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***Degree in Chemistry***

FINAL DEGREE PROJECT  
Synthesis of hypercrosslinked polymers in dispersed media

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## ABSTRACT

The main goal of this project is to understand and adapt the Transfer-dominated Branching Radical Telomerization (TBRT) process to be able to work in a water-based system in order to minimize the use of volatile organic compounds (VOCs). To properly understand the TBRT process, experimental data obtained from solution polymerization has been compared with the data obtained from the simulations, and although the model follows the trends that occur, some improvements must be done to fully represent the real-life process. The transition from a solvent-based media to a water-based has been successful as it has been possible to perform the TBRT process in miniemulsion and by means of dispersible polymers, thus obtaining water dispersions. It has been proved that the TBRT process is capable of synthesizing hyperbranched polymers with high molecular weights but avoiding the formation of gel. The characterization of the polymers obtained from both the miniemulsion and dispersible polymers has been carried out by employing different techniques. The main conclusion has been that although the obtained polymer is capable of forming film and has a controllable molecular weight, as well as a really low gel content and a total vinyl bond conversion, some improvements must be done in order to employ them for certain applications.



## LABURPENA

Proiektu honen helburu nagusia "Transfer-dominated Branching Radical Telomerization" (TBRT) prozesua ulertzea eta hau uretan oinarritutako sistema batean lan egin ahal izateko egokitzea da, konposatu organiko lurrunkorren erabilera minimizatzeko. TBRT prozesua behar bezala ulertzeko, soluzioan egindako erreakzioetako datu esperimentalak simulazioetatik lortutakoekin alderatu dira, eta ereduko datuek esperimentalen joerei jarraitzen dien arren, hobekuntza batzuk egitea beharrezkoa da benetan gertatzen den prozesua ongi adierazi ahal izateko. Bestalde, esan beharra dago disolbatzaile organikotan oinarritutako ingurune batetik uretan oinarritutako ingurune batera trantsizioa egitea lortu dela; izan ere, TBRT prozesua miniemultsioan eta polimero dispertsagarri bidez egitea lortu da. Frogatu da TBRT prozesua gai dela pisu molekular handiko polimero hiperadarkatuak sintetizatzeko, baina gel-eraketa saihestuz. Miniemultsiotik zein polimero dispertsagarriekin lortutako polimeroen karakterizazioa hainbat teknika erabiliz egin da. Ateratako ondorio nagusiak izan dira lortutako polimeroak gai direla filmak sortzeko, pisu molekular kontrolagarria dutela, gel-eduki oso baxuak dituztela eta lotura binilikoek konbertsio totala lortu dela. Hala ere, hobekuntza batzuk egitea beharrezkoa dela ikusi da, hauek aplikazio jakin batzuetan erabili ahal izateko.



# IDENTIFICATION AND CONSIDERATION OF SUSTAINABLE DEVELOPMENT GOALS

This project is related to some of the sustainable development goals that the Basque Country University has. There are 18 sustainable development goals in total, 17 of which are related to the goals of the “2030 Agenda for Sustainable Development Goals” and one extra goal has been added by the Basque Country University.

As my research mainly focuses on adapting preexisting processes to be able to use them in a water based media instead of a solvent based media, it is strongly related to the twelfth and the thirteenth points as the first one is related to sustainable production, which is the case as less volatile organic compounds are employed, and the same happens in the second one as this is related to the climate action, which can be affected by the substances that are released to the atmosphere.

Another key point of the project is that the polymers synthesized could be tuned in the future in order to be fully degradable, relating it to the third point, which is the one that is about the good health and good being, as if the polymers produced can be modified to be fully degradable, the problems that residual plastics such as microplastics cause on our health would be mitigated.

# 1. INTRODUCTION

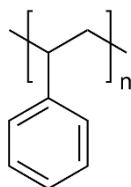
## 1.1. Polymers

Polymeric materials have been essential in the history of humanity as many materials that have been used by humans such as wool, wood, leather... are, indeed, composed of polymers such as cellulose, starch, proteins... Even if the natural polymers mentioned before have been used for a long time, it wasn't until the last century that humanity utilizing synthetic polymers with tailored properties, in order to design them for specific applications<sup>1,2</sup>.

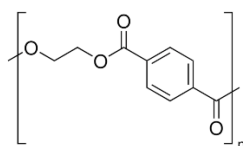
Anyhow, we still rely on natural polymers to a great extent for many things. The main reason behind this being that natural polymers tend to be more degradable than their synthetic counterparts<sup>3</sup>.

There are two main polymerization techniques<sup>4</sup>: chain growth polymerization, in which monomers are added into the main chain one by one, and step growth polymerization where reactions between functional groups present in the monomers take place, giving dimers, tetramers... as a result<sup>5</sup>.

On the one hand, chain growth polymerization usually creates polymers with a carbon backbone (Figure 1), and this can sometimes cause challenges in end-of-life disposal, as degrading a chain formed by carbon-carbon bonds is not easy. On the other hand, polymers synthesized by step growth polymerization tend to contain heteroatoms, forming bonds such as oxygen-carbon bonds in the case of polyester or polyether and nitrogen-carbon bond in the case of polyamides (Figure 2)<sup>6</sup>, which in general are more inherently degradable.



**Figure 1.** Polymer synthesized by chain-growth polymerization.



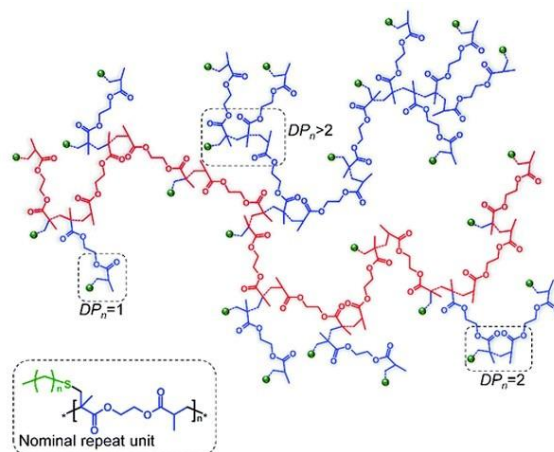
**Figure 2.** Polymer synthesized by step growth polymerization.

Recently some polymerization techniques have been developed that allow us to combine the benefits of chain growth polymerization, such as the ability to perform free



radical polymerization, and the structural properties of step growth polymerization, such as the possibility to have heteroatom-carbon bonds in the polymer backbone, making the polymer easier to be degraded. One example of this is transfer-dominated branching radical telomerization of divinyl monomers<sup>7</sup>.

The previously mentioned transfer-dominated branching radical telomerization (TBRT) is a useful method for synthesizing hyperbranched polymers by employing divinyl monomers with a free radical chain-growth chemistry. It works by using a high concentration of chain transfer agent in order to control the chain growth, generating the possibility to form high molecular weight branched polymers without reaching the gel point. It must be mentioned that the TBRT process combines the benefits of the chain growth processes with the structures of step-growth polymers (Figure 3) and leads to polymers in which the nominal repeat unit contains ester bonds in the backbone.



**Figure 3.** Branched polyester obtained from the TBRT of EGDMA and DDT<sup>7</sup>.

Although TBRT has been demonstrated for a number of cases in solution polymerization, the trend is to migrate from polymerization techniques that employ large amounts of volatile organic compounds towards the techniques that minimize the use of those compounds<sup>8</sup> or, simply avoid them by employing water as a continuous phase.

## 1.2. Polymerization techniques

Radical polymerization can be conducted in a number of ways including in bulk, solution, suspension and emulsion, with another modification of emulsion called miniemulsion. Neither the suspension nor the bulk polymerization will be covered, as these are less related to this project.



When it comes to emulsion or miniemulsion they both work under similar principles, although with some key differences that will be discussed below. The main difference being where the polymerization takes place.

### 1.2.1. Solution polymerization<sup>2,9</sup>

Solution polymerization, which has been mentioned before, is a simpler polymerization technique when comparing it to the emulsion or the miniemulsion polymerization. In this technique the monomer is dissolved in an organic solvent, and an initiator that is soluble in said solvent is added.

When the initiator decomposes and gives radical species those radicals will react with the monomer, thus creating a monomer with an active radical that can undergo different paths. The most common path for the radical monomer is to react with another monomer, and that monomer can keep on reacting with monomers, creating a full chain in less than a second. This continues until it reacts with another radical, giving a termination reaction that can take place either by combination, resulting in a chain with the combination of the monomers in both chains, or it can give a disproportionation termination, creating two chains, each with the amount of monomer that they had before the termination reaction, but one of them having a double bond at the end.

Another option is that while the chain is propagating the radical can be transferred to multiple things in the reaction media such as to the solvent, a monomer unit, another polymeric chain, another monomer unit in the same chain (creating a small branch), or even to a CTA that can be added to the reactor in order to control the molecular weight, as the chain transfer reduces the molecular weight of the chain.

It's important to note that although with this technique the control over the temperature is better than when doing a bulk polymerization, is not as good as with other techniques that use water as the continuous phase. That's because although a solvent is present, and the viscosity won't increase as quickly as in the case where no solvent is present, it will still increase as higher conversions are obtained. Another important problem of this polymerization type is the use of an organic solvent, which in most cases is better to be avoided as they are usually highly volatile, bad for the environment and bad for our health.

### 1.2.2. Emulsion polymerization<sup>9,10</sup>

In emulsion polymerization the main elements in a reactor tend to be a water-soluble initiator, monomer (or multiple monomers when the objective is to create



copolymers), an emulsifier and the water phase. Sometimes a chain transfer agent is also added to aid in the control of the molecular weight. It's important to note that in this kind of polymerization enough emulsifier must be added to surpass the critical micelle concentration (CMC), as when this concentration is surpassed, the emulsifier has already stabilized all the interphases and it has started creating micelles in the continuous phase.

The emulsion polymerization takes place in three distinct stages:

1. In the first stage the emulsifier will first place itself in all the interphases. If as previously mentioned the emulsifier concentration exceeds the CMC, micelles will form, and a fraction of the monomer inside the droplets will pass to the water phase, and from there to the micelles, thus forming an equilibrium between the monomer in the droplets, in the solution and in the micelles.

As the initiator employed is soluble in water, this will create radicals in the water phase, that will then react with monomers in said phase, forming oligomers. The mentioned oligomers can either keep reacting with monomers and growing until they reach a size where they are so hydrophobic that a fraction of the emulsifier in the micelles will migrate to them, to stabilize them (homogeneous nucleation). Another option is that the oligomers can enter a micelle and keep reacting with the monomers inside it (heterogeneous nucleation). This stage will continue until all the micelles disappear through the previously mentioned mechanisms, thus fixing the number of particles.

2. After the first stage the particles will continue to grow by consuming the monomer inside the micelles, and as the monomer in the micelles is in an equilibrium with the monomer in the aqueous phase and in the monomer droplets, the consumption of the monomer in the particles will force the monomer in the solution to migrate to the particles, and the monomer in the droplets to migrate to the solution. This stage will continue until all the monomer in the droplets has been consumed.
3. This stage is the last one and will continue until the end of the polymerization. Through it, the remaining monomer present in the water and in the particles is



slowly consumed until there is no monomer left to react, and the conversion is of 100%.

### 1.2.3. Miniemulsion polymerization<sup>11,12</sup>

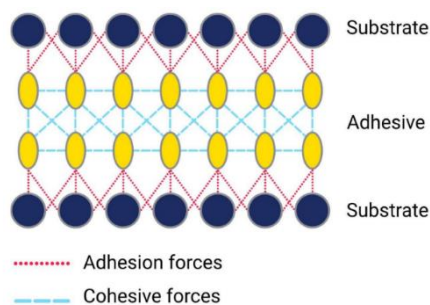
In the case of miniemulsion the monomer droplets are broken into small droplets by applying a source of energy to them. This energy can come from different sources, but a common source is to expose the droplets to ultrasound with a sonicator. Once the droplets are broken, they are stabilized by the surfactant and in some cases by a co-stabilizer, as sometimes the presence of only the emulsifier is not enough to stabilize the small and unstable droplets.

Referring to the polymerization process, opposed to the emulsion polymerization, what it happens in the micelles that later become particles or in the water, and once in precipitates it is stabilized by the emulsifier, in the case of miniemulsion the polymerization mainly takes place inside the previously broken monomer droplets.

## 1.3. Applications<sup>13–15</sup>

As polymers have a large variety of structures they can be employed in a variety of situations. This project focuses specifically on polymers dispersed in aqueous media, especially those that can be later used as adhesives or coatings<sup>1</sup>. Adhesives function by chemically and physically bonding two objects, whilst coatings are applied as thin layers to form films that will protect substrates from environmental factors such as atmospheric salinity, humidity or UV radiation.

Adhesives and coatings both rely on adhesive and cohesive forces on the interfaces and inside their structures (Figure 4). On the one hand, adhesive forces come from secondary bonding between the adhesive or coating molecules located at the interface and the molecules located on the surface of the substrate. On the other hand, cohesive forces are internal forces that take place on the adhesive or coating itself and hold together the adhesive or coating molecules. The effectiveness of adhesives and coatings depends on the synergy between these forces, but it must be mentioned that the exact mechanism remains unclear.



**Figure 4.** Adhesive and cohesive forces in an adhesive holding two things together<sup>16</sup>.

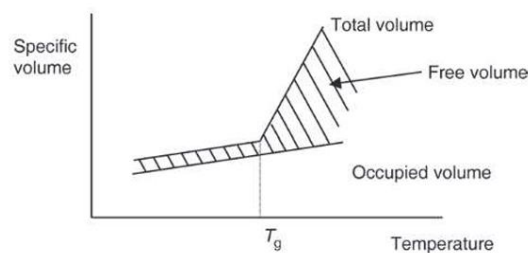
It must also be stated that coatings, are not the same as paints, as their main purpose is to protect the substrate where they are located through physical and chemical processes forming thin films via solvent evaporation, crosslinking, or polymerization<sup>13,14,15</sup>. Although paints can also protect the surface, their main use is to improve the appearance of the substrate.

### 1.3. Film formation<sup>15</sup>

To properly understand how the previously mentioned coatings are used and created, we must first understand how films form, as this is the process that turns the coatings from liquid to solid once they are applied in the desired surface.

When a coating is applied over a surface, at first it will be wet, and as time passes it will solidify becoming a homogeneous. To understand how that transformation takes place we must understand how the polymers behave when they are within a solvent or dispersed in a media and when they are applied in a substrate.

When the coating is stored, it will behave as a viscous liquid, this is due to it being above its glass transition temperature ( $T_g$ ) thanks to it being mixed with the solvent or continuous phase. Once the coating is applied onto the desired surface the  $T_g$  must be elevated to be higher than the temperature in the place where it's being applied so that it stays below the  $T_g$ . The  $T_g$  is an important concept, as it will give information about the movement of the polymeric chains. On the one hand, when the polymer is under its  $T_g$  it will behave as a rigid solid as the chains won't be able to move at all because the free volume is not that large. On the other hand, when the polymer it's above the  $T_g$  although it won't be as viscous as a liquid, the chains will be able to move, because the free volume will be much larger (Figure 5).



**Figure 5.** Effect of the glass transition in the specific volume<sup>15</sup>.

So, for a coating to be effective, it must have a  $T_g$  above room temperature when it's being stored, but the  $T_g$  should be higher than the room temperature once it has been applied. That increase in  $T_g$  can be achieved essentially through two different ways. These are solvent evaporation and chemical reactions.

In the case of thermoplastic coatings, historically the method used to increase the  $T_g$  was the evaporation of the solvent. Quite a lot of coatings rely on solvent evaporation nowadays even though it has many downsides, the main being that for them to be effective, the molecular weights must be high enough so that the chains are able to entangle. Therefore, the viscosity of the polymeric solutions is high, so to counteract that, the polymer is usually diluted so that the coating has an appropriate viscosity at the time of being applied. As the solid content is quite low, multiple layers of this type of coatings must be applied to reach a thick enough barrier to be effective. Since this type of coatings are mostly solvent and those solvents are usually toxic and bad for the environment, their use is slowly going down and they are being replaced by other type of coatings.

Other coating types employ a combination of mechanisms such as the previously explained evaporation of the solvent as well as some chemical reactions that build up the molecular weight and crosslink the system. As those processes take place, the  $T_g$  increases gradually.

Another type of coatings are the solventless crosslinking ones, such as powder paints. In this type of coatings solid particles are sprayed onto a surface, and then upon heating them the particles soften and flow, so that coalescence takes place. After that initial phase the temperature is increased more, leading to an increase in the molecular weight. Once the gelation point is reached the surface appearance becomes set.

Finally, there are the disperse phase polymer systems, which are the main focus of this project, as they have some advantages respect to other systems. The benefit of



using this kind of system is that the problems of using high molecular weight thermoplastics have been overcome.

The advantages of these systems are the low viscosity even when using high molecular weights thanks to the polymer being in the form of particles dispersed in an aqueous phase and thus making the viscosity independent of the molecular weights of the polymer inside the particles. Another important advantage is the low Volatile Organic Compounds (VOCs) present in the system<sup>8</sup>, making it a preferable option when trying to reduce the use of those organic compounds.

Film formation from a latex takes place in three distinct steps:

1. After application of the latex in a non-porous surface, water and the organic co-solvents begin to evaporate, thus raising the solid content of the latex. Consequently, the polymeric particles begin to get closer to each other.
2. For successful film formation, the particles must coalesce by overcoming repulsive forces. The driving forces behind the coalescence are thought to arise from capillary forces as particles get close to each other or the surface energy reduction as the sub-micron particles form a continuous film. The main driving force can be either or a combination of the previously mentioned. The main result is that the spherical particles are deformed into a closed packed polyhedra, reducing the air gaps between the particles.
3. Finally, polymer chains must diffuse through particle interface, which means that in the case of ambient systems the  $T_g$  of the polymer in the interface must be below the ambient temperature. This doesn't mean that the  $T_g$  of the polymer is low. The organic co-solvents or compounds placed to aid in the coalescence will plasticize the polymer long enough so that coalescence takes place, but then they will evaporate and the  $T_g$  of the polymer will increase, making the polymer a solid at ambient temperature. Another option can be to create a multilayer or gradient composition particles by using certain techniques to obtain particles with low  $T_g$  outer layers capable of undergoing coalescence, but with a core with higher  $T_g$  that will provide the rigidity in ambient temperature.



## 2. OBJECTIVE

The main goal of this project is to develop the use of the TBRT process for polymers in dispersed media.

To do so, first the TBRT process must be better understood. To achieve this objective, the impact of varying the amount of chain transfer agent on molecular weight has been studied in solution. Following this, the objective of the work focused on the TBRT process for synthesis of colloidal polymers. To do so, a number of dispersions were formed using miniemulsion polymerization or by synthesis of dispersible polymers by TBRT. Finally, these polymer dispersions were tested for potential applications in coatings by studying the glass transition temperature ( $T_g$ ), particle size, MFFT and the tensile strength (where usable film have been obtained in the experiments).

In summary, the main objectives are three:

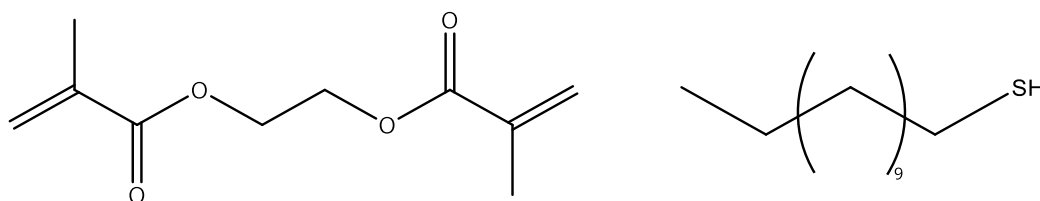
1. Develop an improved mechanistic understanding of the TBRT process.
2. Synthesize hyper crosslinked polymers dispersed in water capable of forming films.
3. Characterize the obtained polymers with regards to mechanical behavior through different techniques.



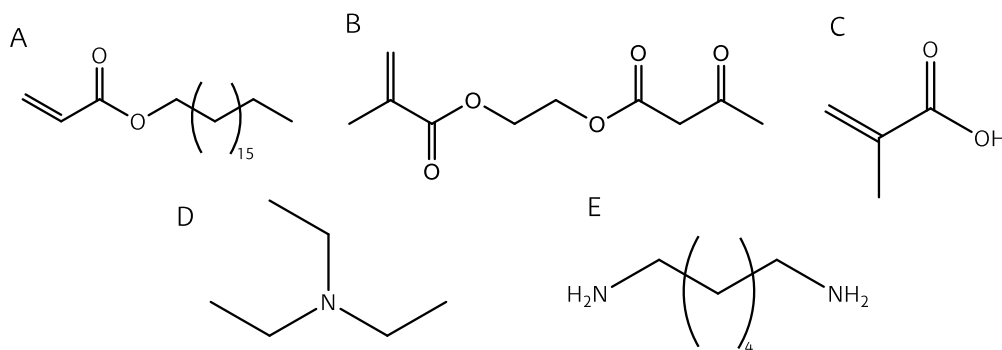
### 3. EXPERIMENTAL PART:

#### 3.1 Reagents and components:

Ethylene glycol dimethacrylate (EGDMA) (Figure 6), 2,2 -Azobis(2-methylpropionitrile) (AIBN), stearyl acrylate (Figure 7), sodium dodecyl sulfate (SDS), methacrylic acid (MAA) (Figure 7), triethylamine (TEA) (Figure 7), 2-(Methacryloyloxy)ethyl acetoacetate (MAEA) (Figure 7), ammonium hydroxide, hexamethylenediamine (HMDA) (Figure 7), methanol, and deuterated acetone were provided by Sigma-Aldrich, whilst the toluene, and both the GPC grade and technical grade tetrahydrofuran (THF) were provided by Scharlab. The dodecanethiol (DDT) (Figure 6) was provided by Fluka and the deuterated chloroform was provided by Eurisotop.



**Figure 6.** Molecule of EGDMA on the left and DDT on the right.



**Figure 7.** Molecule of stearyl acrylate (A), MAEA (B), MAA (C), TEA (D), HMDA (E).



## 3.2. Different polymerization procedures

### 3.2.1. Solution polymerization

When solution polymerizations were carried out, different [EGDMA]/[DDT] ratios (Table 1) were prepared in a beaker. Then 0.01 g of AIBN was added, as well as enough toluene to make the solid content 50%. Once everything had dissolved, it was transferred to a round bottom flask and a sample for the NMR was taken. Later, it was sealed with a septum. To purge the reactor, a nitrogen inlet was placed, as well as a needle to relieve the pressure inside the flask, and the purging was done for 15 minutes while stirring the contents of the flask. After the purging was completed, the flask was lowered to an oil bath at 70 °C, and it was held there while stirring for 24 hours.

**Table 1.** Experiments changing [EGDMA]/[DDT] in solution.

Experiment	[EGDMA]/[DDT]	Precipitation
1	0.51	
2	0.74	
3	0.78	YES
4	0.83	
5	0.97	
6	0.48	
7	0.73	
8	0.79	NO
9	0.86	

Once the 24 h had passed two different procedures were followed:

- The first five reactions were precipitated after a sample for the NMR was taken, by using ice cold methanol in a 1:10 ratio while stirring. Then it was left there until everything settled at the bottom, and it was decanted to separate the precipitate from the methanol. Once the separation was done, the precipitate was left in an aluminum capsule to dry inside the fume hood until all the methanol evaporated. It is important to mention that no precipitation was carried out in experiment 5 as it formed gel.

- The other four reactions were finished by simply leaving them to dry on an aluminum capsule once a sample for the NMR was taken.

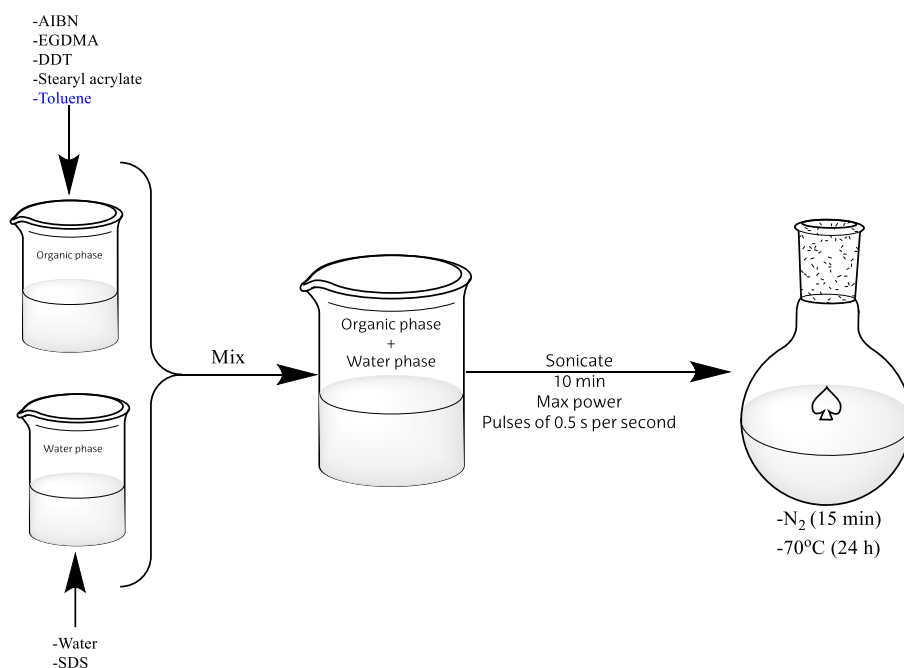
Finally, another experiment was conducted (Table 2) to see how the molecular weight and the conversion evolved during the reaction. For this experiment, the experimental procedure was the same as for the previous ones where no precipitation was carried out, but samples were taken during the reaction, and to ensure that no oxygen entered the flask, instead of only purging for 15 minutes, a constant N<sub>2</sub> inlet and outlet was kept.

**Table 2.** Analysis of the evolution of conversion and molecular weight.

Experiment	[EGDMA]/[DDT]	Precipitation
10	0,80	NO

### 3.2.2. Miniemulsion polymerization

The miniemulsion reactions were carried out to analyze how different variables such as the solid content, the presence of toluene or the total amount of reagents affected the polymer (Table 3). Although some parts of the formulation varied slightly from one reaction to another, the following scheme was followed (Figure 8).



**Figure 8.** Scheme of miniemulsion experiments (in blue the extra procedure that was followed in certain reactions).



To prepare the reactions the water phase and the organic phase were prepared separately. The water phase consisted of enough deionized water to reach the desired solid content, and SDS, which was added corresponding to 2% of the weight of water. After that, the organic phase was prepared, which consisted of enough EGDMA and DDT to reach the desired proportion, 0.01 g of AIBN except in experiment 14 where all amounts were doubled, so 0.02 g were used, and finally the co-stabilizer stearyl acrylate, which was added corresponding to 4% of the weight of the organic phase.

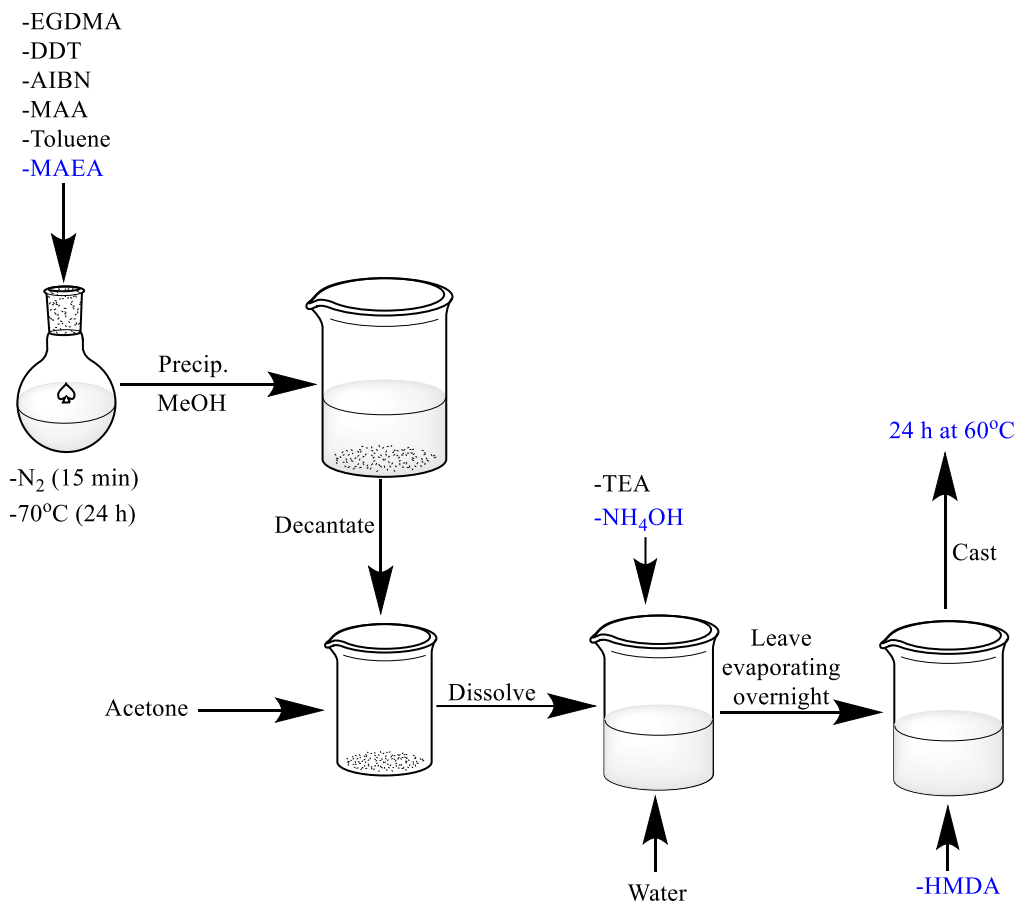
Once both phases were prepared, the organic phase was added to the water phase, while the second one was being stirred. After both phases were combined, they were placed on an ice bath in the small sonicator (Hielscher-UIS250V) and it was sonicated for 10 minutes at the maximum power with pulses of 0.5 s per second. Once the sonication was done, a sample was taken for the NMR and the rest was placed on a round bottom flask that was sealed and then purged using the same procedure as in the solution polymerizations. Once it was purged, the flask was lowered to an oil bath at 70 °C for 24 hours. Finally, once the reaction had finished a sample was taken for the NMR and the rest was kept in a glass vial for later use.

**Table 3.** Miniemulsion reactions with different variables.

Experiment	[EGDMA]/[DDT]	SC (%)	Total mass (g)
11	0.85	40 (50% toluene)	9.7
12	0.83	40	4.8
13	0.86	30	6.5
14	0.85		12.9

### 3.2.3. Dispersible polymers

These reactions were carried out in pairs following the following scheme (Figure 9), as the precipitate obtained in the first reaction was later employed when creating the dispersion (Table 4, e.g. experiment 15.1 is paired with experiment 15.2):



**Figure 9.** Scheme of dispersible polymer experiments (in blue the extra procedure that was followed in certain reactions).

**Table 4.** Dispersible polymer experiments.

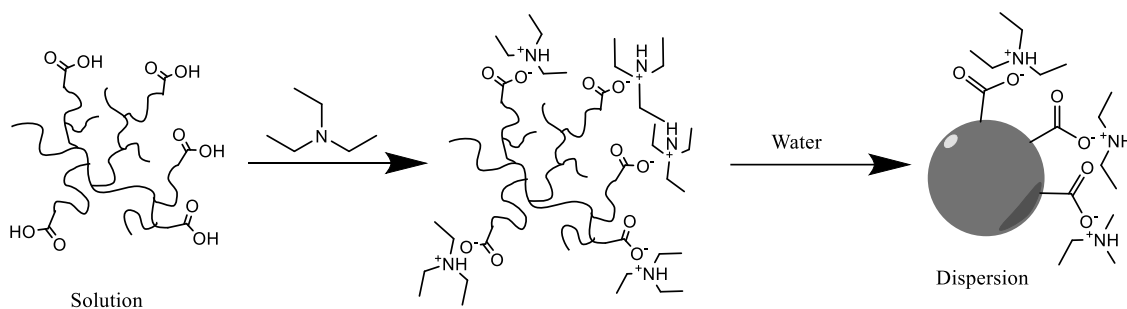
Experiment (1)	[EGDMA]/[DDT]	Experiment (2)	Amount of precipitate (g)
15.1	0.5	15.2	0.5
16.1		16.2	
17.1	0,45	17.2	1
18.1		18.2	2

- The first set of experiments labeled as "Experiment (1)" (Table 4) were carried out using the same procedure as the experiments carried out in solution (Table 1) with a slight variation, as when combining the reagents, MAA was added as a monofunctional monomer, in an amount equivalent to 10% of the sum of both EGDMA and DDT in mass. After the reaction was finished, a precipitation was carried out using the same procedure as in the solution polymerization reactions

where precipitation was done, but more time was required for everything to settle at the bottom. Similar to the other experiments, two samples, one before and one after the reaction were taken to measure the conversion using NMR.

- The second set of experiments labeled as “Experiment (2)” (Table 4) consisted of creating a dispersion from the precipitate obtained on the first set of reactions. First a sample of the precipitate was weighed, and then dissolved in a glass vial, with enough acetone, so the solid content was 60%. After the precipitate was dissolved, TEA was added in a proportion of 1:1 in moles respect to the MAA present in the sample of precipitate. After the previously mentioned steps, water was added to create a dispersion that had a 20% solid content. Finally, the vial was left with the lid open inside a fume hood to evaporate the acetone and reduce the viscosity, getting as a result a latex.

The process of creating the dispersion can be seen in Figure 10:



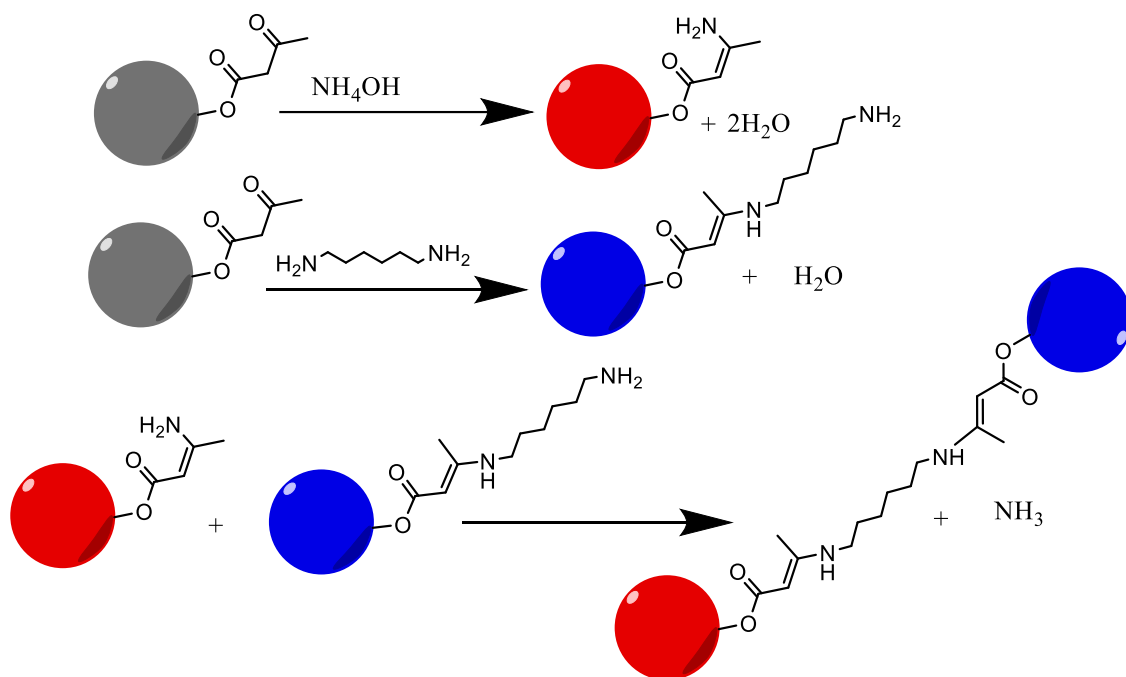
**Figure 10.** Transition from solution to dispersion.

In the last experiment, 18\* (combination of 18.1 and 18.2), although it appears on the same table as the rest of experiments (Table 4), the formulation was slightly altered, but the experiment was carried out following the same procedure as the previous ones. The two differences on the first part of the reaction were that double of the amount of everything was used, as well as the addition of MAEA as a co-monomer, this being 5% of the combined mass of EGDMA and DDT. The rest of the experiment, including the sample taking for the conversion calculation, was done the same way as the other experiments, finalizing the reaction with a precipitation.

The second part of the experiment was the same until the latex was obtained, but once that step had been reached, ammonium hydroxide was added on a 2:1 ratio of mols respect to the MAEA, and was kept stirring for 2 hours, so it reacted completely. The next step consisted of adding HMDA on a 1:1 mol ratio respect to the MAEA,

but as HMDA has 2 amine molecules, half of mols of HMDA were added respect to the MAEA mols, and after making sure that everything was properly mixed it was casted into a silicone mold<sup>17</sup>.

The process of crosslinking can be seen in Figure 11:



**Figure 11.** Crosslinking with MAEA, ammonium hydroxide and HMDA molecules.

Once the latex had dried it was removed from the mold and a sample for the tensile test and GPC were taken. After that, the rest of the film was placed on the oven at 60 °C for 24 hours and more samples were taken for the GPC and the tensile test.

### 3.3. Characterization techniques

#### 3.3.1. Soxhlet<sup>18</sup>

This is a fundamental extraction technique employed to extract specific compounds from solid samples by using a continuous solvent extraction method. The extractor is composed of various parts like the Soxhlet extractor apparatus with some kind of sample holder and a siphon mechanism, a condenser and a heating mantle.

With this technique the gel % present in the sample has been measured, and it has also helped when doing the GPC measurements. It has been done by placing a filter paper with some drops of latex inside the Soxhlet extraction apparatus and connecting this to a flask filled with technical grade THF up to 70% and to a condenser. By heating the flask at the bottom, the THF was refluxed, and then it condensed in the Soxhlet



extractor apparatus, covering the filter paper with the latex drops completely. Then when the THF reached a certain point, the siphon forced it back to the flask.

By repeating the process over a timespan of 24h, at the end only the non-soluble part, also known as the gel, is left in the filter paper and all the polymer is dissolved in the flask. To measure the gel % the filter paper was weighed ( $W_1$ ), then after adding the latex it was left to dry, and the weight was measured again ( $W_2$ ). Finally, after the extraction it was left to dry one more time ( $W_3$ ) and a simple equation was applied to get the result (Equation 1).

$$gel \% = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

**Equation 1.** Equation used to calculate the gel % in the latex.

### 3.3.2. Gel permeation chromatography (GPC)<sup>19</sup>

The GPC is a very useful analytical technique mainly used for the separation and characterization of polymers based on their size or hydrodynamic radius. It measures the relative size of the chains in dissolution, so it must be calibrated before use, as it is not an absolute technique. It is a liquid-solid chromatography, so it contains a solid stationary phase and a liquid mobile phase. The separation mechanism instead of consisting in chemical interactions between the solid phase and the particles, it relies exclusively on the size of the polymer in solution.

It works by using columns packed with beads, and these are full of pores of different sizes. Then a flowing liquid containing the previously dissolved polymer continuously passes through the spaces between the beds, or even through the pores inside them. The separation of the different polymeric chains is based on the difference on the hydrodynamic volume between them. On the one hand, the larger chains have larger hydrodynamic volume, and thus the retention time will be smaller, as they will enter less pores and they will mostly pass through the space between the beds. On the other hand, the small chains will have smaller hydrodynamic volume, so they will enter most of the pores in the beds, making the retention time much larger when comparing it with larger chains. The retention time mentioned before is measured with some kind of detector, that most of the time measures the IR refractive indices.

During this project, the GPC has been used to determine the molecular weights of the polymer, as well as for analyzing the molecular weight distributions, and to do so, the samples were prepared using two different procedures. The samples that did not contain gel were left to dry, and then 5 mg were weighed and placed in a small vial with





1 mL of GPC grade THF to get samples with a concentration of 5 mg/mL. Once it was dissolved, it was filtered (0.45  $\mu\text{m}$  pore size) and added to another vial. Then a drop of toluene was added to it to serve as the reference. The other method was employed when the sample contained gel, and it consisted of performing the Soxhlet extraction mentioned before, and then leaving the THF that was used for the Soxhlet in a vial inside a fume hood during a week to evaporate the THF and leave the polymer at the bottom of the vial. Then the procedure was the same as in the case where no gel was present.

Although the samples were injected by the GPC technician, the setup employed consisted of a Shimadzu LC-20A pump, a Waters 717 autosampler, a Waters 2410 differential refractometer detector as well as three columns (Styragel HR2, HR4 and HR6 with pore sizes ranging from  $10^2$  to  $10^6$  Å). The measurements were carried out at 35 °C using THF (tetrahydrofuran) as the mobile phase at a flow rate of 1 mL/min, and the standards employed to prepare the calibration were of polystyrene.

### 3.3.3. Dynamic light scattering (DLS)<sup>20</sup>

This is a useful technique for characterizing nanoparticles, determine the stability of colloidal dispersions or to analyze proteins and biomolecules by employing light dispersion. In this project, the characterization of the nanoparticles has been the main reason for employing this technique, as it has allowed the measurement of the size of polymeric particles present in the latex.

For preparing the samples a small amount of latex was placed in a disposable cuvette and then it was diluted with Milli-Q water until the inside of the cuvette was almost clear. After that, the cuvette was sealed with a cap, and it was left for 5 minutes to stabilize. Once it was stable it was introduced into the DLS machine (Zetasizer Nano ZS, Malvern Instrument, Zetasizer Software) and the measurement of the particle size was done by selecting the measurement type "generic measurement for latex".

### 3.3.4. Nuclear Magnetic Resonance (NMR)<sup>21,22</sup>

The NMR is a well-known non-destructive technique that can be employed for multiple things such as for analyzing the structure of a molecule when paired with other techniques, as the Fourier Transform Infrared Spectroscopy (FTIR), or it can also be used to follow the conversion of a reaction by doing multiple  $^1\text{H}$ -RMN spectra. The second case has been the one employed in this project.

The NMR machine (Bruker AVANCE 400 MHz) employs a large magnet to create two energy states by aligning the magnetic fields that generate the atoms with its



magnetic field. Then by irradiating the sample with radio frequency waves, the nuclei absorbs that energy, transitioning between different nuclear spin states. The resonance frequency at which these transitions take place depends on the magnetic environment of each nucleus, influenced by the surrounding electronic environment, generating differences in the shielding and, consequently, creating different chemical shifts. The different chemical shifts give the possibility to distinguish different nuclei depending on their environment<sup>19,20</sup>.

In the case of this project the signals of the vinyl bonds of EGDMA have been followed to determine the conversion, and for the internal reference the signal of toluene ( $\delta=7.0-7.5$  for both solvents)<sup>23</sup> has been used. In the case where toluene was already present in the media nothing was done, but when no toluene was employed during the reaction a small amount was added (5% concentration respect the final volume). On top of the previously mentioned, all the samples were prepared with a concentration of 40-50% respect to the solvent.

On top of the mentioned, is important to note that in the case of analyzing the conversion of solution polymerization deuterated chloroform was employed, whereas in the case of the polymerizations carried out in miniemulsion, deuterated acetone was employed, as it is miscible with water present in the sample, that was not removed because the signals of water ( $\delta_{\text{Acetone-d}}=2.84$ )<sup>23</sup> did not interfere with the ones of vinyl bonds ( $\delta=5.5-6.5$  for both solvents)<sup>7</sup>.

For calculating the conversion, the areas of the vinyl bonds mentioned before were measured by using the toluene signals as an internal reference, and then two simple equations (Equation 2 and 3) were applied by comparing the areas before the reaction with the ones during or after the reaction and considering the toluene concentration present in the sample.

$$[\text{Vinyl bond}] = \frac{(CPH)_{\text{vinyl bond}} \times [\text{Tol}]}{(CPH)_{\text{Tol}}}$$

**Equation 2.** Equation for calculating vinyl bond concentration.

$$\text{Vinyl Conversion}(\%) = \frac{[\text{Vinyl bond}]_0 - [\text{Vinyl bond}]_t}{[\text{Vinyl bond}]_0}$$

**Equation 3.** Equation for calculating the conversion of the Vinyl bonds.



### 3.3.5. Differential scanning calorimetry (DSC)<sup>24</sup>

The DSC is a thermoanalytical measurement that can be performed on many different types of materials. It is mainly used to determine the melting and crystallization temperatures, as well as the glass transition temperature, which is the main reason behind the use of this technique during this project.

During the measurement, a sample of 3-10 mg is placed in the DSC machine (DSC Q 2000, with QSeries as software) inside a hermetic pan, and another empty pan is also inserted in the machine to serve as a reference. Then both pans are heated, and the amount of heat required to keep both pans at the same temperature is measured. When phase transitions take place, a change in heat required to keep both pans at the same temperature takes place. The reason behind that change, is the fact that transitions can be exothermic or endothermic. The temperature range employed was of -80 to 80 °C, with a temperature increase of 10 °C/min and cycles of heating-cooling-heating were performed.

### 3.3.6. Tensile test<sup>25</sup>

Tensile tests are used to study how different materials behave under tension load. Normally, a sample is placed in the machine, while it is being held in place with some clamps, and a tensional force is applied until the sample is broken. It must be stated that through the test the amount of force applied to the sample and the elongation are measured constantly, but to analyze the properties normally a stress-strain curve is plotted by dividing the force by the cross-sectional area to obtain the stress, and by dividing the change in length by the initial length to obtain the strain.

To prepare the samples for the test, the latex can be casted into a mold with the desired shape, or it can be casted into a larger mold and then it can be cut with an appropriate machine. Then after the tensile test machine (TA. HDplus, Stable Micro System, with Exponent as software) is calibrated after which the probe is placed on it, and it starts elongating it at a speed of 4.2 mm/min until it is broken. Once a stress-strain curve is plotted, multiple parameters such as the Young modulus, the yielding point and the strain at fracture have been obtained from it.

## 4. RESULTS AND DISCUSSION

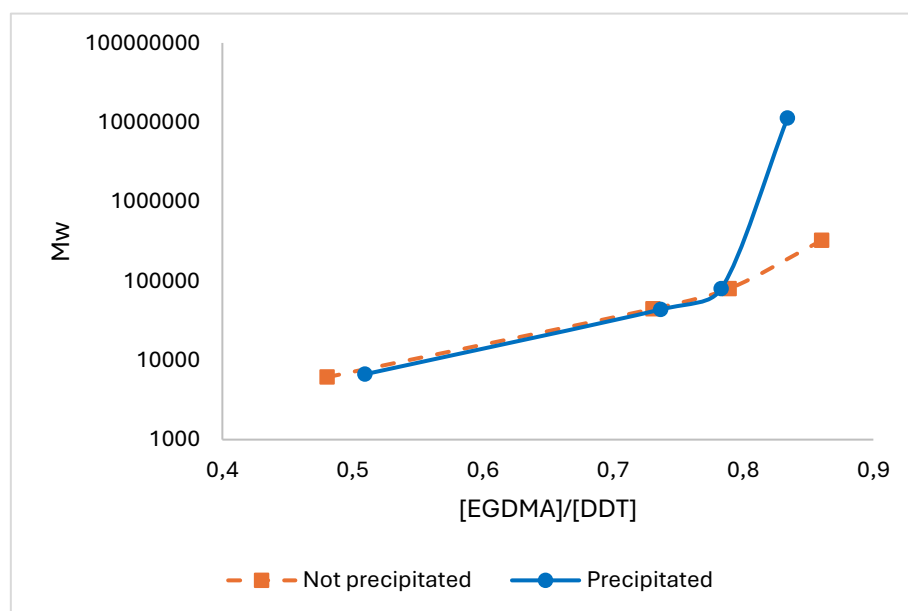
As it has been specified on the experimental part, during this project three main paths have been followed in order to understand the TBRT process and adapt it to be used in dispersed media.

### 4.1. Solution polymerization

When performing the reactions in solution mainly two things have been studied, these being the evolution of the molecular weights when modifying the monomer to chain transfer ratio on precipitated and non-precipitated samples, as well as a comparison of the non-precipitated samples with a model. It must be noted that the conversions of all the reactions have been calculated with the NMR and a conversion of ~99% of the vinyl bonds, which were the ones employed for calculating the conversion was obtained in every reaction.

#### 4.1.1. Analysis of the molecular weight

To study the evolution of the molecular weight, experiments varying the EGDMA to DDT ratio were conducted (Table 1), and the molecular weights obtained in each reaction was plotted against the corresponding  $[EGDMA]/[DDT]$  ratio (Figure 12).



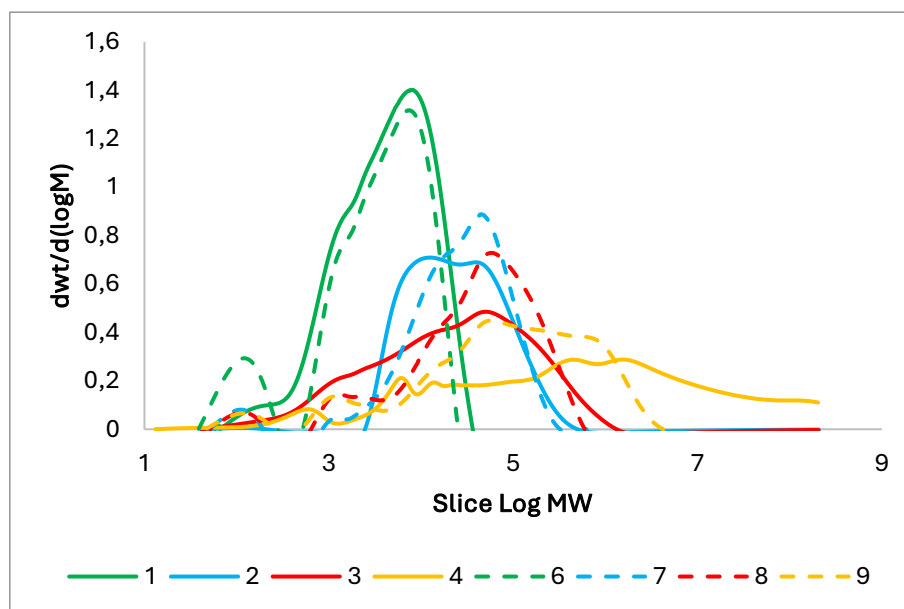
**Figure 12.** Evolution of Mw when changing the  $[EGDMA]/[DDT]$ .

It is clear from the results that increasing the  $[EGDMA]/[DDT]$  ratio, or in other words, reducing the amount of DDT has a direct impact on the molecular weight. This is explained because the DDT is a chain transfer agent, and the radical transfer from the

monomer to the chain transfer agent is really favored, so the Mw ends up decreasing dramatically, as the chains undergo transfer before they can become really large.

It is also interesting that in the case with largest  $[EGDMA]/[DDT]$  ratio there is a bigger difference between the precipitated reaction and the non-precipitated one. This can be explained if we consider that when doing the precipitation, the smallest chains are not precipitated, so the precipitate becomes richer in the higher molecular weight chains, thus increasing the overall molecular weight.

If the molecular weight distributions are analyzed (Figure 13) the same conclusion can be obtained, as the distributions of the experiments with larger  $[EGDMA]/[DDT]$  ratio are overall flatter and appear more shifted to the right, indicating a higher molecular weight.



**Figure 13.** Molecular weight distributions of different reactions (continuous lines represent precipitated samples, whereas the discontinuous lines represent the non-precipitated samples).

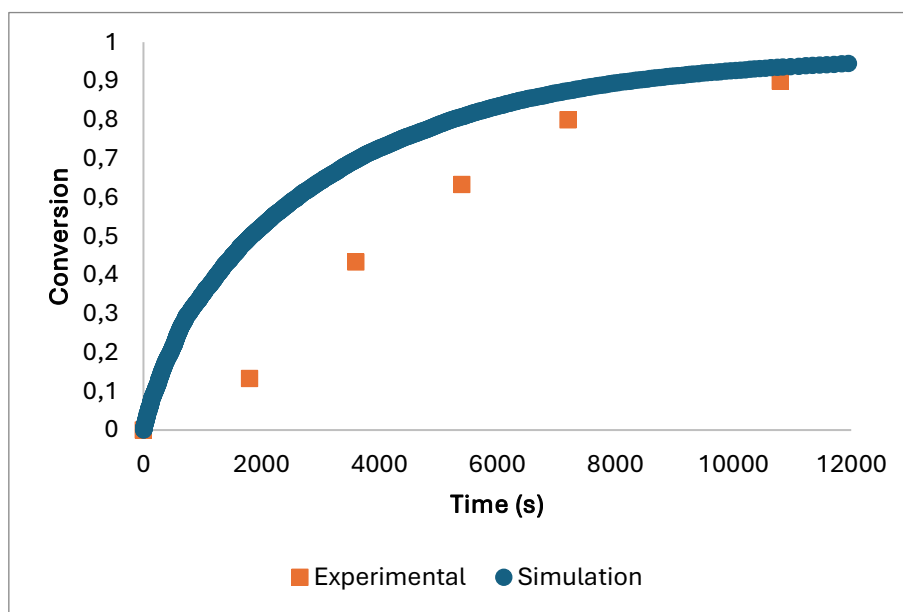
It must be noted that the differences between the molecular weight distributions of the precipitated and the non-precipitated samples can be caused by the results of experimental errors that took place when repeating the reactions and are not entirely caused by the differences in the procedure.

#### 4.1.2. Comparison with model

To better understand the TBRT process, a model based on the kinetic Monte Carlo simulation that was previously employed for analyzing the formation of styrene and divinylbenzene networks was adapted to fit the system that is studied in this project<sup>26</sup>. This was done by substituting the kinetic parameters of the previous

monomers with the ones of EGDMA, and also considering the transfer to chain transfer agent and the subsequent re-initiation of the polymer chain growth on top of the reactions that were also considered for the previous case such as the initiation, propagation and termination reactions. After performing the simulations, experimental data from the non-precipitated reactions was used in order to understand the problems that the model had, aiming to improve it as much as possible, so it represented the reality as close as possible, giving us a better understanding of the TBRT process.

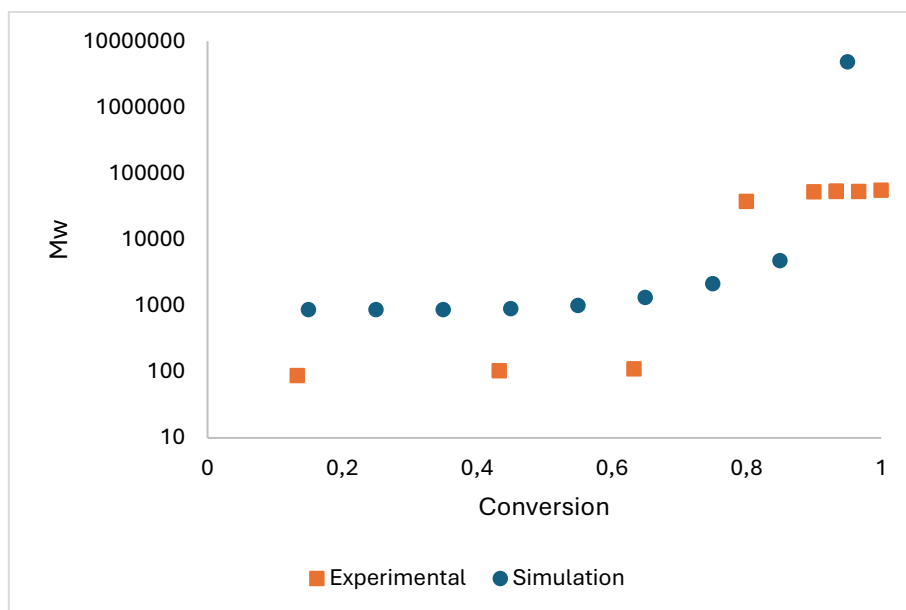
To start comparing the experimental data with the one obtained with the model a reaction was carried out with a  $[EGDMA]/[DDT]$  ratio of 0.8, where samples were taken during the reaction as mentioned in the experimental part, and then the conversion of the vinyl bonds was calculated for each sample as stated in the previous section. Then a simulation was performed using the same  $[EGDMA]/[DDT]$  ratio and both conversions were plotted in the same graph (Figure 14).



**Figure 14.** Evolution of the conversion over time with a  $[EGDMA]/[DDT]$  ratio of 0.8.

The results show that although the tendency is similar in both the experimental and the simulated reactions, they are not exactly the same, meaning that there are some mechanisms present in reality that are not perfectly represented in the simulation.

The next thing that was studied was the evolution of the molecular weight, as the conversion increased during the reaction (Figure 15). It was done by performing GPCs of the previously mentioned samples and plotting the against the previously used simulation.

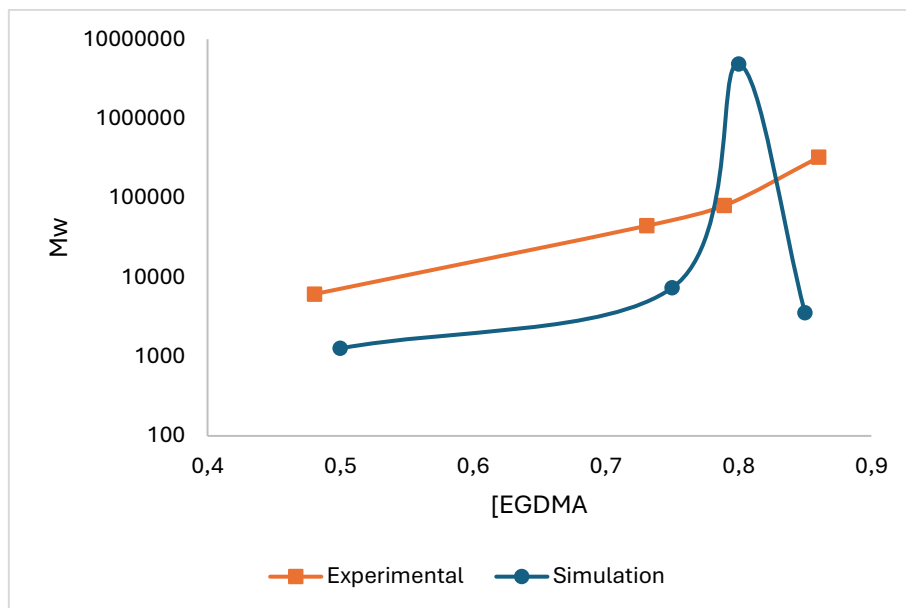


**Figure 15.** Evolution of molecular weight with a  $[EGDMA]/[DDT]$  ratio of 0.8.

From the results it can be seen that in both the experimental and the simulated molecular weights remain constant until a certain point in the conversion is reached, where both molecular weights increase a lot, until they reach their maximum. The mentioned increase can be related to the crosslinking of the system that takes place at relatively high conversion.

As it has happened when analyzing the evolution of the conversion, there are some discrepancies between the experimental and the simulation, that are caused because the simulations predict an exponential increase in the molecular weight when high conversions are obtained, resulting in the formation of gel, whilst in reality no gel point was observed. The aforementioned might be caused because although in reality reactions between high molecular weight, highly branched macromolecules have low probability, the model assumes equal reactivity between all functional groups. In the future this is something that can be included in the model to better describe the experimental results.

On top of the previously mentioned, the effect of changing the  $[EGDMA]/[DDT]$  ratio on the molecular weight was also compared with the model, by plotting the molecular weights obtained during different reactions with the ones obtained from simulating reactions with equivalent ratios and a conversion of 95% (Figure 16).



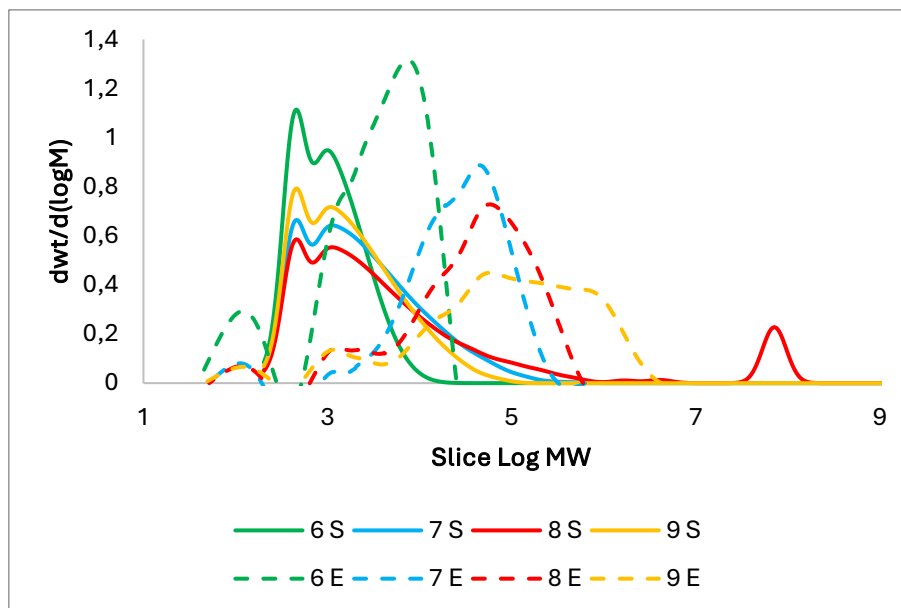
**Figure 16.** Evolution of molecular weight with different  $[EGDMA]/[DDT]$ .

It is clear from the results that although there is a similar tendency on the low  $[EGDMA]/[DDT]$  ratios, the experimental results have a larger molecular weight until the ratio of 0.8 is reached, where the molecular weight in the simulation abruptly increases.

The sudden increase in molecular weight that has been just mentioned is because the model creates a lot of gel, when the reality is that almost no gel forms through the whole reaction. After the increase, there is a drop in molecular weight that is caused because the model creates so much gel that the molecular weight becomes so large, that escapes the processing capabilities of the model.

Finally, the molecular weight distributions obtained experimentally were also compared with the ones obtained with the model, by comparing the distributions obtained experimentally with the simulations with the corresponding ratios and a conversion of 95% as before (Figure 17).





**Figure 17.** Comparison of the simulated (S) molecular weight distributions with the experimental ones (E).

As the results show, in all the cases the distributions obtained from the model are shifted to the left, indicating a lower molecular weight, except in the case where the  $[EGDMA]/[DDT]$  ratios are large, where another peak can be seen at the right, indicating that it has an extremely high molecular weight, as it can be expected from a gel.

In the case of the highest  $[EGDMA]/[DDT]$  ratio there is no peak and the molecular weight appears to be lower than in the other cases, but this is due to it having a molecular weight so large that exceeds the capacities of the model, as it has been stated before.

If the experimental results are compared with the one from the model, they appear more shifted to the right, indicating a higher molecular weight, but an absence of gel, as there is no peak on the extreme right side. As previously commented, these discrepancies are likely due to the incorrect assumptions about the relative reactivities of double bonds in highly branched, high molecular weight polymers.

## 4.2. Miniemulsion polymerization

After performing the miniemulsion as explained in the experimental part, multiple parameters were measured to study how the transition from an exclusively solvent based media to a dispersed media with solvent still present affected the polymer. After that the impact on the properties of the polymer when transitioning to a fully dispersed media without any kind of organic solvent was also analyzed.



To study the differences when performing the previously mentioned changes, experiments with  $[EGDMA]/[DDT]=0.85$  were performed as explained in the experimental part and the results were placed into a table (Table 5).

**Table 5.** Conversion, molecular weight and particle size when performing the reaction with different conditions.

Type of reaction	Conversion of vinyl bonds %	Mw (Da)	Particle size (nm)
Solution	99	245105	-
Miniemulsion with toluene	99	644601	110,5
Miniemulsion without toluene	99	2217999	103,8

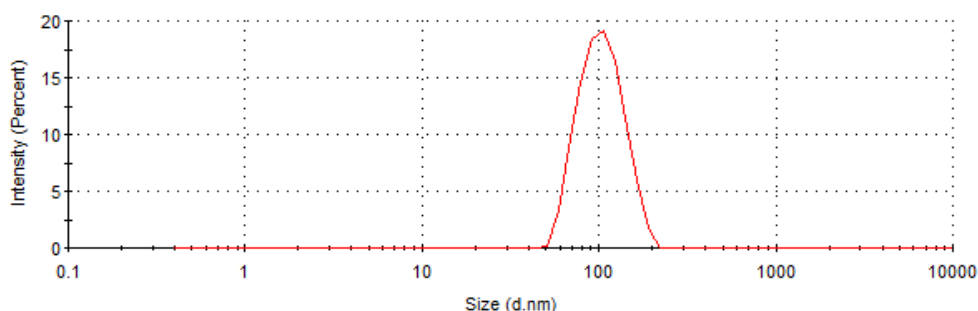
Taking into account that a conversion of ~99% of vinyl bonds has been obtained through the three experiments, the other two characteristics can be properly compared.

When comparing the molecular weight of the different experiments a clear trend that shows an increase in the molecular weight when transitioning from a solvent media to a dispersed media can be observed. This can be easily explained if we consider one of the key factors of emulsion and miniemulsion polymerizations, that is, the compartmentalization, that hinders the termination reactions, and promotes the formation of higher molecular weight polymeric chains.

When comparing the particle size, it must be considered that no particles are formed in solution polymerization. When looking at the other two cases a similar particle size can be observed, indicating that a proper dispersion had formed. Furthermore, the gel fraction was also measured in the case of the miniemulsion without toluene, getting as a result a ~1.2% of gel fraction.

After doing the previous comparisons, a further characterization of one of the experiments was carried out. The experiment that consisted in a miniemulsion without toluene, with a solid content of 30% and a conversion of ~99% was chosen for this.

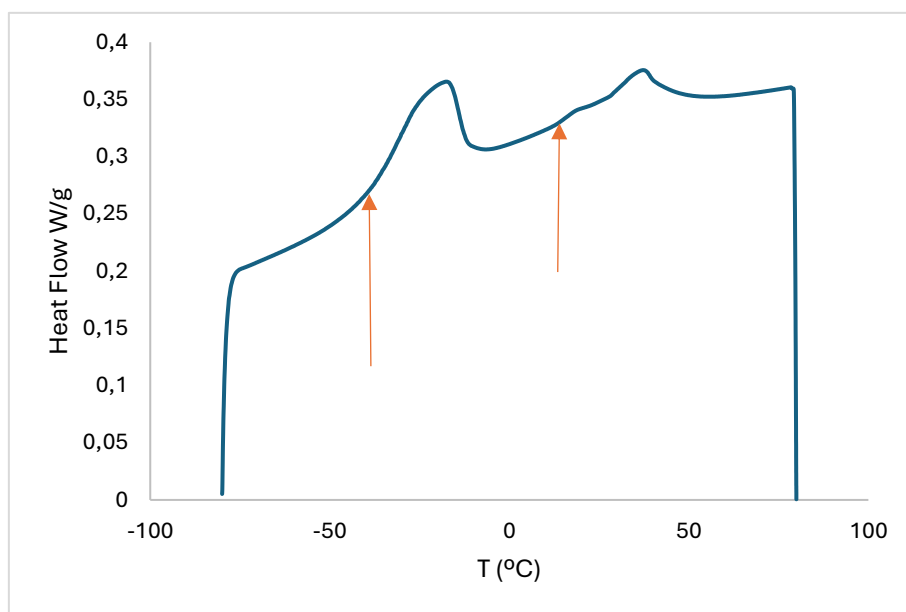
To start with the characterization techniques, the first one to be performed was the DLS, by taking the latex obtained and following the procedure mentioned in the experimental part.



**Figure 18.** Particle size distribution of experiment 14.

In the particle size distribution obtained from the DLS (Figure 18) a single peak can be seen. The presence of a single and narrow peak indicates that most of the particles have a similar size, this being 97.5 nm. This result indicates that the miniemulsion process has been carried out properly, and a good dispersion with homogeneous particles has been obtained.

After studying the particle size of the latex, the next thing was to study the thermal properties of the polymer by performing a DSC as explained previously. After treating the results obtained from the DSC, a graph was plotted by putting the temperature in the X-axis and the heat-flow in the Y-axis (Figure 19).

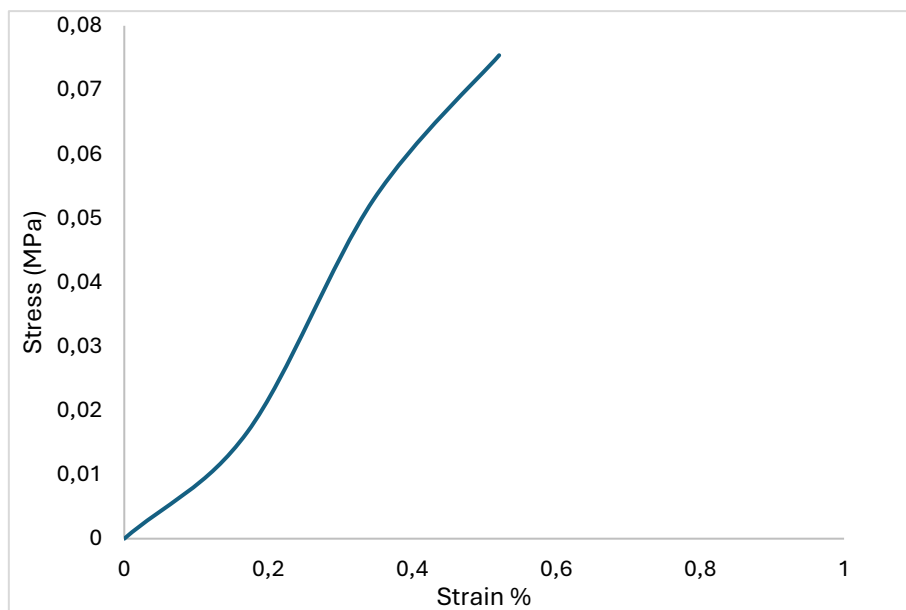


**Figure 19.** DSC of polymer obtained from miniemulsion.

From the results it can be seen that the polymer has two  $T_g$ s (shown by the orange arrows). The main hypothesis for this is that the main polymerization has taken place inside the particles, thus giving a  $T_g$  of approximately  $-40\text{ }^\circ\text{C}$ , in agreement with previous results from solution polymerizations<sup>27</sup> using the same monomer/CTA composition. The origin of the second  $T_g$  located around  $20\text{ }^\circ\text{C}$  is less clear but may be

the result of some polymerization that takes place in particles formed by homogeneous nucleation, resulting in a second site of polymerization where the monomer/CTA composition is richer in EGDMA.

The latex was used to cast a film at room temperature and tensile tests were performed. By doing the test, some stress and strain values were obtained and plotted together (Figure 20).



**Figure 20.** Distribution of the particle size in the latex.

After performing the tensile test, it is clear that the sample is both weak and brittle. This result might be surprising, as the main  $T_g$  is located at around  $-40\text{ }^\circ\text{C}$ , and at room temperature, it should therefore have a more ductile behavior. One hypothesis for this poor mechanical behavior is that, although inside the particles there is a good degree of crosslinking, the highly branched nature of the polymer synthesized by TBRT may result in poor interpenetration between chains of different particles, resulting in poor mechanical properties.

### 4.3. Dispersible polymers by TBRT

In this case a first reaction was carried out in solution in order to synthesize the polymer, following the procedure explained in the experimental part. Then in a second step the polymer was dissolved in acetone, the methacrylic acid molecules present in the chain were neutralized by adding TEA and finally the solution was dispersed in water as stated in the experimental part. To better understand how different variables such as the molecular weight of the polymer obtained in the first reaction, or the presence of a

crosslinking agent affected the properties of the polymer multiple characterization techniques were employed.

First, it must be clarified that although in the experimental part multiple experiments have been carried out with the same [EGDMA]/[DDT] ratios, only the last ones will be shown, the main reason being that these are more relevant because a further characterization has been carried out, giving us a better understanding of its properties.

A comparison of two reactions with conversions of ~99% and different [EGDMA]/[DDT] was made and the obtained molecular weights and particle size, as well as the physical appearance of the latex were compared (Table 6).

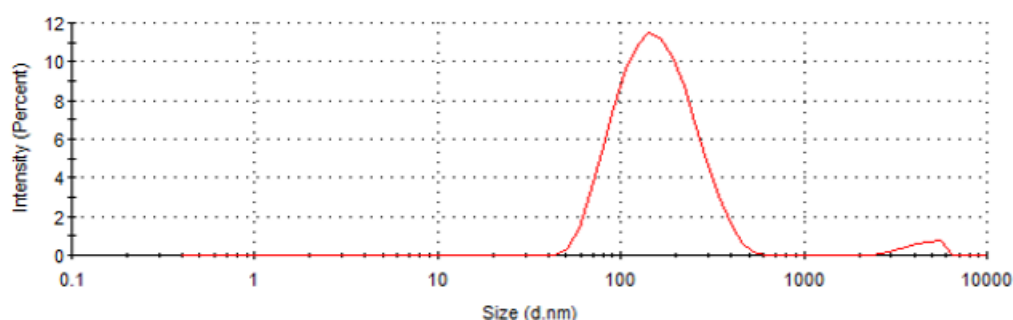
**Table 6.** Comparison of Mw and Particle size when changing the [EGDMA]/[DDT] ratio.

Experiment	Mw (Da)	Particle size (nm)
15*	8770	284.1
17*	4203	130.5

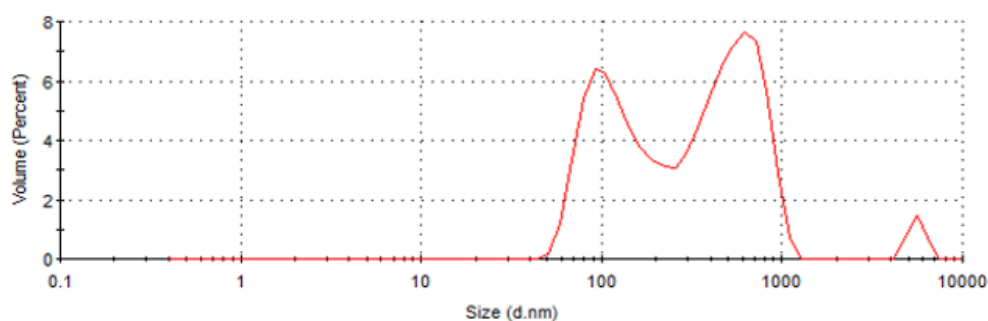
\*The sum of both reactions mentioned in the experimental part (e.g. 15.1+15.2=15\*)

Although at first glance it can be confusing to see how the molecular weight is reduced at the same time as the particle size, it must be considered that the ratio between monomer and CTA is altered between them, containing more CTA in the second one.

The [EGDMA]/[DDT] ratio of experiment 17\* was chosen for a further characterization mainly because the obtained dispersion was more homogenous, both macroscopically and microscopically (Figure 21). The reason was that in the case of experiment 15\* a larger particle size and poly dispersity index were observed (Figure 22), and a homogeneous dispersion was not achieved even after following the whole procedure.

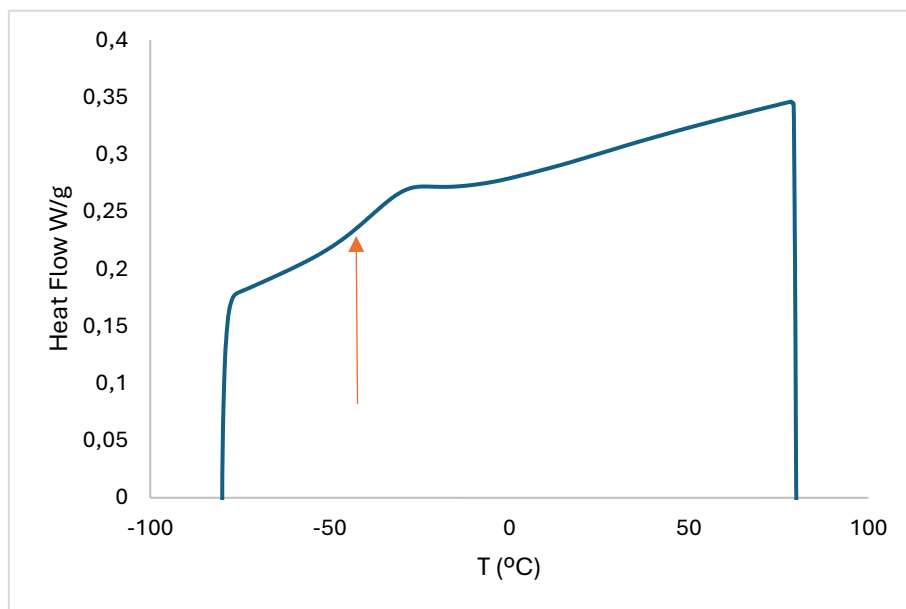


**Figure 21.** Particle size distribution of experiment 17\*.



**Figure 22.** Particle size distribution of experiment 15\*.

Following the previously mentioned, a study of the thermal properties of the selected sample was carried out by performing a DSC as stated previously, similar to the case of miniemulsion (Figure 23).

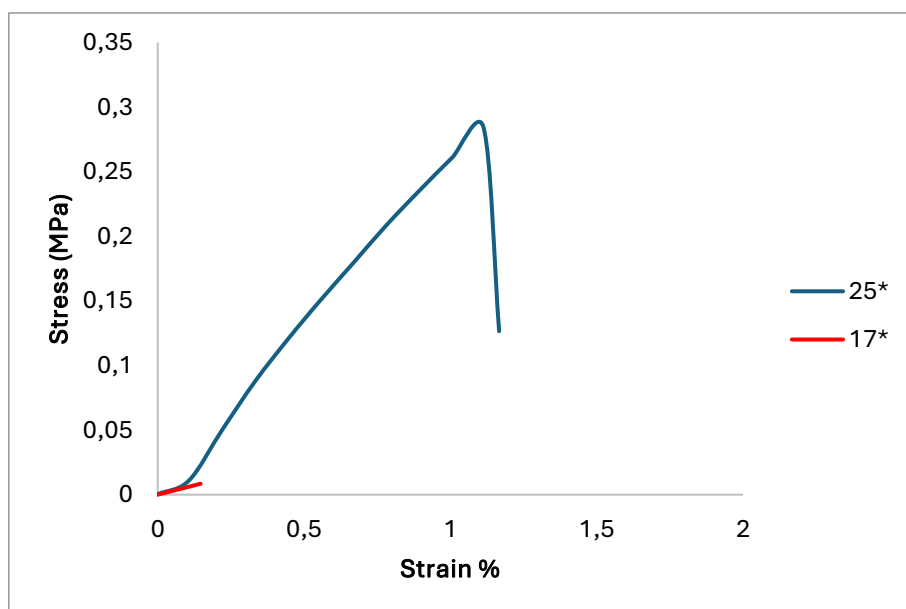


**Figure 23.** DSC of polymer obtained from dispersible polymers.

In this case only a single  $T_g$  can be observed at around  $-40\text{ }^\circ\text{C}$  unlike in the DSC obtained from the miniemulsion (Figure 19). The single  $T_g$  can be explained by considering that the whole polymerization process happens in solution during these experiments, unlike the case of the miniemulsion ones, where even though the majority of the polymerization takes place inside the previously broken monomer particles, a small part can polymerize outside the particles, as explained in the previous part.

After measuring everything previously mentioned, some tensile tests (Figure 24) were carried out following the same procedure as in the case of the miniemulsion, to determine the mechanical properties of the polymers obtained from the dispersible

systems. As the mechanical properties of the polymer obtained from the previously explained route were really weak because of the low molecular weight needed to be able to disperse it properly, some changes in the formulation were done to improve the low molecular weights. Although the [EGDMA]/[DDT] ratio was not altered, MAEA was added in the first step to incorporate the reactive acetoacetoxy group into the polymer. Before film formation one equivalent of ammonium hydroxide and HMDA were added to crosslink the polymer during film formation. Finally, the sample was cured on the oven, so it crosslinked even more, resulting in a higher molecular weight. Although before the sample was cured on the oven looked quite flexible, after the curing process it became more rigid, and some bubbles appeared in the probe (Figure 25).



**Figure 24.** Tensile test results from the dispersible polymer experiments.

As it can be observed in the stress-strain curves, on the one hand, the polymer obtained from the experiment 17\* is a weak and brittle, as it has a strain at fracture that is of 0.14% and a tensile strength of 0.008 MPa. Although the results indicate one thing, it must be stated that when handling the sample, it showed some kind of flexibility, so the poor results might be caused by the extremely low thickness of the sample. On the other hand, the polymer from experiment 25\*, where a crosslinking agent was employed, and was cured on the oven overnight, has a strain at fracture that is of 1.11% and a tensile strength of 0.284 MPa. When comparing both results, the sample that was kept inside the oven for 24 hours, although it had some bubbles (Figure 25), has a much better properties when comparing it with the polymer from experiment 17\*, where no

crosslinking agent was employed, meaning that some crosslinking reactions have occurred.



**Figure 25.** Appearance of the bubbles in the probe after curing.





## CONCLUSIONS

During this project the TBRT process was studied in depth and adapted to be used in dispersed media. To do so, the process was studied in solution and compared with a model. On top of that, reactions were also carried out by miniemulsion and dispersible polymers were synthesized.

The solution polymerization experiments proved that the molecular weight of the polymer could be effectively modified by altering the ratio between the EGDMA and DDT. Higher EGDMA/DDT ratios resulted in increased molecular weights, caused by a decrease in the chain transfer agent, which aids in the termination reactions. Additionally, the lack of precipitation of smaller chains led to a higher molecular weight in some precipitated samples compared to non-precipitated ones, although the difference is not noticeable most of the time. A model was also employed to simulate the TBRT process, showing that while trends between experimental and simulated data were similar, certain real-world phenomena were not fully captured, leading to some differences between the experimental and simulated data.

The transition from solvent-based to dispersed media in miniemulsion showed significant impacts on polymer properties. The molecular weight increased in dispersed media due to compartmentalization, which limits termination reactions. A good final particle dispersion was achieved, with a narrow particle size distribution indicating that the miniemulsion was carried out successfully. The thermal analysis showed two glass transition temperatures, which suggested that the polymerization took place inside and outside the particles. Despite the low  $T_g$  observed, mechanical testing showed the polymer was weak and brittle, probably because of the lack of crosslinking between different particles.

The dispersion experiments showed that a high chain transfer agent proportion was needed in order to get chains with low enough molecular weights, so they could be dispersed in order to create a homogeneous latex. Thermal analysis showed that only a single glass transition was present, indicating that unlike in the case of miniemulsion, the polymerization occurred uniformly. Similar to the polymer obtained from miniemulsion, in this case the mechanical properties also showed a weak and brittle polymer. These mechanical properties could however be improved by crosslinking the chains during film formation.



## ONDORIOAK

Proiektu honetan, TBRT prozesua aztertzeaz gain, hau fase dispartsoan erabiltzeko egokitu da. Horretarako, soluzioan egindako polimerizazioak aztertu eta eredu batekin konparatu ondoren, polimerizazioa miniemultsioan egin, eta polimero dispartagarriak ere erabili dira, horretarako formulazioko hainbat elementu aldatuz.

Soluzioan egindako polimerizazioek frogatu dute polimeroaren pisu molekularra kontrola daitekeela, EGDMAren eta DDTren arteko erlazioa aldatuz. [EGDMA]/[DDT] erlazioa handituz, pisu molekularra handitu egiten da, kate-transferentziako agentearen kontzentrazioak behera egiten baitu. Horrez gain, prezipitazioa burutzean, kate txikiak ez prezipitatzeak batez besteko pisu molekularra handiagoa izatea eragiten du. Hala eta guztiz ere, aipatu behar da kasu gehienetan prezipitatutako eta prezipitatu gabeko laginen arteko desberdintasuna ez dela nabarmena izan. TBRT prozesua simulatzeko eredu bat ere erabili da, eta argi gelditu da, datu esperimentalen eta simulatuen arteko joerak antzekoak izanda ere, esperimentalki gertatzen diren zenbait fenomeno ez daudela guztiz ondo errepresentatuta, desberdintasunak ikus baitaitezke simulatutako datuen eta esperimentalen artean.

Bestalde, disolbatzailetan oinarritutako inguruetik uretan oinarritutako ingurunera egindako trantsizioak eragin garrantzitsuak izan ditu polimeroen propietateetan. Pisu molekularra handitu egin da modu nabarmen batean dispartsoetan konpartimentalizazioaren ondorioz, honek amaiera erreakzioak ematea zailtzen baitu. Partikulak behar bezala sakabanatzea lortu da, partikula tamainaren distribuzio estu bat lortu baita, adieraziz miniemultsioa modu egoki batean eman dela. Horrez gain, analisi termikoak beira-trantsizioko bi temperatura erakutsi ditu, eta horrek adierazten du polimerizazioa partikulen barruan eta kanpoan gertatu dela. Hala ere,  $T_g$  balioa baxua izan arren, proba mekanikoez erakutsi dute polimeroa ahula eta hauskorra dela, ziur asko partikulen arteko saretze faltagatik.

Azkenik, polimero dispartagarriekin egindako esperimentuekin ikusi da kate-transferentziako agentearen kontzentrazio altua behar dela pisu molekular txiki kateak lortzeko, eta polimeroa modu egoki batean dispartsatu ahal izateko. Analisi termikoak erakutsi du beira-trantsizio bakarra dagoela, miniemultsioaren kasuan ez bezala, adieraziz polimerizazioa modu uniforme batean eman dela. Hala ere, miniemultsioetik lortutako polimeroak bezala, kasu honetan ere propietate mekaniko



ahulak erakutsi ditu polimeroak, baina ikusi da propietate hauek hobetzeko aukera dagoela filma sortzen den bitartean kateak saretuz.



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