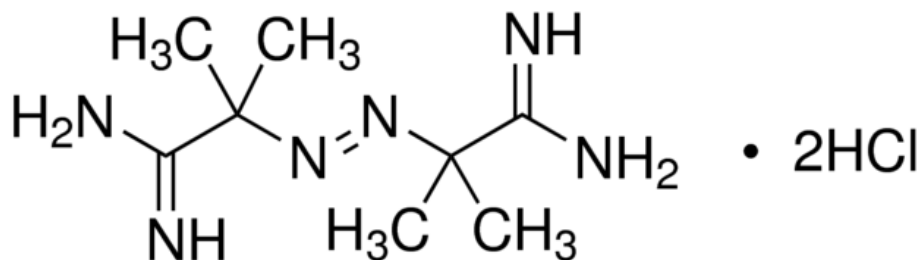
Figure 35: 2,2′-Azobis(2-methylpropionamidine) dihydrochloride.

- **Benzoyl peroxide**

Benzoyl peroxide (BPO) consists of two benzoyl groups bridged by a peroxide link (Figure 36).
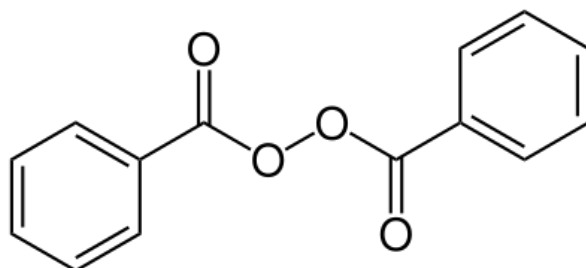
Figure 36: Benzoyl peroxide.

It is one of the most important organic peroxides in terms of applications and the scale of its production. It is used as a radical initiator to induce polymerizations. Other major applications include its antiseptic and bleaching properties. It is a solid powder and it is soluble in organic solvent. As an example, its decomposition reaction is showed in Figure 37.
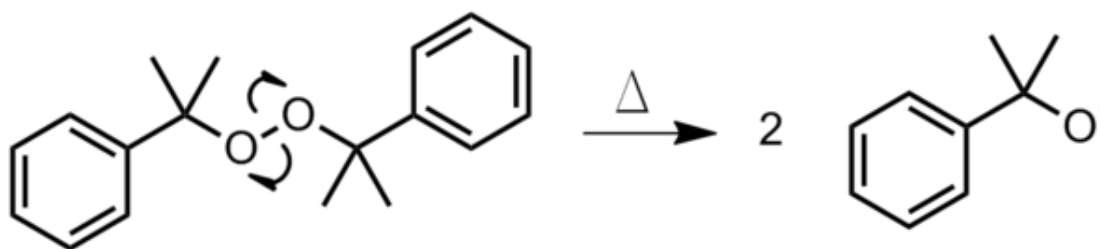
Figure 37: Decomposition reaction of BPO.

Table 6 summarizes all the different initiators tested in this work.

Table 6: List of initiators adopted to generate radicals.

Compounds	Producers	Purity	Molecular Weight [Da]	Physical state
BPO	Aldrich	70%	242.23	Solid
H_2O_2	Aldrich	30%	34.01	Liquid
APS	Aldrich	99%	228.20	Solid
KPS	Aldrich	99%	270.32	Solid
$FeSO_4$	Aldrich	99%	278.01	Solid
AAPH	Waco	99%	271.19	Liquid

2.1.4   Surfactants

The name surfactant stand for surface active agent for the ability to reduce the surface tension between two immiscible phases. [69]

This compound is an amphiphilic molecules: it has both a lipophilic (tail) and a hydrophilic (head) part (Figure 31(a)).
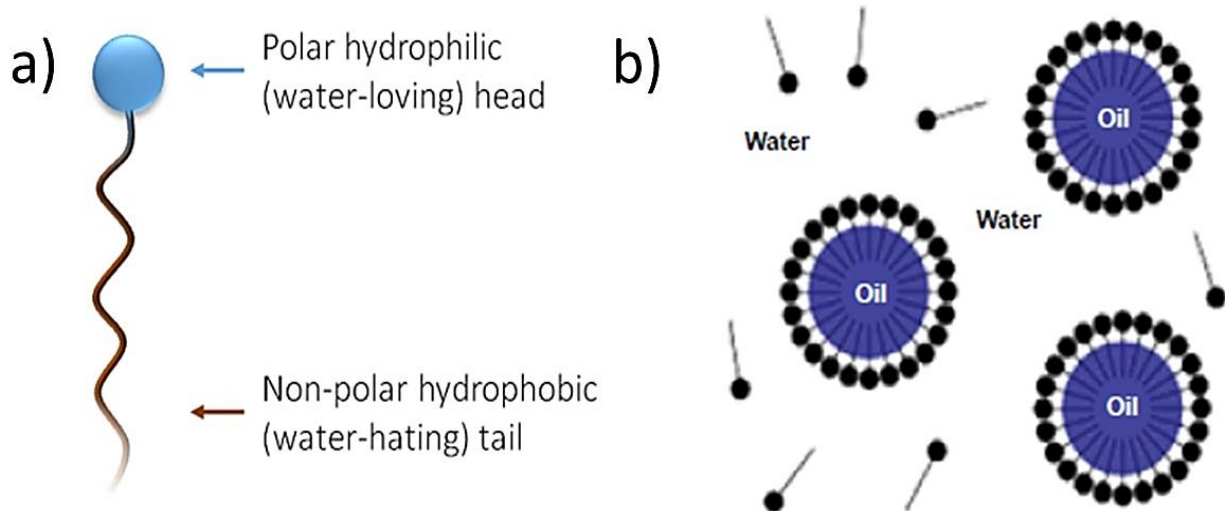
Figure 38: a) Surfactant structure, b) Surfactants arrangement around the oil drops.

It is very important in the emulsion processes, where there are the oil and the water phases, because of the steric repulsion that avoid the coalescence of the droplets. More in detail, the surfactant plays the role of a stabilizer on the drop surface, bringing to a reduction of surface area that otherwise expands leading to an unstable system with consequent separation of the two fluids. [8] According to their structure, surfactants exhibit a very strong tendency to migrate to interfaces and to orientate themselves in a way in which the polar group (head) lies in water and apolar group (tail) is placed out of it, eventually in oil. Figure 38(b) shows the stabilization of the oil drops by surfactants that cover the surfaces with the tail linked to the oil drops and the head linked to the water phase. There are different families of surfactants, as shown in Figure 39: nonionic, anionic, cationic and zwitterionic.
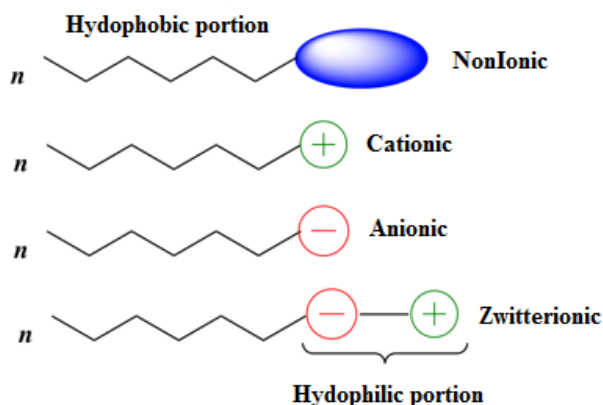
Figure 39: Classification of surfactants.

In this work, a range of mild nonionic surfactants have been tested. According to the absence of charges, they have less interaction with the charge of the monomer, resulting in more stability, formulating flexibility and wider compatibility. They are stable in mild acids, alkalis and electrolytes. As mentioned before an important parameter for the selection of the surfactant is hydrophilic-lipophilic balance (HLB). It is possible to establish the right value of HLB in order to develop a stable emulsion, according to the type of reactants involved.

In this work, two different surfactants have been adopted, Tween 80 and Span 80.

- **Sorbitan monooleate - Span80**

Sorbitan monooleate (Span80) is produced by the dehydration of sorbitol. Its structure is reported in Figure 40.
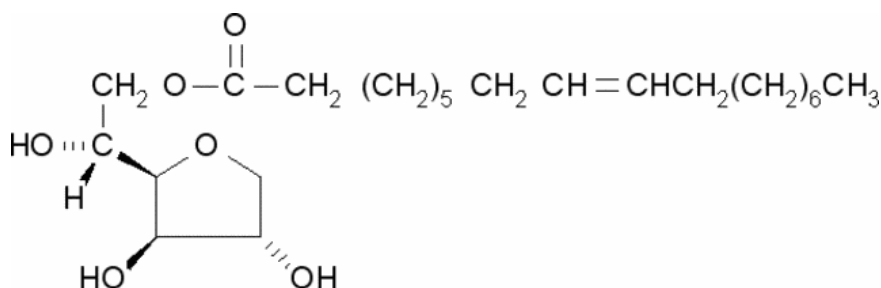
Figure 40: Sorbitan Monooleate.

Span 80 has an HLB of 4.3.

- **Polyethylene glycol sorbitan monooleate - Tween80**

Polyethylene glycol sorbitan monooleate (Tween80) is simply ethoxylated Span80 (Figure 41).
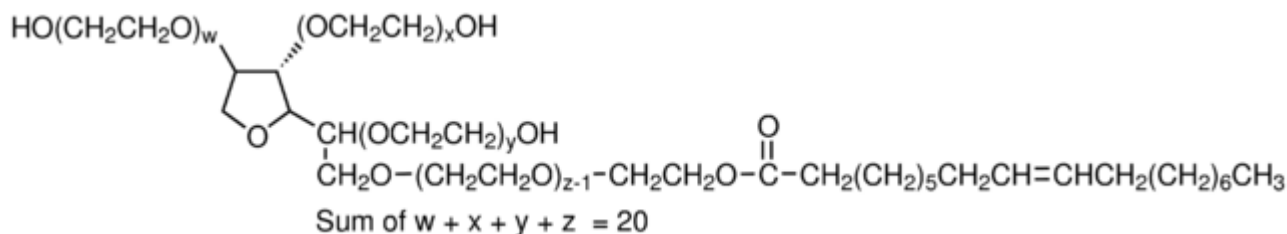
Figure 41: Polyethylene glycol sorbitan monooleate.

Tween80 is hydrophilic, so it is soluble in water and dilute solutions of electrolytes.

Its HLB is 15.

Table 7 shows the two surfactants used in this work with their properties.

Table 7: Surfactants

Compounds	Producers	Purity	HLB	Physical state
Span80	Aldrich	99%	4.3	Liquid
Tween80	Aldrich	99%	15	Liquid

2.1.5   Solvent

All the formulations prepared in this work involve a solvent. The use of solvents in a formulation has several functions. It allows to easily transport the reagents, so its solubility, especially if they are solid. In addition, it can be very useful in the exothermic reaction because, with its evaporation, can remove the heat from the reaction. The solvent mainly used in this work is deionized water. It is able to dissolve hydrophilic initiators in the oil-based mixture and it is necessary to prepare the emulsions. In this work oil-based solvents are not used for their safety concerns and toxicity. In the section 2.5, it is reported the procedure adopted to produce emulsion without having oily solvents.

2.2 Methods and Experiments

In this section all the recipes and the procedures to obtain the final materials are described.

2.2.1   Requirements and Operative Conditions

The formulations are specialties chemicals and are sold on "what they can do": it means that are sold according to their specific functions. After some attempts reported in previous works, this Thesis focuses on the possibility to exploit bicomponent mixture solutions. A bicomponent formulation is composed by two different mixtures that must be in contact to perform the wanted function. In this case the two mixtures must be pumped, using some tubes or metallic rods directly in the wanted zone; once they are in contact and at the right temperature, they must be able to form a solid after few time. In laboratory attempts an average temperature of 60°C is assumed in order to prevent polymerization to occur spontaneously. It is studied the behaviour of different formulation. The requirement that the product must satisfied are:

- The final polymer must be solid and with good mechanical resistance, especially in compression.
- The reaction must rapidly occur, at most in 30 minutes.
- The reaction mechanism can be a FRP or a frontal polymerization. The last one has the advantage to avoid problems related to the inefficient mixing. In fact, in this case, when the two mixtures touch themselves just in one point occurs the complete polymerization of the system. In fact, when the two mixtures are in contact, the redox couple starts the reaction that generates the heat wave which trigger the decomposition of the initiator and the propagation of the front.
- The two mixtures must be stable in storage condition.

- The whole procedure and each components use in the final formulation must be under safe condition (temperature, reagents, pressure)

Three different pathway are selected to get the right formulation and product: FRP, FP and emulsions.

2.2.2   Selection of the Materials

To find out the best formulation, a selection of the most suitable materials is necessary in order to respect the previous needs and requirements. The strategies used for each pathways are presented below

2.3 Pathway 1: FRP

In this case, the idea is to investigate more in detail the differences that are obtained in the final polymer changing one of three main players at time; it means the understanding of the influence on the final material of the monomer, the crosslinking agent and the initiator. For this reason, numerous reactions tests with hydrophilic formulations have been made. Before showing the results, the procedure consist in two mixtures: the first one, called mixture A contains the monomers, the crosslinking agents and, in case of FP, an initiator; while the second one is made up of the initiator and the solvent (Mixture B). From a safety point of view it is better to avoid to put in the same mixture initiator and monomers from the beginning. The two mixtures were mixed together and the reactions occurred in glass vials placed in the stove at 60°C. The reactions were tested also at 25°C to be sure that polymerization does not occur either when the mixture A and B where put together and for the mixtures A and B took separately. Tests were monitored at following

time intervals: time 0, the beginning, 30 minutes, 1, 2, 4, 24 and 48 hours after the addition of mixture B in A. From previous works, a basic formulation has been obtained (Table 8).

Table 8: Starting formulation.

All the percentages are in weight. The percentage of crosslinking agent, solvent and initiators are referred to the quantity of monomer; Y is linked to the initiator used.

Mixture A		Mixture B	
Monomer [g]	Crosslinking Agent [g]	Initiator [g]	Solvent (H_2O)[g]
X	30%X	5%X	Y

This composition was the best formulation developed that worked well even changing the monomer. After the preparation of the sample, so the addition of the two solutions, it has been shacked for few seconds and then let it react. All the considerations that have been made on consistency were performed by testing the final material with a spatula. The two mixtures A and B are always stable both at 25° and at 60° C. For each samples, four mixtures A and four mixtures B are prepared: two of them are used for stability tests (mixtures alone) at 25°C and 60°C, while the others are mixed together putting mixture B into A to check their reactivity at both temperatures.

2.3.1 Evaluation of the solubility of the initiators

Before starting the experiments with the combination of different components, it is mandatory to evaluate the solubility of the initiators in water, so the amount of solvent that needs to be added to the reactive system to dissolve a precise amount of initiator. By weighing the same amount of

initiator and adding water in small doses, has been identified the minimum quantity of water necessary to dissolve the different initiators. In order to have a more reliable understanding on the solubility values, three replicates for each initiators were prepared and the results are reported in Table 9.

Table 9: Solubility tests for the water soluble initiators

All the measurement were performed at room temperature with manual stirring for 10 seconds

Initiator	Solubility
KPS	0.061g/g
APS	0.140g/g
AAPH	0.233g/g

AAPH shows the highest solubility in water, on the contrary KPS has a solubility lower than 100 mg/ml. Once the solubility of the water soluble initiators it is known, it is ease to evaluate the correspondent amount of water (Y in table 8, always a % of monomer) to be added to the mixture B, considering the quantity of monomer X used in the mixture A (the initiator is the 5% of the monomer):

$$Y_i = \left(\frac{5X}{solubility_i}\right)\% \quad ; \quad \text{i=different initiators}$$

2.3.2 Optimization of the formulation

In order to find out the best formulation in term of solid material with specific mechanical properties, different monomers have been tested using the different initiators, taking into account their solubility, as previously studied.

2.3.3   TMAEC as a monomer

In this set of experiments, TMAEC has been used as the only monomer in the mixture A for all the samples. At the same time, the quantity of crosslinking agent EGDMA is changed together with the kind of initiator and the amount of solvent in mixture B, according to its solubility (Table 9). In each reaction, only one component at time has been varied, keeping constant all the others. This is very important to understand the influence of each compound in the final properties of the materials. All the different experiments involved in the optimization using TMAEC as monomer are reported in Table 10.

Table 10: Optimization study using TMAEC as a monomer.

All the percentages are in weight [g]. The percentages of crosslinking agent and initiators are referred to the quantity of monomer, while the solvent quantity Y depends on the solubility of the selected initiator

	Mixture A		Mixture B			
Sample	TMAEC	EGDMA	KPS	AAPH	APS	H_2O
R1	X	-	5%X	-	-	Y
R2	X	60%X	5%X	-	-	Y
R3	X	30%X	5%X	-	-	Y
R4	X	30%X	-	5%X	-	Y
R5	X	30%X	-	-	5%X	Y

These reactions were all performed both at 25°C and at 60°C to test the reactivity of the bicomponent mixture A + B. At room temperature, all the samples were stable and it was not possible to appreciate any changes of the system. On the contrary, the results of the reactivity at 60°C showed some significant variations inside the systems. In fact, it was possible to see the formation of a gel in all the samples. It was not possible to appreciate the influence of the EGDMA

in the samples R1, R2 and R3 because the final consistency was more or less the same. The worst samples is R5, the one with APS as initiator. In fact, even after 4 hours, there was still some liquid over the gel. For this reason, APS was not anymore considered to be part of the final formulation.

2.3.4 PEGMA300 and PEGMA500 as monomers

A similar procedure is adopted using PEGMA 300 and 500 instead of TMAEC, and using different amount of EGDMA. In all these reaction KPS as initiator is used (Table 11).

Table 11: Tests with monomer PEGMA 300 and PEGMA 500.

All the percentages are in weight [g]. The percentages of crosslinking agent and initiators are referred to the quantity of monomer, while the solvent quantity Y depends on the solubility of the selected initiator

	Mixture A			Mixture B	
Sample	PEGMA 300	PEGMA 500	EGDMA	KPS	H_2O
R6	-	X	30%X	5%X	Y
R7	-	X	45%X	5%X	Y
R8	X	-	30%X	5%X	Y
R9	X	-	45%X	5%X	Y

PEGMA 500 has a longer chain than PEGMA 300 so the aim is to investigate how this property can affect the behavior of the final polymer. In any case, it is expected that the resulting polymer is harder than the one obtained using TMAEC as a monomer, with which the result was a gel. Also in this case the single mixtures are always stable at both temperatures, 25°C and 60°C. In addition, no

reaction occurs at 25°C for the first hours (after a day the A + B mixture polymerizes). All the samples at 60°C react within the time span desired of 1 hour and give a hard and compact, white polymer with no liquid phase. In particular, samples R6 and R8 show the best result in term of hardness of the final materials. For this reason they were adopted as starting point for further formulation changes.

2.3.5   Combination of PEGMA 300 and Lauryl Acrylate

Starting from the information collected from the previous tests (Sections 2.3.3 and 2.3.4), the following three experiments were performed by adding different amount of PEGMA 300 and LA in order to try to obtain a polymer with the desired mechanical properties, that it is still able to be formed in the required time frame (30 minutes-1 hour). In fact, LA is an acrylate so it reacts earlier in the system, but it gives a softer polymer; on the contrary, PEGMA 300, being a methacrylate, gives a hard solid but in a longer time. All the experiments are reported in Table 12. The mixture B is the same of R8 in Table 11, while the mixture A changes.

Table 12: Tests of monomer mixture A.

All the percentages are in weight [g]. The total quantity of monomers is always X. The percentages of single monomers are referred to the total quantity of monomer, instead the percentages of crosslinking agent are referred to the quantity of monomer.

	Mixture A			
Sample	TMAEC	PEGMA 300	LA	EGDMA
R10	-	80%X	20%X	30%X
R11	10%X	70%X	20%X	30%X
R12	10%X	70%X	20%X	15%X

The idea was to use only PEGMA 300 and LA, but the reaction is too fast, so TMAEC was added as a sort of diluent, but the resulting material still had liquid on it. Therefore, the amount of EGDMA was reduced, no more liquid is obtained but the consistency is not good enough and the polymer is fragmented. To conclude, R6 and R8 are still the most promising result.

2.3.6   AAPH initiator

To better investigate the effect of AAPH as initiator, two more tests have been performed (Table 13). Samples R16 and R17 are the same of the previous R6 and R8 (Table 11), but in this case AAPH takes places of KPS.

Table 13: Tests with PEGMA 300, PEGMA 500 and AAPH.

All the percentages are in weight [g]. The percentages of crosslinking agent, solvent and initiators are referred to the quantity of monomer, while the solvent quantity Y depends on the solubility of the selected initiator

	Mixture A			Mixture B	
Sample	PEGMA 500	PEGMA 300	EGDMA	AAPH	H_2O
R16	X	-	30%X	5%X	Y
R17	-	X	30%X	5%X	Y

The results obtained are very similar to the previous ones. It means there is no significant difference among the two kinds of initiators.

2.3.7   Effect of different crosslinking agents: EGDMA and pEGDA

Crosslinking agents are used to increase the crosslink between the polymeric chains in order to increase the mechanical resistance of the three-dimensional solid polymer. The principal needs that

a crosslinking agent must fulfill are the miscibility with the monomers and the increase of mechanical resistances. For this reason, two sets of three reactions have been prepared using KPS and AAPH as initiators, and two different crosslinking agents have been tested, EGDMA and pEGDA (Table 14).

Table 14: Tests with different crosslinking agents and HEA in the mixture A.

All the percentages are in weight [g]. The percentages of crosslinking agent and initiators are referred to the quantity of monomer.

Sample	TMAEC	PEGMA 300	HEA	pEGDA	EGDMA
R13	-	X	30%X	-	-
R14	-	X	-	30%X	-
R15	10%X	90%X	-	-	30%X
R19	-	X	30%X	-	-
R20	-	X	-	30%X	-
R21	10%X	90%X	-	-	30%X

The quantity of crosslinking agent affects the characteristics of solid block. It is worth to note that the mechanical proprieties of the final products reach a maximum with a ratio equals to 30% of monomer. For lower of higher values, the solid does not satisfy the requirements. Reactions R13 and R14 are the same of R8 (that give good results), so it was interesting to investigate which changes occurs by varying the kind of crosslinking agent (pEGDA) and providing another monomer, HEA, instead (in this case the formulation is different: no crosslinking agent but a monomer amount of 130%X). Moreover, comparing the two sets, the difference between AAPH and KPS appears more clearly, with the second that seems to show the best results. Mixture B is the same of R8 for reactions from R13 to R15, and equal to R16 for the other three.

2.4 Pathway 2: FP

In this case the possibility to use the frontal polymerization to develop a novel formulation have been deeply studied. As previously explained in Section 1.4, frontal polymerization is a particular free radical polymerization in which the initiation step is due to a redox reaction. The reactive system is still made up of two mixtures, mixture A and mixture B, having the reducing and oxidant agent dissolved separately. The reaction can occur only when the two mixtures are put in contact, so when the redox reaction among the couple of initiator can happen and produce the heat necessary to develop the front of the reaction. Compared to Pathway 1, related to the use of the classic free radical polymerization, it is not a thermal initiation to produce radicals, but the generation of them occurs after the redox reaction. It means a greater control on the reaction because the beginning of the reaction does not depend on the external temperature. The same optimization study of the Pathway 1 has been performed with a special attention on the selection of the right couple of initiators.

2.4.1   Operative Procedures

For each samples, four mixtures A, four mixtures B were prepared: two of them were used for stability test (only mixtures alone) at 25°C and 60°C; the others were mixed together, by adding mixture B in mixture A to check the reactivity at both temperatures. Mixture A is made up of the selected crosslinking agent (EGDMA), the monomer and the H_2O_2 solution (Mixture C), in this order of preparation. To better mix the solution is recommended to stir/shake the vials for 30 seconds to ensure a good dissolution and intimate mixing among all the components. Mixture B is composed by $FeSO_4$, as the reducing agent, dissolved in water. Then, the $FeSO_4$ solution is added to the mixture A and the final solution is thoroughly mixed. During this step, it is possible to notice the change of the color from colorless to light yellow, during the mixing. Then, the resulting system, without stirring, is put in stove at 60°C.

2.4.2   Selection of the couple of initiators

The selection is based on the solubility of each initiator in the mixture of the monomer and crosslinking agent and in water, the chosen solvent. After this step, it is necessary to check if the couple of initiator is compatible with the requirements of the time and temperature. A list of possible different combinations of water soluble initiators for the hydrophilic formulation is available from previous work and it is reported in Table 15.

Table 15: Possible couple of initiators.

Initiator in mixture B	Initiator in mixture A
APS	FeSO$_4$
KPS	FeSO$_4$
FeSO$_4$	H$_2$O$_2$

As mentioned before, mixture A contains also the monomer and the crosslinking agent. In order to avoid safety concern, it is better to keep separated the oxidant initiator and the reactive compounds. For this reason, the selected couple of initiator is the last one, where the reducing agent, the iron sulphate salt solution (Mixture B) is added to the mixture A that contains the monomers, the crosslinking agent and the oxidant solution (Mixture C).

2.4.3   Formulations tested for pathway 2

Once the couple of initiator was decided, the choice of the right monomers and crosslinking agent follows the same optimization experiments showed before for Pathway 1 (Section 2.3.2). In particular, it has been considered the possibility to use a mixture of PEGMA500 and TMAEC, and EGDMA as crosslinking agent. The possibility to obtain a hard and compact material was studied by 2 mixing steps:

- H_2O_2 solution added into the mixture of the monomers.

- $FeSO_4$ aqueous solution added into the monomer mixture containing H_2O_2.

Table 16 shows the tests done for the determination of the optimal quantity of initiators, even changing the amounts of monomers and crosslinking agents. It is worth to note that in this case, there is also a mixture C, made up of the H_2O_2 solution, together with mixture A (with the monomer and crosslinking agent) and mixture B composed of the reducing agent and the solvent. In particular, mixture C is first mixed in A and then mixture B is added.

Table 16: Tests to optimize initiators.

All the percentages are in weight [g]. The percentages of crosslinking agent and initiators are referred to the quantity of monomer, while the solvent quantity Y depends on the solubility of the selected initiator. The percentages of H_2O in mixture C depends on the desired concentration of the H_2O_2 solution.

	Mixture A			Mixture C		Mixture B	
Sample	PEGMA 500	TMAEC	EGDMA	H_2O_2 [37%v]	H_2O	$FeSO_4$	H_2O
FP1	X	-	40%X	5%X	9.35%X	5%X	Y
FP2	-	X	60%X	5%X	9.35%X	5%X	Y
FP3	80%X	20%X	30%X	5%X	9.35%X	5%X	Y
FP4	X	-	40%X	3%X	9.35%X	3%X	Y
FP5	X	-	40%X	3%X	26%X	3%X	Y
FP6	-	X	60%X	3%X	26%X	3%X	Y
FP7	80%X	20%X	30%X	3%X	26%X	3%X	Y

The amount of the two initiators is always the same so is first necessary to evaluate their solubility in the monomers mixtures and in the solvent. The starting H_2O_2 solution is at 37%v and is used diluted both at 35% and at 10% so the first case required less water content than the second one (9.35% instead of 26% always respect to the total monomers amount). The Y in formulation is instead evaluated from the solubility in water of $FeSO_4$ that is 0.28 g/g. The increase in the quantity of initiators brings a decrease in the time of reaction. For this reason, stability tests must be performed in order to evaluate the right amount of initiator in mixture A (and so in C) that ensures stability at the condition at which the formulation is stored, and no reaction until 60°C.

2.5 Pathway 3: Emulsions

The previous pathways 1 and 2 are related to a chemical transformation of the reactants, because both of them are able to produce a polymer with the desired characteristics. However, all the formulations that are explained and tested before are valid only for hydrophilic mixtures. This is mainly due to the fact that the combination of lipophilic initiators for the redox initiation, like benzoyl peroxide (BPO) and N,N-dimethylaniline (DMA) have some safety and toxic concerns. A possible strategy to overcome this problem is the exploitation and the study of emulsion system. In this case, several lipophilic mixtures A, with monomers and crosslinking agent, have been tested with the hydrophilic mixture B already adopted in the previous solutions. The first point is to test the stability of the emulsion, with the use of surfactants, and then its reactivity.

2.5.1 Stability of the emulsions: operative procedures

Oily phase is prepared starting from the two surfactants, Span 80 and Tween 80. Then the monomer and the crosslinking agent are added and mixed together. To prepare the aqueous phase (mixture B), the initiator, according to the correct solubility values, is put in the vial with water and the solution

is mixed until reaching complete dissolution. At the end, pre-emulsions are prepared by adding the mixture B to the oily phase under constant stirring kept at 800 rpm. Then, the prepared pre-emulsions are stirred at high speed, about 5000rpm, due to the use of a sonicator for 20 minutes. All emulsions are prepared at room temperature and the stability has been checked at different time from 0 to 48 hours in order to estimate their stability.

2.5.2   Reactivity of emulsions

As a starting point, formulation of the white diesel is chosen and the percentages of its components are reported in Table 17.

Table 17: White Diesel formulation.

Gasoline [g]	Water [g]	Surfactant [g]
88%	10.3%	1.7%

In this work, oily phase corresponds to the mixture A, while water phase to the mixture B. Surfactants are instead Tween 80, dissolved in the mixture B, while Span 80 is blended in A. During the attempts, it was tried to vary both the percentages of water and oily phase, the amount of surfactants, and the value of HLB (changing the relative ratio between Tween80 and Span80), so as to obtain an emulsion as stable as possible.

2.5.3   HLB: Griffin's method

HLB is a measure of the lipophilicity or hydrophilicity of a compound. It can be calculated in different ways, but in this specific case, the Griffin's method is adopted Griffin's method is based

on a scale from 0 to 20 and represents the strength of the polar portion (hence, hydrophilic portion) of the molecule (red part in Figure 42). [70]
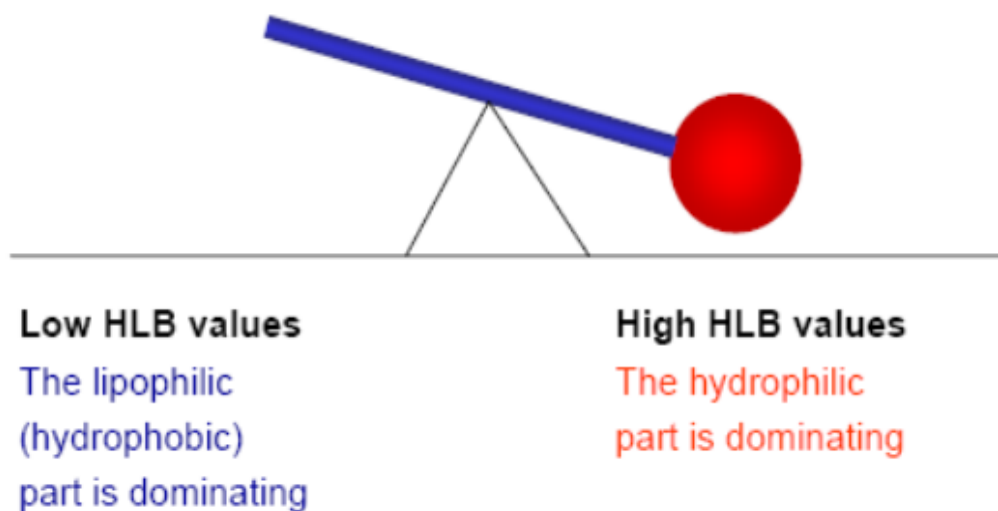
Figure 42: Representation of the HBL of a surfactant.

The theoretically value can be determined with this formula: $HLB=20(Mh*M)$

Where Mh stands for the molecular mass of the hydrophilic portion of the molecule, while M represent the molecular mass of the whole molecule. So, the HLB value is calculated as the ratio between the hydrophilic part and the whole molecule. A value of 0 correspond a molecule which is totally lipophilic, while a value of 20 correspond to a molecule completely hydrophilic. The Griffin's method was initially developed for non-ionic surfactants, then it was extended also to ionic surfactants, capable to have higher value of HLB, due to their ionic properties. Molecules with HLB higher than 10 are hydrophilic and more soluble in water, on the contrary, molecules with HLB lower than 10 are more soluble in the organic phase.

A general classification of the surfactants according to their HLB value is reported in Table 18.

Table 18 : HLB values and expected properties of the surfactants.

HLB Value	Expected properties
From 0 to 3	Antifoaming agent
From 4 to 6	W/O emulsifier
From 7 to 9	Wetting agent
From 8 to 18	O/W emulsifier
From 13 to 15	Typical of detergents
From 10 to 18	Solubiliser of hydrotrope

It is well established that a combination of a high and low HLB emulsifier is often more effective than the use of a single one. Blend of Span 80 and Tween 80 can therefore be used to develop stable emulsions. [71] The first step is to understand the most suitable HLB value for considered formulations. Considering two different surfactants A and B, the final HLB value of the mixture can be obtained as shown below:

$$HLB_{mix} = w_A HLB_A + w_B HLB_B$$

HLB$_{mix}$= HLB value of the final mixture

HLB$_A$**, HLB**$_B$= HLB values of the two surfactants, A and B

w_A**,** w_B= mass fraction of surfactant A and B, respectively.

In this way, knowing the total amount of surfactants in the formulation and varying the ratio between Tween80 and Span80, it is possible to obtain all the values of HLB between 4.3 and 15

(HLB values of the pure surfactants), and find the one that better stabilizes the emulsions (Table 19).

Table 19: Variation of HLB values due to the amount of Tween80 and Span80.

Span 80	Tween 80	HLB
100%	-	4.3
95%	5%	4.835
85%	15%	5.905
75%	25%	6.975
50%	50%	9.65
25%	75%	12.325
15%	85%	13.395
5%	95%	14.465
-	100%	15

2.5.4   Preparation technology

It is worth to note that in the case of the emulsion is very important to take into account also the way used to prepare it. In fact, there are two methods of emulsification: low-energy and high-energy. Only a few examples of low-energy methods are found in the literature. These methods make use of changing the spontaneous curvature of the surfactant forcing a transition from an oil-in-water (O/W) emulsion at low temperatures to a water-in-oil (W/O) emulsion at higher temperatures (phase inversion temperature, PIT). Transition in the spontaneous radius of curvature

can be obtained also by changing (increasing) the water volume fraction. This is the case of emulsion inversion point method, EIP, or catastrophic phase inversion (Figure 43). [72]
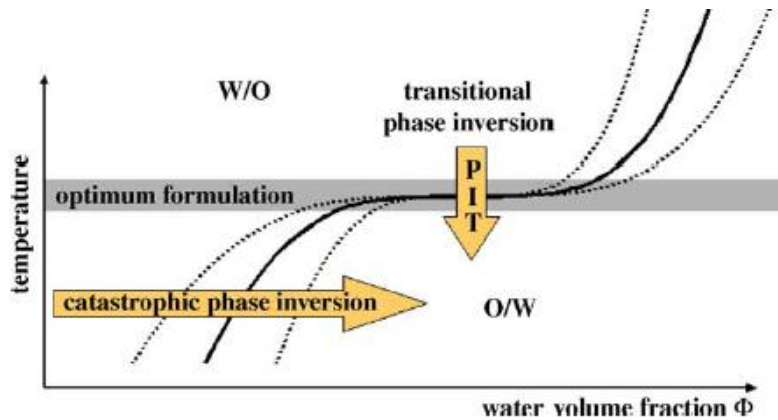
*Figure 43***:** Schematic illustration of both catastrophic and transitional phase inversion for the preparation of finely dispersed O/W emulsions.

The solid black line marks the inversion locus, the dotted lines the hysteresis zone. Within the optimum formulation zone and at the inversion locus, the interfacial tension is minimal. During low-energy emulsification, this ultralow interfacial tension is employed for the formation of finely dispersed droplets, while the final emulsion should be far away from these regions to enhance emulsion stability.

This work is instead focused on the high-energy methods that provide mechanically the deforming forces required to break the droplets into smaller ones, overcoming the Laplace pressure. The high energy input is achieved thanks to the following device: magnetic stirrer, ultrasonic bath and, in particular, the immersion sonicator.

- **Magnetic stirrer**

The magnetic stirrer is a laboratory device that employs a rotating magnetic field to cause a stir bar immersed in a liquid to spin very quickly, thus stirring it (Figure 44). The rotation field is created by a rotating magnet.

Figure 44: Rotation field created by a magnetic stirrer

- **Ultrasonic bath**

This instrument is generally used to dissolve the solute in the solvent. [73] A generator produces high-frequency electrical current that amplifies the mechanical waves in the range of the ultrasounds. The sample is allocated in the water bath in which it is possible to set the operating time and the bath temperature (Figure 45). It is worth to note that the bath temperature is not constant due to the absorption of the ultrasound waves by water.

Figure 45: Ultrasonic bath.

- **Immersion sonicator**

The sonicator is used to obtain nanoparticles by producing ultrasound waves that come out from the tip and then propagate inside the solution (Figure 46). [74]

Figure 46: Sonicator ultrasound waves that break the monomer droplet.

The limitations of this device are related to the difficulties for the scale-up. In fact, the device has a poor efficiency to propagate the waves in the solution and so, more the droplets are far away from the sniffer, less they will be affected by ultrasound waves (in this work the volumes of the samples are small enough not to present this kind of problem). Furthermore, the smaller the droplet size, the more energy and/or surfactant is required, making this preparation route unfavorable for industrial applications. Figure 47 shows the devices used, model UP200S supplied by Hielscher. The solution

is in contact with the sonication tip and the production of pressure waves leads to an increase of the solution temperature [73].

Figure 47: Immersion sonicator.

These were the steps initially adopted for the preparation of the samples:

1) Prepare the mixture A with the Span80

2) Prepare the mixture B with the Tween80

3) Add mixture B into A and vigorously shake with a magnetic stirrer until emulsion formation (40 minutes at 850 rpm); if necessary, mix for other 20 minutes with vortex or ultrasonic bath.

This methodology did not work, because the emulsions were not stable. Another procedure with greater energy input, available in previous work, has been adopted. [62, 63]

This time, emulsions were prepared in two steps:

1) Surfactants (Span80 +Tween80) were mixed into the mixture of monomers and crosslinking agent. Then, pre-emulsions were prepared by adding the mixture B under constant stirring at 800 rpm.

2) The prepared pre-emulsions were stirred at high speed (5000rpm) with immersion sonicator for 20 minutes.

All the emulsions were prepared at room temperature and the stability of the emulsions is evaluated over the time with checks at 30 minutes, 1, 2, 4, 24 and 48 hours.

2.5.5 Formulation

The starting point is white diesel (section 2.5.2). Subsequently, the percentages of aqueous phase and surfactants have been modified in order to optimize each component. Monomers and crosslinking agent are the oily phase, composed by a total monomer equals to X and crosslinking agent equals to 30%X. It is so easy to calculate how much aqueous phase and surfactants are needed in relation to the oily phase that is always a fixed quantity. Four formulations were tested and their compositions are shown in Tables 20-23.

Table 20: Formulation 1 on the model of white diesel.

All the percentages are in weight [g]. The total quantity of monomers is always X. The percentages of the other components are referred to the total quantity of monomer. Z is the largest amount of initiator that can be dissolved.

88%		1.7%	10.3%	
Monomers	Crosslinking agent	Surfactants	H_2O	Initiator
X	30%X	2.51%X	15.22%X	Z

Calculations are:

Gasoline phase $= X + 0.3X = 1.3X = 88\%$

Aqueous phase $= \frac{1.3X}{88} * 10.3 = 0.1522X$

Surfactants $= \frac{1.3X}{88} * 1.7 = 0.0251X$

Despite the previous pathways, in this case, the amount of water is not fixed by the solubility of the initiator, but it is determined by the possibility of having an emulsion. In particular, the amount of water is kept constant for each of the 4 different formulations that have been tested. For this reason the final value of initiator is only 1%X for KPS and 3.5%X for AAPH that is more soluble (this two percentage are referred to the white diesel formulation with a water content of 10.3%). Table 19, 20

and 21 report the results coming from the variation of the water amount in the emulsion. In fact, more water means more initiator, but at the same time it involves stability problems for the emulsion. Likewise, the amount of surfactants has been increased with the idea of better stabilizing the emulsion.

Table 21: Formulation 2.

All the percentages are in weight [g]. The total quantity of monomers is always X. The percentages of the other components are referred to the total quantity of monomer. Z is the largest amount of initiator that can be dissolved.

	86.7%		3%		10.3%	
Monomers	Crosslinking agent	Surfactants		H_2O		Initiator
X	30%X	4.5%X		15.45%X		Z

Calculations are:

Gasoline phase = $X + 0.3X = 1.3X = 86.7\%$

Aqueous phase = $\frac{1.3X}{86.7} * 10.3 = 0.1545X$

Surfactants = $\frac{1.3X}{86.7} * 3 = 0.045\text{X}$

Table 22: Formulation 3.

All the percentages are in weight [g]. The total quantity of monomers is always X. The percentages of the other components are referred to the total quantity of monomer. Z is the largest amount of initiator that can be dissolved.

	92%		3%		5%	
Monomers	Crosslinking agent	Surfactants		H_2O		Initiator
X	30%X	4.24%X		7.06%X		Z

Calculations are:

Gasoline phase $= X + 0.3X = 1.3X = 92\%$

Aqueous phase $= \dfrac{1.3X}{92} * 5 = 0.0706X$

Surfactants $= \dfrac{1.3X}{92} * 3 = 0.0424X$

Table 23: Formulation 4.

All the percentages are in weight [g]. The total quantity of monomers is always X. The percentages of the other components are referred to the total quantity of monomer. Z is the largest amount of initiator that can be dissolved.

82%		3%		15%
Monomers	Crosslinking agent	Surfactants	H$_2$O	Initiator
X	30%X	4.75%X	23.78%X	Z

Calculations are:

Gasoline phase $= X + 0.3X = 1.3X = 82\%$

Aqueous phase $= \dfrac{1.3X}{82} * 15 = 0.2378X$

Surfactants $= \dfrac{1.3X}{82} * 3 = 0.0475X$

It is worth to note that surfactants contains the total amount of Tween80 and Span80 adopted, but their relatively amount depends on the chosen HLB value.

2.5.6   Selection of materials

In order to find out the best formulation to ensure a stable and reactive emulsion, different set of tests were performed. They are collected in Tables 24 -27.

Table 24: Tests on formulation 1

All the percentages are in weight [g]. The percentages of crosslinking agent are referred to the quantity of monomer. The total amount of surfactant is expressed as S and depend on the formulation tested. The tests with subscript "a" have KPS as initiator, those with subscript "b" use instead AAPH

	Mixture A			
Sample	LA	Span80	EGDMA	Tween80
E1a	X	85%S	30%X	15%S
E1b	X	85%S	30%X	15%S
E2a	X	75%S	30%X	25%S
E2b	X	75%S	30%X	25%S
E3a	X	50%S	30%X	50%S
E3b	X	50%S	30%X	50%S
E4a	X	25%S	30%X	75%S
E4b	X	25%S	30%X	75%S
E5a	X	95%S	30%X	5%S
E5b	X	95%S	30%X	5%S
E6a	X	5%S	30%X	95%S
E6b	X	5%S	30%X	95%S

Table 25: Tests on formulation 2.

All the percentages are in weight [g]. The percentages of crosslinking agent are referred to the quantity of monomer. The total amount of surfactant is expressed as S and depend on the formulation tested. All the samples have KPS as initiator.

		Mixture A		
Sample	LA	Span80	EGDMA	Tween80
E7	X	85%S	30%X	15%S
E8	X	75%S	30%X	25%S
E9	X	50%S	30%X	50%S

Table 26: Tests on formulation 3.

All the percentages are in weight [g]. The percentages of crosslinking agent are referred to the quantity of monomer. The total amount of surfactant is expressed as S and depend on the formulation tested. All the samples have KPS as initiator.

			Mixture A		
Sample	LA	LMA	Span	EGDMA	Tween
E10	X	-	85%S	30%X	15%S
E11	-	X	85%S	30%X	15%S
E12	-	X	75%S	30%X	25%S
E13	-	X	50%S	30%X	50%S
E14	-	X	25%S	30%X	75%S

Table 27: Tests on formulation 4.

All the percentages are in weight [g]. The percentages of crosslinking agent are referred to the quantity of monomer. The total

amount of surfactant is expressed as S and depend on the formulation tested. All the samples have KPS as initiator.

		Mixture A		
Sample	LMA	Span80	EGDMA	Tween80
E15	X	85%S	30%X	15%S
E16	X	75%S	30%X	25%S
E17	X	50%S	30%X	50%S
E18	X	25%S	30%X	75%S

Mixtures B are the same for each sample within the same formulation class 1, 2, 3 or 4 as indicated

in Tables 20-23, and summarize in Table 28 below.

Table 28: Mixture B depending on the different formulation.

The percentage of H_2O in the mixture is in weight [g] and is referred to the total quantity of monomer. Z is the largest amount of initiator that can be dissolved in a fixed amount of water.

Formulation	H_2O	KPS	AAPH
1a	15.22%X	Z	-
1b	15.22%X	-	Z
2	15.45%X	Z	-
3	7.06%X	Z	-
4	23.78%X	Z	-

The values of HLB for each emulsion tested is easily obtained from Table 19.

Chapter 3: Results and Discussion

The aim of this chapter is to provide the most significant results coming from the experiments described in the Chapter 2, highlighting the strength and the weakness of each pathways

3.1 Results for Pathway 1

Several different formulations have been investigated, using mainly KPS as initiator and EGDMA as crosslinking agent. The high-boiling hydrophilic monomers used are TMAEC, PEGMA 300 and PEGMA 500.

The operative procedure used to obtain and evaluate the results are summarized below.

1. Add water to KPS and leave the system under magnetic stirring, until complete dissolution at room temperature (mixture B).

2. Add EDGMA to the monomer to obtain mixture A.

3. Add mixture B to mixture A and stir/shake for 30 seconds to mix thoroughly the two solutions. Then, the resulting system, without magnetic stirrer, is put in the oven at 60°C.

4. Evaluate the consistency of the final product over the time, till 48 hours.

The details of all the tests performed are shown in the section 2.3. The monomer TMAEC is not the most suitable monomer for this kind of polymerization: in all the samples, alone or blended with another monomer, the final polymer was not a hard solid, but just a compact jelly polymer easily penetrable, even doubling the amount of crosslinking agent (Figure 48).

Figure 48: Final material made up of TMAEMC, after 1.5h at 60°C.

This behavior is probably due to the fact that TMAEC contains already some water. In fact, the product was supplied by Sigma-Aldrich in a water solution, with a concentration of 80%, as reported in section 2.1. For this reason, PEGMA was selected as the best monomers together with EDGMA, for being the most promising crosslinking agent in term of properties of the final material. (Figure 49)

Figure 49: Samples with A) and without B) EGDMA, after 1 h at 60°C.

The possibility to use AAPH was abandoned for the low capacity of the final material to resist to the pressure of the spatula. (Figure 50) KPS gave better results.

Figure 50: Fragmentation of the solid polymer using the initiator AAPH.

3.1.1   Stability Tests

Once the reactive systems have been identified, it is important to analyse the stability of the mixture A and mixture B at room temperature (25°C) and at 60°C, to avoid unwanted polymerization during the storage condition, when they are not in contact. Table 29 below shows the results of the stability performed on the most promising reaction R6.

Table 29: Stability tests on R6.

Sample	Stability time at 25°C	Stability time at 60°C
R6-Mixture A	>48h	>4h
R6- Mixture B	>48h	>48h

The stability of mixtures A is always between 24 and 96 hours at room temperature, instead at 60°C it is at least 4 hours. The stability of mixtures B, showed in Table 29 is always over the 48h.

3.1.2 Final Formulation

According to the obtained results, the final formulation that shows the best characteristics in terms of stability, mechanical resistance and time of reaction is the one that involves PEGMA 500 (R6). The amounts used to perform the experiments are reported in Table 30, while the final product, after 1 hour of polymerization, is in Figure 51. It is a hard material, difficult to be fragmented into flakes.

Table 30: Final formulation for Pathway 1.

All the percentages are in weight [g]. The percentages of crosslinking agent and initiators are referred to the quantity of monomer, while the solvent quantity Y depends on the solubility of the selected initiator. Numerical values are the real quantities used in the performed tests.

Mixture A		Mixture B	
PEGMA 500	EGDMA	KPS	H_2O
X	30%X	5%X	Y
1.39g	0.417g	0.07g	1.15g
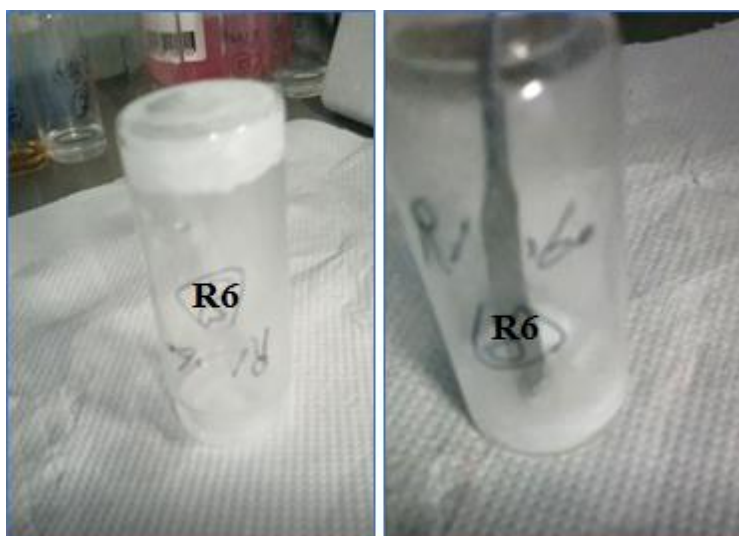
Figure 51: Result using PEGMA 500 and KPS solution.

The system preserves its configuration over the time.To validate these results, it was interesting to observe how the solutions behave increasing the volume. For this reason, scale up tests were performed doubling and decupling the quantities used and, also in this case, the results were good and in line with the previous ones

3.2 Results for Pathway 2

The same monomers have been also used to produce a solid material using a couple of redox initiators to start the polymerization. In this case, the beginning of the reaction is due to the reaction among one oxidant and one reducing agent that generates radicals capable to initiate the frontal polymerization. The selected couple is represent by H_2O_2, as oxidant agent, and $FeSO_4$, as reductant. From a safety perspective, it is better to keep separated the different mixtures to avoid unwanted reactions among monomers and initiators. For this kind of experiment, three different mixtures have been prepared. Mixture A is made up of the hydrophilic monomer and the crosslinking agent, mixture B is the reducing agent in water and mixture C is the oxidant in the aqueous solution.

The step by step procedure used to perform these experiments is summarized below.

1. Prepare solution H_2O_2 at different concentration in water, 10% or 35% (Mixture C).

2. Add water to the powder of $FeSO_4$ to dissolve it (stirring for 30 s) (Mixture B).

3. Add the indicated amount of monomer to EGDMA (Mixture A).

4. Add mixture B to the mixture A and stir/shake for 30 seconds.

5. Then, add mixture B to the resulting system. Stir/shake it for 30 seconds, to mix thoroughly the solutions. During the mixing, it is possible to appreciate the change of the color, from colorless to yellow/brown. This means the redox reaction is happening. Then, the resulting

system, without stirring, is put in the oven at 60°C and checks are done over the time on the consistency of the material

After the optimization of the recipes, the best concentration of the oxidant initiator is 10%, otherwise the reaction is uncontrolled. The selection of the monomers was pretty though. After 2.5 hours, a solid phase was formed, but there was a smooth gel on the surface, as illustrated in Figure 52). The figure refers to the blend of monomers TMAEC and PEGMA 500.

Figure 52: Result using TMAEMC and PEGMA 500 and H_2O_2 at 10%.

The sample in figure is FP7 (section 2.4.3) with ratio between PEGMA 500 and TMAEC of 80:20

The system preserves its configuration up to 8 hours, even if the gel is still there.

3.2.1   Stability Tests

It is important to analyse the stability of the two mixture A, B and C at room temperature (25°C) and at 60°C, to avoid unwanted polymerization during the storage condition. Initially, it was tried to use only two mixtures, A and B. In this case, the solution of H_2O_2 was already in the mixture A and this could lead to problems related to the stability and the safety. The stability is a problem for this formulation, because the H_2O_2 is unstable and reacts inside the mixture: the samples are stable only

1-2 hours at room temperature and 30 minutes at 60°C. For this reason, it was decided to prepare three distinct blends that come in contact only when the reaction must occur. Mixtures B and C take alone are stable at room temperature and 60°C for more than 48 hours. Mixtures A at 25°C is stable for 48 hours as well, while at least for 4 hours when put in stove.

3.2.2   Final Formulation

According to the obtained results, the final formulation that presents the best characteristics in terms of stability, mechanical resistance and time of reaction is the one that involves PEGMA 500 (FP5). The amounts used to perform the experiments are reported in Table 31, while the final product, after 1 hour of polymerization, is in Figure 53.

Table 31: Final formulation for Pathway 2.

All the percentages are in weight [g]. The percentages of crosslinking agent and initiator are referred to the quantity of monomer, while the solvent quantity Y depends on the solubility of the selected initiator. The percentages of H_2O in mixture C depends on the desired concentration of the H_2O_2 solution. Numerical values are the real quantities used in the performed tests.

| Mixture A		Mixture C		Mixture B	
PEGMA 500	EGDMA	H_2O_2 [37%v]	H_2O	$FeSO_4$	H_2O
X	40%X	3%X	26%X	3%X	Y
1.39g	0.55g	0.04g	0.36g	0.04g	0.14g

Figure 53: Best formulation for the frontal polymerization experiments.

It is a hard material and compact material. The system preserves its configuration over the time.

3.3 Results for Pathway 3

The aim of this pathway is the exploitation of emulsions to have a reactive lipophilic mixture A with the same hydrophilic mixture B already tested, with the possibility to investigate a larger number of materials and reactants, including this time all the lipophilic compounds, and try to obtain results comparable to the previous ones. Before having a reactive emulsion, it is necessary to get a stable emulsion. Many tests have been carried out starting from the formulation of a stable W/O emulsion like the one used for the white diesel and gradually adjusting the ratios of liquid phase, oil amount, surfactants and the HLB value. Also the methodology of preparation has been prepared following the high-energy procedure found in the literature [75, 76].In particular,

1. Add water to KPS and leave the system under magnetic stirring, until complete dissolution at room temperature (Mixture B).

2. Add EDGMA to the monomer to obtain mixture A.

3. Blended surfactants (Span80 + Tween80) were mixed into the mixture of monomers and crosslinking agent. Then, pre-emulsions were prepared by adding the mixture B under constant stirring at 800 rpm.

4. In the second step, the prepared pre-emulsions were stirred at high speed (5000rpm) through the use of sonicator for 20 minutes.

5. Evaluate the final stability over the time.

It is worth to note that all the emulsions were prepared at room temperature. As previously mentioned in section 2.1, the lipophilic monomers tested are lauryl acrylate (LA) and dodecyl methacrylate (LMA). LMA shows better stability results. The chosen crosslinking agent is EGDMA and the initiator KPS.

3.3.1   Stability Tests

In order to develop a reactive mixture, it is necessary firstly to find out a stable emulsions. Despite the many experiments that have been done, no formulation was identified, even compared to other work whit similar emulsions (Figure 54). [76]
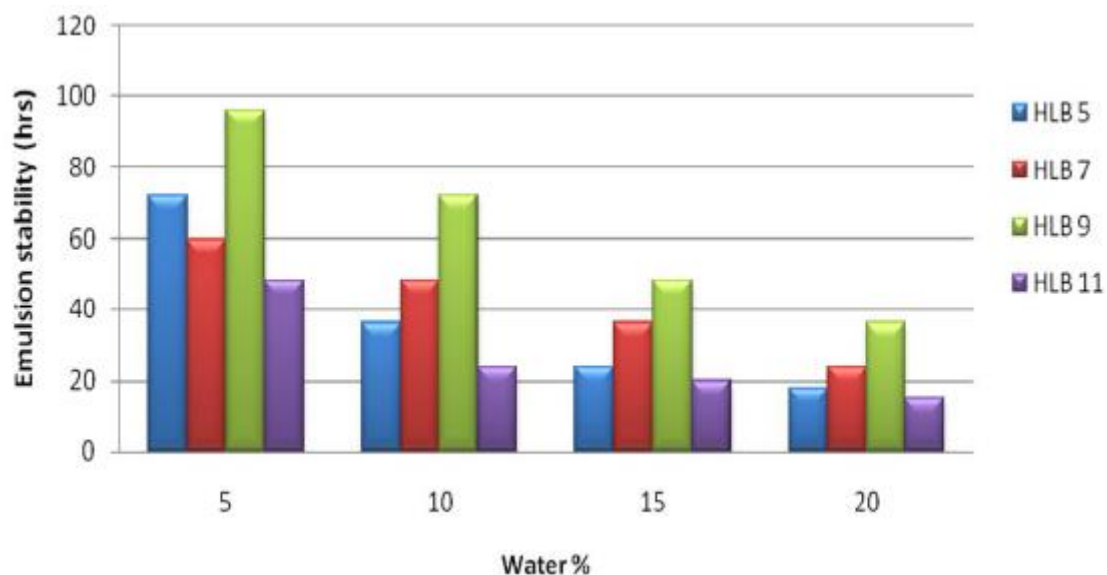
Figure 54: Expected values of stability for emulsions.

In this work, some samples are dissociated even after few minutes from the preparation of the emulsion, others are stable for almost an hour, but in general all of them show phase separation before 2 hours (Figure 55).

Figure 55: Phase separation in emulsion sample after few hours.

Only the sample E13 is stable for 24 hours (Figure 56), it has an HLB of 9.65 and is formulation is reported in Table 32 below.

Table 32: Most promising formulation for a stable emulsion.

All the percentages are in weight [g]. The percentages of crosslinking agent and solvent are referred to the quantity of monomer. The total amount of surfactant is expressed as S and depend on the formulation tested. Z is the largest amount of initiator that can be dissolved. Numerical values are the real quantities used in the performed tests.

Mixture A				Mixture B	
LMA	Span	EGDMA	Tween	H_2O	KPS
X	50%S	30%X	50%S	7.06%X	Z
1.39g	0.029g	0.417g	0.029g	0.098g	0.006g

Figure 56: Most promising sample for the emulsion pathway, after 24h.

3.3.2   Final Formulation

Some reactivity tests were performed on sample E13 also doubling the dose to increase the amount of initiator but no reaction occurs in the time frame analysed (0-48h). This is probably due to the fact that the initiator in formulation is barely the 1% of the monomer. The problem is the low solubility of KPS: it requires a lot of water to be dissolved and this causes a less stable emulsion. Further researches are needed to get a stable but also reactive emulsion through which the desired polymerization can take place

Conclusions and Outlook

The starting point is to obtain a polymer which is solid and with good resistance to compression, within about an hour since the reactants come into contact. Three different pathways have been investigated in which two polymerization techniques were exploited: the Free Radical Polymerization (FRP) and Frontal Polymerization (FP). In particular, new smart formulations for bicomponent mixtures are presented. Mixture A, composed by a monomer and a crosslinking agent, and mixture B, containing an initiator and a solvent. In the case of FP is required also a mixture C containing the oxidant agent. The idea is to explore the possibility to obtain a hard and compact material by dissolving the initiator solution (mixture B) into the mixture of the monomers (mixture A). Most of the work (Pathway 1 and 2) of this research focuses on hydrophilic mixtures, it means that both the monomer and the initiator are water soluble. To understand the mechanism and to optimize the formulations, most of the degrees of freedom of these formulations are investigated: the behaviour of the systems changing the kind and the relative quantities of the monomers and the crosslinking agents, the different types of initiators, the amount of the solvent and the problems of the incompatibility among the materials. The detailed studies presented are the results of the optimization processes of the synthesis involving the use of the thermal activated KPS or the redox couple $H_2O_2/FeSO_4$ as initiators and ethylene glycol dimethyl acrylate (EGDMA) as crosslinking agent. The high-boiling hydrophilic monomers most suitable for both polymerization techniques is poly ethylene glycol methyl ether methacrylate Mw=500 Da (PEGMA 500). It has also been attempted to broaden the research horizon by treating lipophilic mixtures (Pathway 3), initially set aside for the difficulty of finding a lipophilic initiator that meets all the requirements, including safety and reactivity. The idea was to exploit the emulsion between a lipophilic mixture A (with monomer such as Lauryl acrylate and Dodecyl methacrylate) and a mixture B, which is still

hydrophilic and made up of water and the initiator (accordingly to its solubility). Further investigation are required to find out the best solution for the emulsion pathway.

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