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DEGREE IN CHEMISTRY

FINAL DEGREE PROJECT

WATERBORNE FILM FORMING AND CRYSTALLINE POLY(THIOETHER) FILMS FOR BARRIER COATINGS

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INDEX

ABSTRACT

The use of (Polyvinylidene chloride) PVDC in food packaging is very widespread due to its outstanding barrier properties. Nevertheless, the environmental concern regarding the release of chloride has promoted the research of more sustainable alternatives. The use of thiol-ene chemistry seemed to be an interesting alternative to achieve the objective. In this work, glycol dimercaptoacetate (GDMA) and diallyl terephthalate (DATP) monomers were used to synthesize poly(thioether)s with the final purpose of obtaining self-supportive consistent films for barrier properties. Therefore, the reactivity of GDMA and DATP and the effect of different parameters on the molecular weight, polydispersity index and conversion were analysed in bulk photopolymerization in order to optimize the synthesis process. The premature polymerization worsened the reproducibility of the reactions so, therefore, 2,5-di-tert-butylhydroquinone (DBHQ) was used to control it. Afterwards, miniemulsion photopolymerization were carried out to obtain latexes to cast and obtain the aimed films. There, different formulations of GDMA:DBHQ were tried to analyse its possible effects on the mechanical properties and the depolymerization process.

LABURPENA

Polibinilideno kloruroaren (PVDC) erabilera oso zabaldua dago elikagaien paketatzean, izan ere, hesi propietate bikainak ditu. Halere, ingurumenera askatutako kloruroak eragindako kezkak aukera jasangarriago batzuen ikerketa bultzatu du. Tiol-eno kimika aukera ona izan daiteke helburu hau lortzeko. Lan honetan Glikol dimerkaptoazetatoa (GDMA) eta Diallil tereftalatoa (DATP) monomeroak erabiltzen dira poli(tioeter)ak sintetizatu eta oztopatze propietate egokiak dituzten film batzuk lortzeko. Hori dela eta, GDMA-ren eta DATP-ren arteko erreaktibitatea eta gainontzeko aldagaiek pisu molekularrean, polidispertsitate indizean eta konbertsioan duten eragina aztertzen da masa polimerizazioan, prozesua optimizatzeko asmoz. Polimerizazio goiztiarrak erreproduzigarritasuna okertzen duenez, 2,5-di-tert-butilhidrokinona (DBHQ) erabiltzen da arazoa kontrolatzeko. Ondoren, miniemultsio polimerizazioa burutzen da latexak lortu eta, hauek lehortuz, nahi diren filmak lortzeko. Bertan, GDMA:DBHQ formulazio anitz erabiltzen dira, amaierako propietate mekanikoetan eta depolimerizazio prozesuan izan dezaketen efektua aztertzeko asmoz.

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDGs)

The United Nations have set in their agenda 17 general objectives that are supposed to achieve by 2030. Those objectives are related to the sustainable development and the fixing of some of the current issues. As chemistry students, the research projects that are being carried out by us should take into account those objectives, in order to collaborate to achieve the mentioned ambitious objectives.

Firstly, the project suits the objective number 2, which the main is the achievement of zero hunger. This could be achieved, as this project will enhance the food security and duration, helping to bring food to everyone.

In addition, this project could be suitable for the objective number 12, which supports the responsible and consumption and production. However, this point is closely related to the objective 13, which tries to promote the sustainability and the respect regarding the environment. This project tries to find out greener alternatives to the commonly used polymers by producing new polymers in dispersed media, where the use of organic solvents is avoided, and the reactions are carried out in aqueous media. Working in dispersed media would promote the carbon footprint reduction, as the production in dispersed media requires lower energies than in solution or bulk to control the temperature during the reaction. Furthermore, as the PVDC is the polymer which this work tried to substitute, the release of chloride would be avoided.

Moreover, this project is sufficiently aligned with the objective 17, which is based on the partnership to achieve the goals. This project has been developed based on the previous work of different researchers, who have been key to complete the work and to understand the basis of it.

1. INTRODUCTION

1.1. POLYMER COATING FOR FOOD PACKAGING

Polymers have a countless number of applications and coating for packaging is one of the most used one. Currently, packaging represents approximately 60 % of total plastic products[1], with a market value of $ 362,9 billion. This number is expected to increase, as according to some predictions, in 2030 global polymer packaging market is expected to reach $562,3 billion, with an annual growth of 5.7% from 2023 to 2030[2]. Besides this constantly increasing market, many detractors appeared against the plastics in the last decades, especially the ones used in packaging. The massive production of these polymeric products has led to a general concern regarding the generated waste and its management. In fact, 340 million tonnes of waste were generated in the last years, which 46 % of them came from packaging plastics[3]. In this context, the production of polymer packaging with lower environmental impact has become an absolute necessity. The polymer coating industry has already shifted towards the synthesis of waterborne products by polymerization in aqueous dispersed media. These processes allow the production of VOC-free coatings, more sustainable than the traditional solvent-borne coatings.

The field of waterborne polymer coatings for food packaging is widely open in terms of innovation and must cope with some specific requirements. The first purpose of such coatings is to keep the food in optimum conditions until the consumption of it. For that aim, food packaging need to present oxygen and humidity barrier properties. Nowadays, the waterborne poly((vinylidene chloride) (PVDC) is the main coating manufactured industrially for food packaging as it presents outstanding barrier properties[4]. Halogen-free alternatives has to be found as the release of chlorine to the environment related to the current use of PVDC food packaging were reported[5]. It is indubitable that numerous problems related to the current management of plastics should be fixed. Nevertheless, forbidding the use of plastic packaging might not be the best way of tackling the problem. Despite the popular thought that plastic wrapping should be reduced significantly or even banned, appropriate packaging systems are key to reduce the waste generation. For instance, around 20-25 % of food might be wasted due to a lack of an effective packaging system[6]. Thus, the alternative may be finding more sustainable ways of producing and managing the plastic package that are produced, instead of banning them.

Currently, one of the big objectives is to produce more environmentally friendly packaging and avoid the drawbacks that the mentioned PVDC has. Firstly, it is important to know which are the main reasons why the current commercial polymers are so damaging for the nature. The main issue related to this kind of debris is their lifetime, as they can last without being totally degraded between 100 and 1000 years[7]. Furthermore, once started to decompose, microplastics are released to oceans and landfills, generating several problems[8–11]. Therefore, one path to face the mentioned setback would be the production of polymeric products that were not so harmful for the environment after their use. Once started to decompose, products obtained by the degradation of the packaging polymers would be environmentally friendlier and easier to manage than the wastes generated from current plastics. In addition, much less time would be required to degradation take place. Although they are encouraging alternatives, competing against the excellent barrier properties and the low production costs of polyolefin polymers is an ambitious challenge.

In the recent work of Elgoyhen et al.[12], thiol-ene sonopolymerization and photopolymerization in aqueous dispersed media have been reported to be a potential alternative to the mentioned PVDC traditional food packaging[12,13]. The authors reported the synthesis of thiol-ene polymers or poly(thioethers) dispersions in water that yielded to semi-crystalline films after water evaporation at room temperature. The films, suited for the intended application in coating, presented low water uptake (Below 12 % after 1 week) and good barrier properties to water vapour with a water vapour transmission rate of 2(g.mm)/(m2.day). In this work, the authors highlighted the high reactivity of the thiol-ene monomers used in the study that react spontaneously without the addition of initiator. This uncontrolled reaction in the thiol-ene system may induce a lack of reproducibility in the final product, and limit its suitability for industrial production. Although this drawback was turned into an advantage in this work, it should be further addressed to fully tap the potential of poly(thioethers) for packaging application.

1.2. THIOL/ENE CHEMISTRY FOR POLYMER SYNTHESIS

1.2.1. THIOL/ENE RADICAL MEDIATED STEP-GROWTH POLYMERIZATION

Many are the studies that have been done around the thiol-ene chemistry in the last decades. Its potential versatility and a great number of advantages provided by these reactions promoted the mentioned increase, producing a wide range of products such as hydrogels or thin films[14].

The polymerization of thiol-enes is unique, as it is the only radical-mediated step-growth process[15]. The mechanism is reported in Figure 1 for dithiols and dienes monomers. For the initiation process, an initiator decomposes either photochemically or thermally, producing some radicals. As the S-H bond is significantly weak, the hydrogen is abstracted by the radical and yilding to thiyl radicals. Afterwards, propagation step takes place, where an Anti-Markovnikov addition (Less substituted carbon) of thiyl into the alkene occurs. Then, transfer reactions occur, where the secondary carbon radical abstract the hydrogen of another thiol monomer, producing again a thiyl radical. The polymerization takes place by alternation of the propagation and transfer step. Finally, termination occurs by radical recombination.

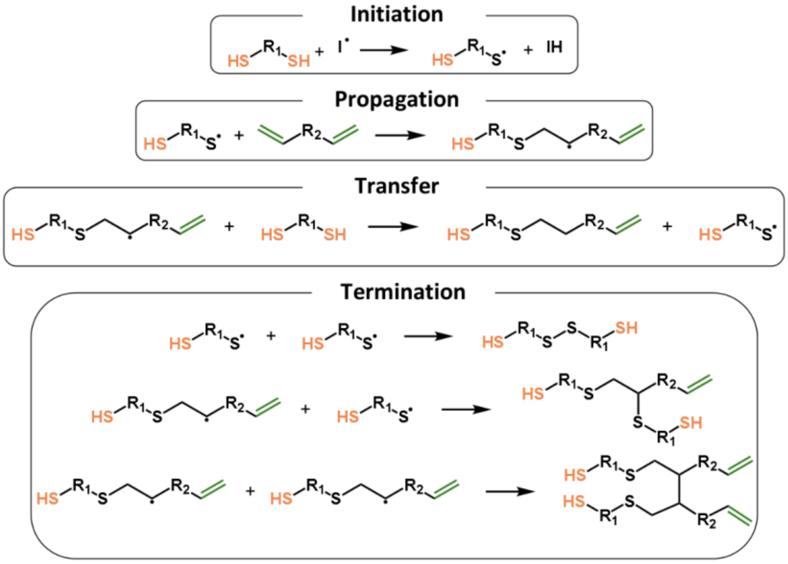

Figure 1. *Step-growth polymerization mechanism of bifunctional thiol and ene monomers*[5].

A long list of benefits could be obtained with this chemistry, such as insensitivity to oxygen and fast kinetics[16]. In addition, the polymer architecture[16–20] can be finely tuned, as bifunctional monomers yield to the synthesis of linear polymers and multi-functional monomers to the synthesis of polymer networks. Moreover, thanks to the mechanism of step-growth polymerization, at 50 % of conversion, there would be dimers in the system, which would lead to a fast monomers consumption. Therefore, the presence of residual monomers at the end of the reaction would almost be inexistent. This is key as the final purpose of the project is to create packaging for food. As there would not be monomers remaining in the final package, the risk of leaking and contaminating the food would be avoided.

However, thiol-ene chemistry also presents some drawbacks. First, the achievement of high molar masses turns quite challenging compared to the polymers synthesized by chain-growth mechanisms. Molar masses are highly sensitive to small stoichiometric imbalances between thiol and ene monomers that could be in the reaction. As the Carothers equation (Eq. 1) shows, for the AA-BB monomers systems polymerized by linear addition with a step-growth mechanism[5], almost perfect molar ratio between the two monomers and almost complete conversion is required to achieve acceptable molar masses. $\bar{X}n$ is the number-average degree of polymerization, p the conversion and r the stoichiometric ratio between both monomers. As mentioned, a small change in the r value would mean a huge change in the final conversion value, affecting directly on the obtained molar masses too.

$$\bar{X}n = \frac{1+r}{1+r-2pr} \qquad \text{(Eq. 1)}$$

As emphasized previously, the instability of the thiol-ene system is one the most significant setbacks that the reaction has. The high reactivity of monomers can lead to premature polymerization. Hence, the reaction starts without the decomposition of initiator, and it is not possible to control properly. As a result, reactions can be remarkably irreproducible, which complicates the design of a reliable reaction. Moreover, as very low radical species are required to trigger the reaction, it is very sensitive to impurities which are capable of generating radicals and abstracting H atoms from the thiol monomer[5]. The instability of thiol-ene system, also known as thiol-ene dark reaction[5], has been reported in the literature. The presence of peroxides and hydroperoxides in the reactional mixture capable to initiate the radical-mediated polymerization seems to be the principal responsible of the spontaneous reaction and can be avoided by using radical scavenger[21]. Thus, for the moment is not possible to scale up the reactions to industrial level, as reproducibility issues are not controlled yet. However, even if there were no impurities in the system, it has been reported that radicals can be generated spontaneously when both monomers are mixed[22].

Furthermore, the obtained films usually present a low glass transition temperature (Tg) and not very high mechanical properties[23].

1.2.2. THIOL/ENE POLYMERIZATION IN AQUEOUS DISPERSED MEDIA

Thiol/ene polymerization has been performed in aqueous dispersed media, as it has been reported to be adequate to obtain coatings after water evaporation[13]. Polymerization processes in dispersed media dealt with some setbacks that bulk or solution polymerization had. The outstanding heat removal capacity and the possibility of obtaining high molecular weight values at the same time as achieving high conversions promoted these techniques. Previous works had shown the possibility of performing thiol-ene photopolymerization reactions in suspension[24], emulsion[25,26] or miniemulsion[12]. Miniemulsion is particularly suited for thiol-ene step-growth mechanism, as it will be explained in the following sections.

1.3. EMULSION POLYMERIZATION

Emulsion polymerization is one of the most used polymerizations in dispersed media. The most used monomers in the synthesis are acrylics, methacrylics, acrylamide, styrene or vinyl acetate. In this process, monomers are dispersed in a surfactant containing aqueous phase, above the critical micellar concentration. Polymerization starts in the aqueous phase (homogeneous nucleation) and after nucleation the process continues inside polymer particles. However, as the surface area of micelles is far bigger than the one of monomer droplets, most of the polymeric chains will be formed by either homogeneous or heterogeneous nucleation[27].

Despite being a very interesting mechanism, there are some limitations. A proper diffusion of monomers in water is key to allow either homogeneous or heterogeneous nucleation. Therefore, highly hydrophobic monomers are inadequate to polymerize by the mentioned mechanism and other processes must be used to produce those kinds of polymers in dispersed media. Miniemulsion polymerization is one of the most promising alternatives to this issue.

1.4. MINIEMULSION POLYMERIZATION

In miniemulsion process monomer droplets are formed thanks to the use of high energy equipment such as sonicator or homogenizers, as presented in Figure 2. The resulting droplets present a lower size, which means a higher surface area that needs to be stabilized by the surfactant. Therefore, surfactant molecules that were stabilizing micelles diffuse in water and stabilize monomer droplets, making the micelles disappear. Unlike in emulsion polymerization, polymers are formed just in particles and not in micelles, so that the hindered diffusion is not a problem anymore. Solving the diffusivity issue is especially interesting for thiol-ene chemistry, where, as mentioned above, stoichiometric ratio is crucial for the polymerization process and the final properties of the product.

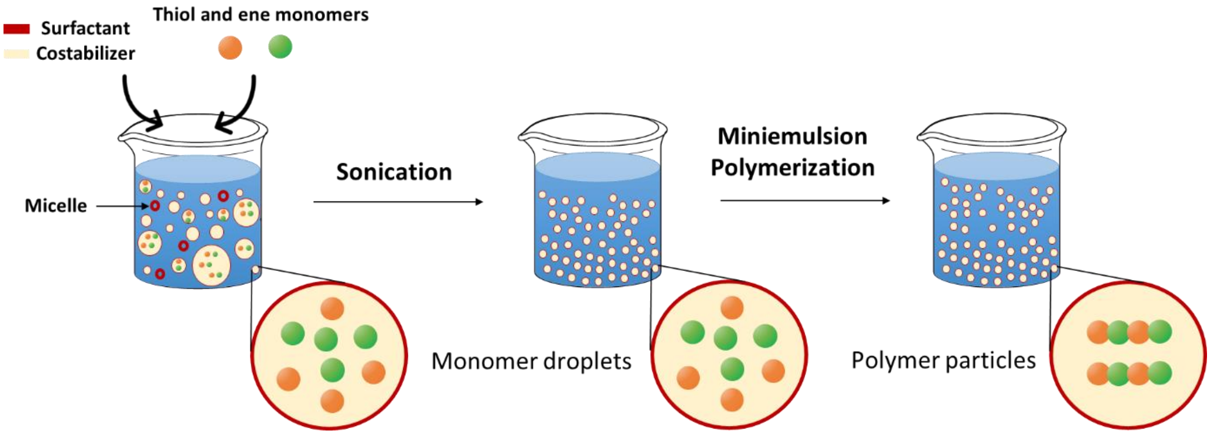

Figure 2. *Thiol-ene miniemulsion polymerization process*[5].

The fact that this process is performed in dispersed media is interesting regarding the sustainability and being respectful with the environment, as stated previously. Furthermore, it seems especially adequate to carry out step-growth processes due to the 1:1 ratio between thiol and alkene monomers, required to obtain high molecular weight polymers. Moreover, using a photoinitiated process is suited for the miniemulsion process, as the light penetration is better than in other cases because of the lower droplet size than in emulsion process for example.

Nevertheless, miniemulsion polymerization has some other drawbacks such as the requirement of a sonication step to obtain the small droplet, which would increase the final cost of the process. In addition to the surfactant, other stabilizing agents like costabilizers could be used to control diffusional degradation (Ostwald ripening) and coagulation and, hence, improve the mentioned instability[27]. Hexadecane is one of the most used costabilizers, although the low compatibility with some monomers and the environmental concern due to its presence in the final latex would make preferable the removal of those components. Moreover, relatively low solid contents and significant surfactant concentrations are required to obtain small droplet sizes, which is not worthwhile enough from an industrial viewpoint.[28]

1.5. FILM FORMATION PROCESS

The film formation process of a polymer dispersed in water consists of the evaporation of the water, obtaining a continuous polymer layer in the end. As shown in Figure 3, the process can be divided into 3 main steps[29].

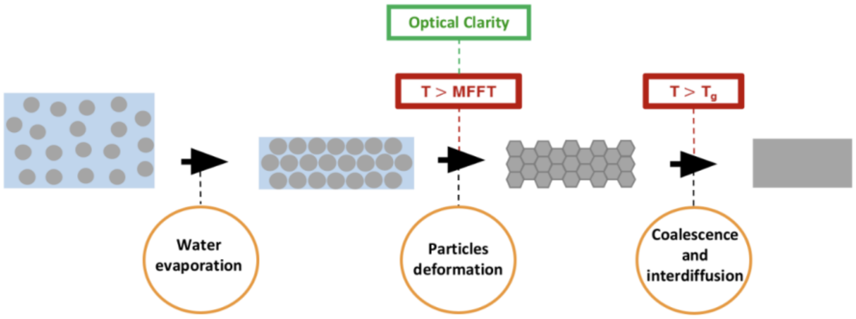

Figure 3. *Film formation process steps*[5]*.*

Firstly, the water of the latex starts to evaporate, making the polymer particles get closer to the adjacent ones. Afterwards, and above a certain temperature known as the minimum film formation temperature (MFFT), particles start to deform until a continuous film without cavities is formed. At this point, no water remains in the film which becomes transparent, and the mechanical properties are meaningfully poor. Finally, above the glass transition temperature (Tg) of the polymer coalescence takes place, and the particles lose their integrity. Some interdiffusion of the polymer chains through particles takes places due to Brownian motion, providing with some physical entanglements and making the film consistent. This last step is determinant in the final properties of the film.

In case of having soft latex particles, when working with polymer that presents a low Tg, the interdiffusion of polymer chains can efficiently occur at room temperature. In spite of that, too soft particles would generate soft, tacky, and poor mechanical properties films. In the other way, if the particles are too hard (with polymer with high Tg), the films should be dried at high temperature for the polymer chains to efficiently interdiffuse and form a consistent film. So, obtaining a film will depend on the glass transition temperature (Tg) of the polymer and the conditions at which the film should be casted.

2. OBJECTIVES

Following the work of Elgoyhen et al., the main objective of this work is to obtain waterborne thiol-ene coatings that can be used as food packaging. For that aim, the dithiol monomer glycol dimercaptoacetate (GDMA, Figure 4) and diallyl terephthalate (DATP, Figure 4) has been selected as they have been reported to form films for coating applications[12].

Figure 4. *Chemical structure of the monomers GDMA and DATP*

In a first part, the lack of stability of the system GDMA-DATP is addressed, as it should be overcome in order to develop a solid and reproducible synthesis process. The spontaneous reaction of GDMA and DATP was first studied in bulk conditions in order to understand the reactivity of both monomers and try to find the most optimum conditions for performing later the reaction in dispersed media. The effect of reaction time and photoinitiator concentrations of the final molecular weight (Mw) of GDMA-DATP polymer were examined.

The use of radical inhibitor 2,5-di-tert-butylhydroquinone (DBHQ) was chosen to prevent the spontaneous reaction and improve the reproducibility. The effect of DBHQ on the final Mw was investigated.

Once the reactivity between both monomers was understood and the effect of different parameters were studied, the reactions were carried out in dispersed media, specifically in miniemulsion process. The obtained films were characterized by different techniques in order to evaluate the water uptake, or the effects of DBHQ on the final mechanical properties or the depolymerization.

3. EXPERIMENTAL SECTION

3.1. MATERIALS

Ethylene glycol bis-mercaptoacetate (GDMA, 95%) was gently provided by Bruno Bock Chemische Fabrik GmbH & Co. Diallyl terephthalate (DATP, 98%), Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO, >98 %), and Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (TPO-Li, >98 %) were purchased from TCI. Used without any modifications. 2,5-Di-tert-butylhydroquinone (DBHQ, >99%) was acquired from Acros organics and with >99% purity. Sodium Dodecyl sulfate (SDS, >98,5 %), was aquired from Sigma. All chemicals were used as received, without further purification. De-ionised water was used as dispersant for miniemulsion polymerization.

3.2. BULK PHOTOPOLYMERIZATION

Bulk photopolymerizations were carried out in 2 mL vials, where GDMA and DATP monomers were mixed with a targeted 1 : 1 stoichiometric ratio. The photoinitiator TPO was added to the monomer mixture, with different weight percent (w%), based on the monomers mass. The bulk formulations with different amount of photoinitiator and the calculated stoichiometric ratio are listed in Table 1.

Table 1. *Experimental reactants ratios of bulk polymerization experiments*

Reaction	m_{GDMA} (g)	m_{DATP} (g)	m_{TPO} (g)	m_{DBHQ} (g)	GDMA : DATP mol ratio	GDMA:TPO mol ratio	TPO (w%)	GDMA:DBHQ mol ratio	TPO:DBHQ mol ratio
B1	0,5263	0,6074	0,0026	-	1 : 1,022	1 : 0,003	0,23	-	-
B2	0,5230	0,6019	0,0031	-	1 : 1,014	1 : 0,004	0,27	-	-
B3	0,5299	0,6006	0,0061	-	1 : 0,998	1 : 0,007	0,54	-	-
B4	0,5222	0,5865	0,0056	-	1 : 0,989	1 : 0,007	0,50	-	-

B5(1)	0,5194	0,6051	0,0057	-	1 : 1,026	1 : 0,007	0,51	-	-
B5(2)	0,5268	0,5982	0,0059	-	1 : 1,000	1 : 0,007	0,52	-	-
B6(1)	0,5243	0,5905	0,0061	0,0011	1 : 0,992	1 : 0,007	0,55	1 : 0,002	1 : 0,283
B6(2)	0,5250	0,6073	0,0059	0,0011	1 : 1,019	1 : 0,007	0,52	1 : 0,002	1 : 0,292
B7(1)	0,5312	0,6051	0,0056	0,0027	1 : 1,003	1 : 0,007	0,49	1 : 0,005	1 : 0,756
B7(2)	0,5401	0,6185	0,0062	0,0027	1 : 1,009	1 : 0,007	0,54	1 : 0,005	1 : 0,682
B8(1)	0,5253	0,6061	0,0053	0,0053	1 : 1,016	1 : 0,006	0,47	1 : 0,010	1 : 1,567
B8(2)	0,5251	0,6052	0,0059	0,0053	1 : 1,015	1 : 0,007	0,52	1 : 0,010	1 : 1,408

The mixture was stirred for 3 minutes to fully dissolve the TPO, and subsequently exposed to UV light for 1 hour under stirring in the UV chamber.

3.2. MINIEMULSION PHOTOPOLYMERIZATION

The next step was the performance of photopolymerization reactions in miniemulsion. Same bifunctional monomers were used but other elements were added. Table 2 gathers the data about used reactants and ratios.

Table 2. *Experimental reactants ratios of 20 % solid content attempts in miniemulsion.*

Reaction	**m_{GDMA} (g)**	**m_{DATP} (g)**	**m_{TPOLi} (g)**	**m_{DBHQ} (g)**	**GDMA : DATP mol ratio**	**GDMA:TPO mol ratio**	**TPO (w%)**	**GDMA:DBHQ mol ratio**	**TPO:DBHQ mol ratio**
M1	6,3158	7,1701	0,0651	-	1 : 1,001	1 : 0,008	0,48	-	-
M2(1)	6,3056	7,1624	0,0652	0,0126	1 : 1,000	1 : 0,008	0,48	1 : 0,002	1 : 0,267
M2(2)	6,3205	7,1765	0,0656	0,0122	1 : 1,000	1 : 0,008	0,49	1 : 0,002	1 : 0,246
M2(3)	6,3141	7,1731	0,0659	0,0135	1 : 1,001	1 : 0,008	0,49	1 : 0,002	1 : 0,271
M3	6,3135	7,1798	0,0654	0,0389	1 : 1,002	1 : 0,008	0,48	1 : 0,006	1 : 0,787

M4	6,3205	7,2013	0,0655	0,0640	1 : 1,004	1 : 0,008	0,48	1 : 0,010	1 : 1,293
M5	6,3253	7,1855	0,0654	-	1 : 1,001	1 : 0,008	0,55	-	-

20 wt% of solid content miniemulsion based on the monomers GDMA and DATP were prepared. The aqueous and organic phases were prepared independently in two different beakers. Regarding the aqueous phase, water and SDS were mixed and stirred for few minutes. The organic phase was prepared by mixing, GDMA and DBHQ in a first step. In that way, the formation of radicals by GDMA can be prevented. Afterwards, DATP was added to GDMA, and the organic phase was kept stirring 3 minutes. Once both phases were stirred, organic phase was poured into the aqueous phase. Subsequently, the dispersion was introduced in the sonicator with the purpose of creating small, dispersed droplets into the aqueous phase. The sonication was carried out using a Branson digital sonifier. Sonication was performed for 5 minutes, with 1 s on and 0,5 s off pulsed program, with 80 % of amplitude. After the sonication, 0,5 mn/w% TPO-Li photo initiator was added, and the dispersion was introduced in a reactor and placed inside the UV chamber at room temperature and 700 rpm of stirring speed. Photopolymerization process was performed for 1 hour using the UV chamber with at a wavelength of 368 nm with an irradiance of 7wW/cm^2.

3.3. FILM FORMATION

After the poly(thioether) latexes were obtained by miniemulsion photopolymerization, film casting process took place in each reaction with the objective of evaporating the water and obtaining a consistent film. Latexes were poured into silicon moulds and dried at a temperature of 25 °C and a relative humidity of 55 %. Once all the water was evaporated, a couple of weeks were required to have the film in optimum conditions, and then, demould it.

3.4. CHARACTERIZATION

3.4.1 PROTON NUCLEAR MAGNETIC RESONANCE (^{1}H-NMR)

NMR is one of the most used spectroscopic techniques worldwide. This method takes advantage of an intrinsic property of fundamental particles, the spin. As the particles forming the atoms are fermions, their spin values are not entire numbers. The composition of the nucleus is vital to determine its magnetic properties. Atoms which have an even value of protons and neutrons will present a nuclear spin quantum number equal to zero, $I = 0$. Hence, there will not be any angular momentum, and so, neither a magnetic field. Nevertheless, atoms containing an odd number of protons and neutrons, will present $I \neq 0$[30]. Therefore, an angular momentum and magnetic field would appear. The last ones are useful in this technique, as the spin states are sensitive to external magnetic fields. After the samples nucleus being exposed to a big magnetic field, a second alternate magnetic field is applied orthogonally to perturbate the alignment. Finally, the nucleus recovers its original state, and the released energy is collected by a detector. The obtained data will be used to create the final image on the computer screen using Fourier transform[30,31].

During these experiments, NMR was carried out with the objective of calculating the conversion of the reaction. Each reaction had 3 spectra; the one in time 0, the one taken before reaction started and another one after reaction ended. For preparing sample tubes, 20 mg of samples were placed in a vial and 0,5 mL of deuterated Dimethylsulfoxide (DMSO-d^6) were used to dissolve it. The analysis was using the Bruker 400 MHz at 25 ºC.

For calculating the conversions two signals were chosen, one from the DATP monomer and the other from the poly(thioether) molecule. As shown in Figure 5, the proton adjacent to the ester group showed a shifting of 4,81 ppm in the case of DATP monomer. However, once polymerized, the same proton showed a shift of 4,32 ppm[5].

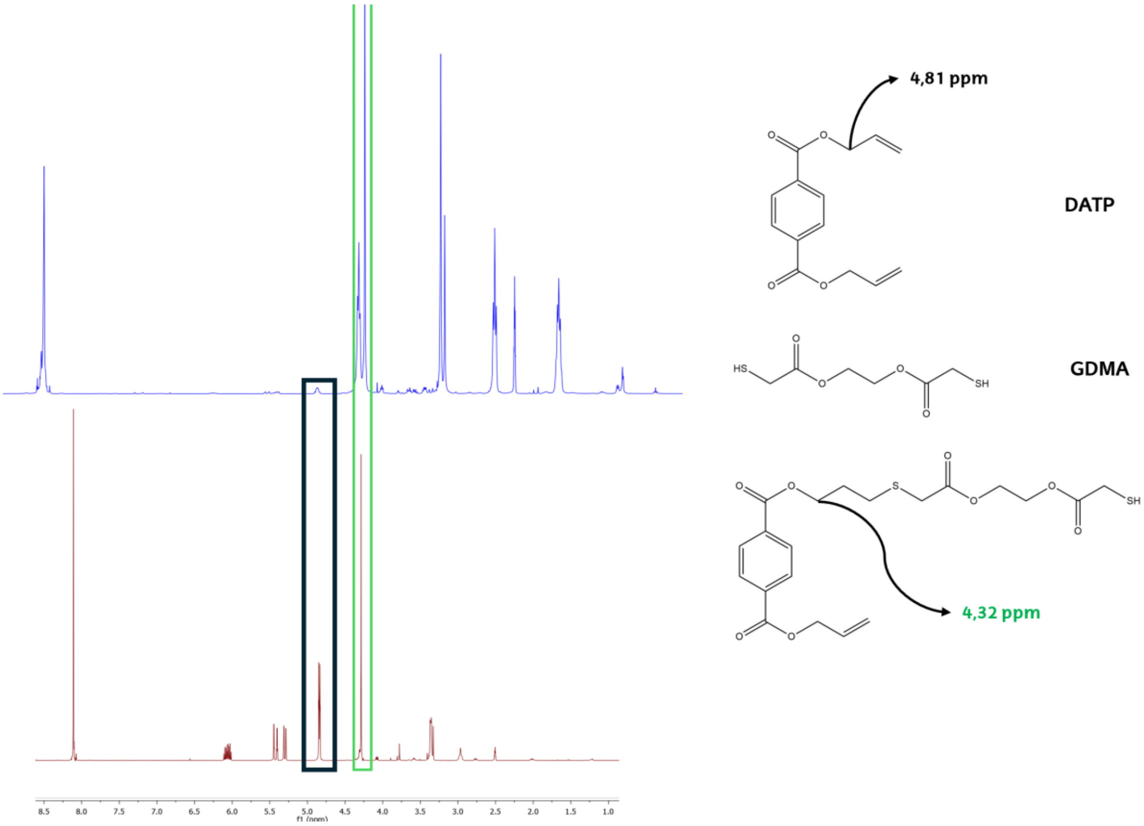

Figure 5. *T0 (Below) and final (Above) GDMA-DATP proton NMR spectra.*

Thus, integrating the mentioned signals, we could calculate the conversion using the equation 2 (Eq.2).

$$\text{Conversion} = \frac{I_{4,32\text{ ppm}}}{I_{4,32\text{ ppm}} + I_{4,81\text{ ppm}}} \qquad \text{(Eq.2)}$$

3.4.2 GEL PERMEATION CHROMATOGRAPHY (GPC)

GPC was one of the most important characterization techniques of all the project. The determination of the molecular weight in the samples was crucial to check the validity of the polymerization process and to follow the previously mentioned depolymerization during the time. The technique is a liquid chromatographic technique, which is based on the time that molecules chains with different hydrodynamic volume will need to go through a porous capillary. Chains with higher hydrodynamic volume will not be able to go through the pores, making a shorter way and hence requiring less time to cross the capillary. Regarding smaller chains, as they can go through the pores, more time will be required to get to the end, as their way will be more tortuous. Once our sample crosses the capillary, the software considers the required time and based on it, a distribution of molecular weights was given.

The GPC machine, which was calibrated with a polystyrene (PS) sample, was equipped with one pump (Shimadzu LC-20AD), three columns (Styragel HR2, HR4 and HR6) and a refractive index detector (Waters 2410). In addition, measurements were carried out at 35 ºC and a flow rate of 1 mL/min.

Samples were prepared by weighting approximately 1 g of dry polymer and dissolved in GPC grade THF, to get a concentration of 5 mg/mL. Afterwards, samples were filtered using a filter with a pore size of 0,45 µm from Scharlau. Finally, 1 drop of toluene, acquired from Scharlab, was added to the solution, which will be the reference to, afterwards, calculate the molecular weight values.

3.4.3 TURBISCAN

Turbiscan was used to check the colloidal stability of the system after the sonication process. Having a colloidally stable system for a certain amount of time was crucial for the development of the reactions, as the system should be at least stable while the photopolymerization process was being performed. Measurements were done using the equipment Turbiscan Lab. A turbiscan analysis was carried out every time that a reaction was done by placing a bit of the dispersion into a vial. The vial was filled ¾ parts approximately and it was placed inside the turbiscan machine. The measurements were done at room T, as the photopolymerization step was done in the same way. Afterwards the software was programmed to make an analysis every 5 minutes for 1 h, and, after that, one analysis every 30 minutes for 3 h. As the photopolymerization step lasted 1 hour, 3 hours of scanning was enough to ensure the stability of the dispersion during the process.

3.4.4 DYNAMIC LIGHT SCATTERING (DLS)

DLS is a light scattering technique, which is based on the measurement of a scattering of a light with a constant frequency. The scattered light is detected at different angles over the time, allowing the determination of the particle size and the polydispersity[32].

In this step, measurements were carried out using a Zetasizer Nano ZS and with Zetasizer software. Samples were prepared by taking one drop of dispersion or latex into a plastic cuvette and diluting it with distilled water until getting a transparent solution. Afterwards, the cuvette was placed inside the Zetasizer and the software made the required measurements to determine the average particle size and the polydispersity index in the dispersion.

3.4.5 CAPILLARY HYDRODYNAMIC FRACTIONATION (CHDF)

CHDF is a chromatographic technique which is used to determine the particle size and its distribution. The distribution is determined by the required elution time, where due to the velocity profile of the fluid, particles of different sizes will have a different average velocity[33].

Samples did not need to be prepared, as the latex was used as it. The measurements were done with a flow rate of 1,4 mL / min at 35 °C and with the detector at 200 nm. The carrier liquid was the 1X-GR500 (Matec) and the samples were diluted to the 0,6 % regarding the total mass. The results were interpreted using the software Matec 2.3 version.

3.4.6 WATER UPTAKE

Water uptake of the poly(thioether) films was measured due to the great importance of it in relation to the polymer chains degradation. The method consisted of preparing 3 samples of the same dimensions and weights. Once the weight at time 0 was determined, the samples were introduced into a bottle full of distilled water. Afterwards, samples were taken out and dried using paper, before measuring their weight again in the balance. Based on the weight difference with respect to the beginning sample, the amount of water absorbed by it was obtained. Firstly, measurements were done every 1 h for 9 hours, in order to ensure how much water was absorbed by the sample. Subsequently, measurements were done 1 per day for 5 days. Then, another measurement was done after 21 days, with the purpose of getting results on a wider range of time. Finally, samples were dried in the oven at 60 ºC and the weights were compared to ensure that there was not any material loose during the process.

3.4.7 TENSILE TEST

Tensile test is used for measuring the mechanical properties of a material, where a sample holded by clamps is subjected to a certain force, deforming and breaking it. Afterwards, stress-strain curves are obtained from where different parameters can be calculated.

To prepare the samples, after being the film totally dried, standardised probes were obtained using a mechanical press. The analysis were carried out with TA.HD plus texture analyzer (Stable Micro Systems Ltd., Godalmming UK) at a strain rate of 0,42 cm/s. Data was processed using the software Exponent.

3.4.8 RAMAN SPECTROSCOPY

Raman spectroscopy is a vibrational spectroscopic technique which is based on the excitation of the molecules using visible or infrared (IR) light. Thus, molecules vibrate and certain energy is released, which is used to determine different structures[34].

To get the analysis, the final polymers were dried and once the water was evaporated, no further treatments were required. Measurements were done using a Renishaw InVia Raman spectrometer, joined to a Leica DMLM microscope.

4. RESULTS AND DISCUSSION

4.1 BULK PHOTOPOLYMERIZATION

Bulk photopolymerization reactions were performed to analyse the effects of some reaction parameters, as it is the simplest system. Starting from more complex systems would add different variables that could affect to the reactivity, making the analysis more difficult. Firstly, the effect of photoinitiator concentration and reaction time were analysed in Mw, PDI and conversion values. The main objective of it was to find out the most optimum conditions to carry out the reaction between GDMA and DATP monomers. Moreover, the reproducibility of the reactions was analysed by making 3 attempts for each of them.

The effect of TPO amount on the final Mw and conversion of GDMA-DATP polymer was investigated. For that aim, different polymerizations were carried out with different photoinitiator concentrations. As it is shown in Figure 6, GDMA and DATP bulk photopolymerization were carried out with TPO concentrations (wt%) of 0,25 %, 0,5 % and 1 %. Herein, the reactional mixture were subjected to UV light for 1 h and it was maintained constant for all the reactions.

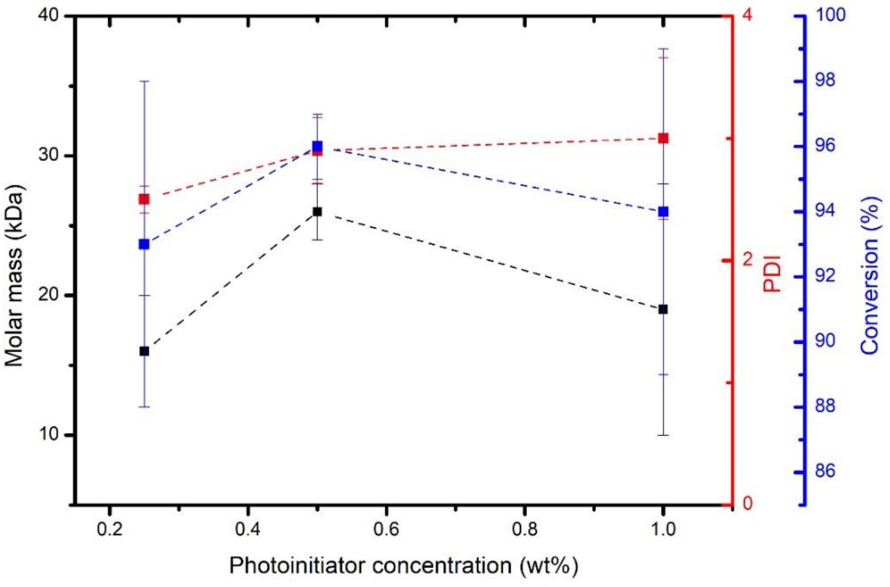

Figure 6. TPO concentration effect on Mw, PDI and conversion.

After analysing results from Figure 6, it seemed that the best results regarding reproducibility were obtained at 0,5 % TPO concentrations, as the error bars were significantly narrower than for the other concentrations. In addition, Mw values increased from 0,25 % TPO concentration to 0,5 %, whereas at 1 % TPO concentration Mw values decreased again. Regarding 1 wt % TPO reactions, more radicals were created which might had a significant impact on the termination by radical recombination, increasing them. Thus, smaller chains may have been created, showing the decrease in Mw values shown in Figure 6. In the case of the 0,25 % and 0,5 % [TPO], it might have not been high enough to have an impact in radical formation, making the increase in termination reactions almost negligible.

The effect of reaction time was investigated by carrying out photopolymerization of GDMA and DATP for 1 h, 3 h and 6 h, using a constant photoinitiator concentration of 0,25 wt % in all the reactions. Figure 7 shows the final results, where there was not any clear trend in any of the analysed parameters with the change of reaction time. The clearest result might be that increasing the reaction time, reproducibility issues were slightly controlled for some parameters, despite being far from a perfectly reproducible reaction. Hence, it seemed that increasing the reaction time no further advantages were obtained, concluding that 1 h of photopolymerization was enough to perform the reaction.

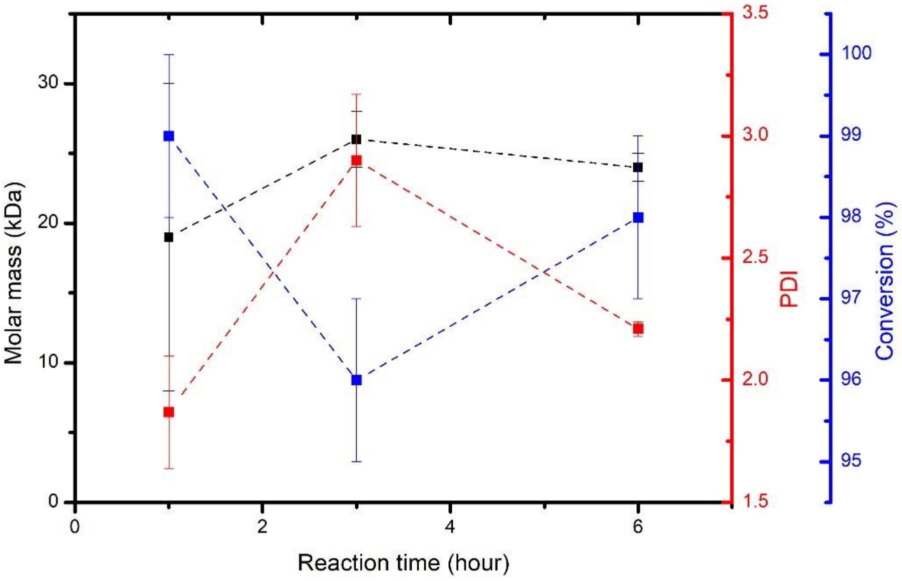

Figure 7. *Reaction time effect on Mw, PDI and conversion.*

As the obtained results after characterization did not show a good reproducibility of the reaction, a phenomenon was taking place, which avoided the correct polymerization process. It has been reported by Elgoyhen et al.[5] that the monomers GDMA and DATP reacts spontaneously, without the addition of a radical inhibitor. In this work, electron paramagnetic resonance measurements evidenced the formation of thiyl radicals in the neat monomer GDMA, capable of initiating the GDMA-DATP polymerization. To further investigate the origin of the thiyl radicals, the authors performed MALDI-ToF mass spectroscopy analysis on the neat GDMA monomers, and reported the presence of dimers, trimers and tetramers. These are known to be oxidation products of thiols, through the formation of disulfide bonds. Raman spectroscopy indeed confirmed the presence of disulfide bonds in the GDMA-DATP polymer backbone. Disulfide bonds are capable of undergoing rapid exchange with thiyl radicals, which could initiate the radical mediated step-growth polymerization when mixed with DATP. The authors proposed a possible mechanism for the self-initiated polymerization between GDMA and DATP, and is reported in Figure 8.

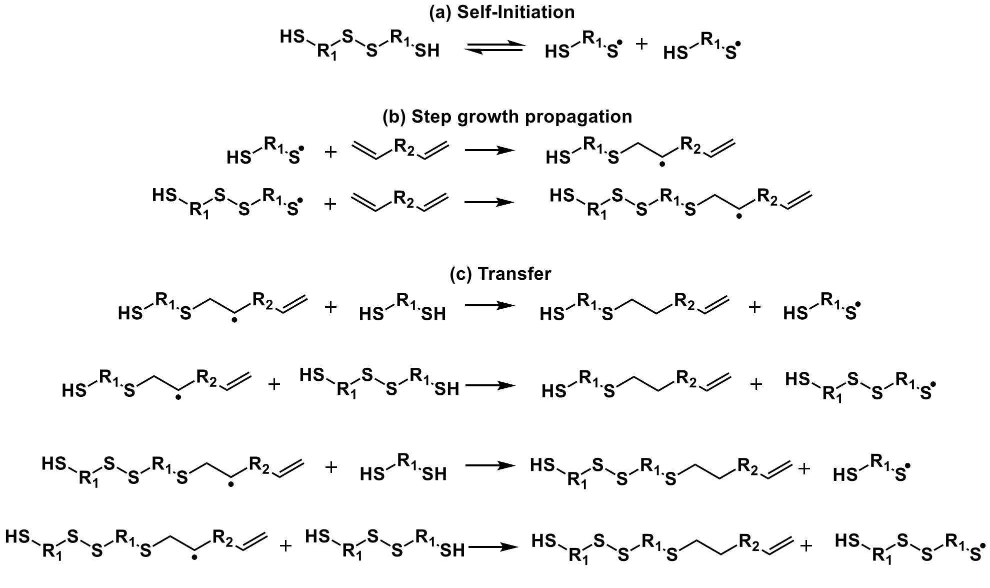

Figure 8. *Proposed mechanism for the self-initiated polymerization between GDMA and DATP*[5].

The unwanted premature reaction and the presence of GDMA oligomers in the reactional mixture that create stoichiometric imbalance between the monomers drastically worsen the reproducibility of thiol-ene reaction, already hard to achieve because of the nature of step-growth polymerization.

However, it has been reported that premature polymerization could be controlled by the addition of a radical scavenger as DBHQ[5]. Therefore, reactions were repeated under same conditions but with the addition of little amounts of DBHQ, necessary to control thiyl radicals formation but not enough to stop the polymerization process initiated by the addition of a photoinitiator. As it had been reported, the GDMA was the responsible for the generation of some thiyl radicals, which afterwards led to the unwanted premature polymerization process. Hence, in practice, DBHQ was first mixed with GDMA to quench thiyl radicals, and later mixed with DATP.

4 reactions were performed; one reference without any radical inhibitor and other 3 with different GDMA:DBHQ molar ratios, as reported in Table 3. As it had been reported, radicals coming from the GDMA may react with each other, giving way to S-S bonds in the structure[5]. Moreover, those S-S bonds seemed to be dynamic. Hence, once the S-S bonds were broken, radical scavengers could catch the radicals and avoid joining again. Our hypothesis was that a reduction of the presence of S-S bonds would occur when increasing the DBHQ amount. A Raman spectrum was done to each sample, with the purpose of checking if the hypothesis made was correct. Figure 9 and Table 3 gather the spectrums and the presence of S-S bonds in each of the reactions.

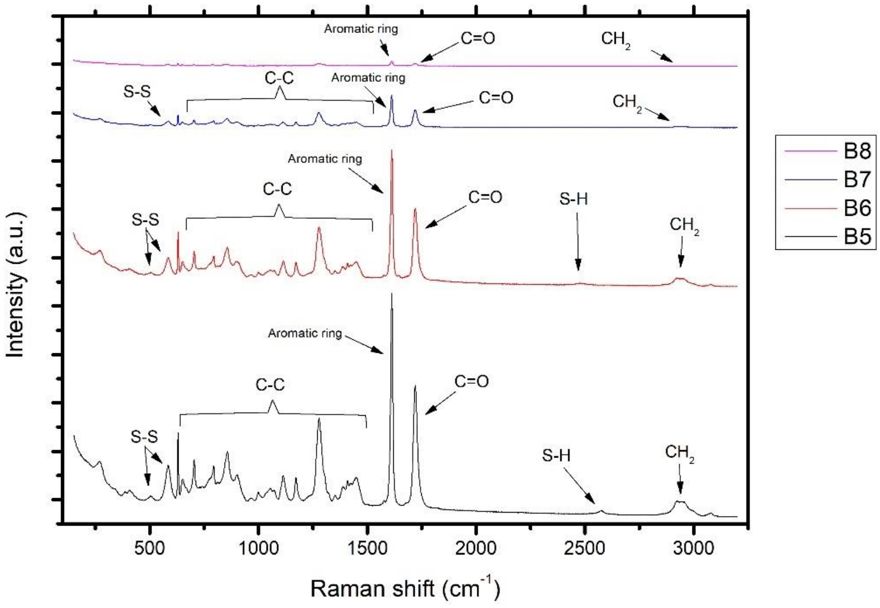

Figure 9. *Raman spectrums of bulk polymerization of GDMA and DATP monomers with different DBHQ ratios.*

Table 3. *Aromatic ring : S-S bond ratios for bulk polymerization reactions.*

Reaction	GDMA:DBHQ	Relative intensities (Aromatic ring : S-S bond)
B5(1)	X	1 : 0,311
B6(1)	1 : 0,002	1 : 0,210
B7(1)	1 : 0,005	1 : 0,205
B8(1)	1 : 0,010	1 : 0,373

After analysing the data above, we could conclude that DBHQ did not have the expected effect, as there was a clear S-S bond presence in all the reactions. Furthermore, increasing the DBHQ ratio regarding the thiol monomer did not show a clear decrease in S-S bond presence along all the formulations. Although B5, B6 and B7 seemed to present S-S bond reduction when increasing the DBHQ ratio, reaction with the highest DBHQ ratio was the one with the more S-S bonds too. Therefore, the formation of disulfide bonds was not controlled by the addition of radical scavenger, even in high amounts.

The final molecular weight values of the bulk photopolymerization with different DBHQ amounts were measured by the GPC to check if the radical scavenger affected the extend of the polymerization process. Table 4 gathers the information about GDMA:DBHQ and TPO:DBHQ molar ratios.

Table 4. *Mw masses for bulk photopolymerization.*

Reaction	GDMA:DATP molar ratio	GDMA:DBHQ molar ratio	TPO:DBHQ molar ratio	Mw (kDa)	Conversion (%)
B5(1)	1 : 1,005	X	X	15	>99
B5(2)	1 : 1,000	X	X	5	94
B6(1)	1 : 1,040	1 : 0,002	1 : 0,283	10	90
B6(2)	1 : 1,019	1 : 0,002	1 : 0,292	15	94
B7(1)	1 : 1,028	1 : 0,005	1 : 0,756	4	70

B7(2)	1 : 1,009	1 : 0,005	1 : 0,682	17	97
B8(1)	1 : 1,015	1 : 0,010	1 : 1,567	9	89
B8(2)	1 : 1,015	1 : 0,010	1 : 1,408	16	96

The obtained results firstly confirmed the irreproducibility of the GDMA:DATP photopolymerization. However, as it in shown in Table 4, GDMA:DATP molar ratio was not accurate enough for a step-growth polymerization process, generating big reproducibility issues. Furthermore, as mentioned previously, different DBHQ proportions were used to try to prevent the spontaneous polymerization but not to stop the radical polymerization initiated by TPO. However, the spontaneous polymerization was not controlled and might have worsened the results, making the bulk photopolymerization even more irreproducible. Regarding the photopolymerization step, it was not hindered by the presence of DBHQ, even if it was added in higher amount than the photoinitiator, as the conversion values were above 90 % almost in all the cases. Thus, more radicals were created apart from the ones coming from TPO decomposition, which DBHQ was not able to neutralize and stop the reaction.

4.2. MINIEMULSION PHOTOPOLYMERIZATION

4.2.1. PREPARATION OF MINIEMULSION

Afterwards, GDMA-DATP photopolymerization in miniemulsion were performed. For that aim, GDMA and DATP monomers were mixed in an aqueous solution containing the surfactant. One reference reaction (M1) was performed without the DBHQ and other 3 reactions were carried out with different GDMA:DBHQ ratios (M2, M3 and M4). Moreover, the reaction M2 was performed 3 times, in order to check the reproducibility. The formulations are detailed in Table 5.

Table 5. *M1,M2,M3 and M4 formulations.*

Reaction	GDMA : DATP mol ratio	GDMA:TPO mol ratio	GDMA:DBHQ mol ratio	TPO:DBHQ mol ratio
M1	1 : 1,001	1 : 0,008	-	-

M2(1)	1 : 1,000	1 : 0,008	1 : 0,002	1 : 0,267
M2(2)	1 : 1,000	1 : 0,008	1 : 0,002	1 : 0,246
M2(3)	1 : 1,001	1 : 0,008	1 : 0,002	1 : 0,271
M3	1 : 1,002	1 : 0,008	1 : 0,006	1 : 0,787
M4	1 : 1,004	1 : 0,008	1 : 0,010	1 : 1,293

In the reactions where DBHQ was added, it was firstly added to GDMA monomer to neutralize the thiyl radicals and, afterwards, DATP monomer was added to them. As it had been reported, the addition of a costabilizer such as hexadecane was not an option due to the GDMA monomer insolubility on it[5]. Afterwards, sonication was performed to get small droplets. As the energy provided by this step was significant, the possible effects were analysed.

Firstly, a proton NMR was done after the sonication step to check if it had triggered the polymerization of GDMA and DATP or if the DBHQ had been able to prevent it. Table 6 collects the obtained data.

Table 6. *Conversion values of M1, M2, M3 and M4 after sonication step.*

Reaction	**GDMA : DATP mol ratio**	**GDMA:DBHQ mol ratio**	**Conversion after sonication (%)**
M1	1 : 1,001	-	95
M2(1)	1 : 1,000	1 : 0,002	90
M2(2)	1 : 1,000	1 : 0,002	86
M2(3)	1 : 1,001	1 : 0,002	85
M3	1 : 1,002	1 : 0,006	92
M4	1 : 1,004	1 : 0,010	88

As observed in NMR results, the energy of the sonication was enough to trigger the polymerization process, obtaining values between 85 % and 95 % of conversion. Although high molar masses are not obtained until reaching close to 100 % of conversion, we could not ignore the fact that the reaction was almost completed after this step. Hence, the reaction was not taking place in the interested step, photopolymerization. Adding DBHQ could not efficiently prevent the polymerization occurring during sonication step. On the other hand, the data in the Table 6 showed that the increase of DBHQ amount regarding the GDMA monomer caused a decrease of the Mw values after the sonication step, which was the main aim. Although the polymerization step occurred in all the cases, when the DBHQ quantity was increased, the polymerization degree was slightly lower. Hence, the DBHQ was acting in the desired way but not as much as wanted.

Increasing DBHQ quantities until controlling the premature polymerization was not a realistic alternative, as the quantities were already significant, and it remains in the final coatings, which is not interesting for the final properties. Although the premature polymerization was a drawback for the miniemulsion photopolymerization process, it had been reported that taking advantage of it, a sonopolymerization process could be performed[12]. Nevertheless, this alternative is not going to be discussed in this work.

Furthermore, the colloidal stability of the dispersions was analysed too, as the dispersion should have been stable at least during the time that the polymerization process was completed. As the extra energy provided by the sonication step might affect the stability, a turbiscan spectrum of each of the reactions was obtained, where the backscattered light was used. Figure 10 is one of the examples of the obtained turbiscan spectra and the rest will be presented in the appendix.

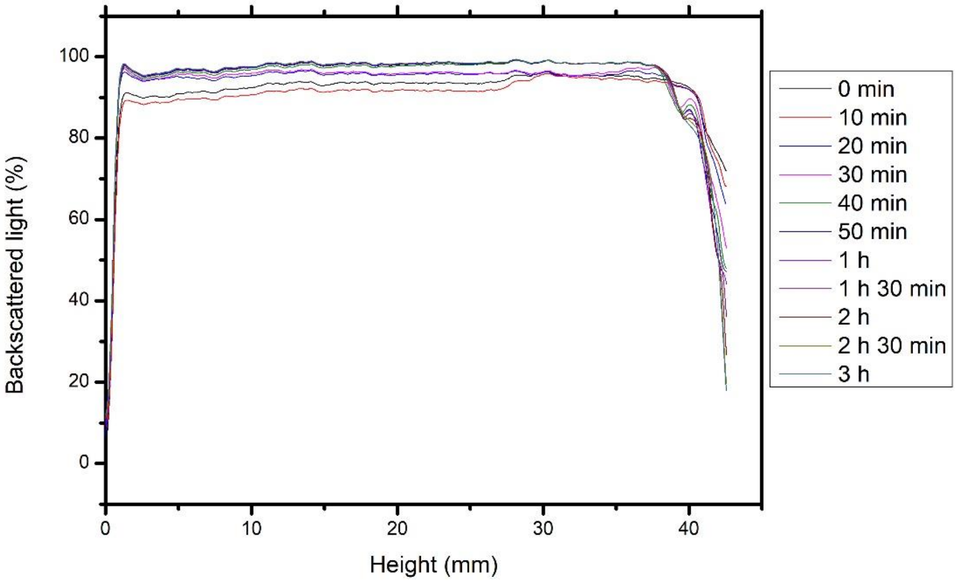

Figure 10. *Turbiscan spectrum of M2(1) reaction.*

After sonication step, colloidally stable miniemulsions were obtained for at least 3 hours, as emphasized by the repeatability of the backscattered signal over time obtained by turbiscan analysis. Nevertheless, as the NMR results showed, the conversion after the sonication was always above the 85 %. Thus, the stability might exist due to the formation of oligomers, which are less prone to diffuse in water, and not because of the intrinsic stability of the dispersion of our monomers in water. Thus, Mw after sonication were analysed by GPC, to confirm the triggering of the reaction due to the applied energy. Table 7 collects the Mw data of M1, M2, M3 and M4.

Table 7. *Mw values of M1, M2, M3 and M4 after sonication step.*

Reaction	**GDMA : DATP mol ratio**	**GDMA:DBHQ mol ratio**	**Mw after sonication (kDa)**
M1	1 : 1,001	-	13
M2(1)	1 : 1,000	1 : 0,002	8
M2(2)	1 : 1,000	1 : 0,002	7
M2(3)	1 : 1,001	1 : 0,002	5
M3	1 : 1,002	1 : 0,006	7

M4	1 : 1,004	1 : 0,010	7

As it was shown in Table 7, significant Mw values were obtained after sonication, which matched with the data obtained by the NMR and turbiscan, as the GDMA-DATP monomer pair started to react. Moreover, it was observed that M1 reaction, which did not have DBHQ presence, had the highest Mw values, whereas the rest Mw values were lower. Thus, these results confirmed that the addition of DBHQ could slightly hinder the polymerization of GDMA-DATP after sonication, but not prevent it.

Afterwards, DLS analysis were performed to each reaction after sonication, with the purpose of obtaining the particle size and check the evolution of this parameter along the different steps of the polymerization. Table 8 collects the particle size data obtained by DLS.

Table 8. *Particle size values of M1, M2, M3 and M4 after sonication step.*

Reaction	**GDMA : DATP mol ratio**	**GDMA:DBHQ mol ratio**	**Particle size after sonication (nm)**
M1	1 : 1,001	-	217
M2(1)	1 : 1,000	1 : 0,002	390
M2(2)	1 : 1,000	1 : 0,002	338
M2(3)	1 : 1,001	1 : 0,002	220
M3	1 : 1,002	1 : 0,006	360
M4	1 : 1,004	1 : 0,010	560

Based on the data shown in Table 8, it was observed that the reaction with no addition of radical scavenger presented the lowest particle size, whereas the reaction with the highest DBHQ amount had the biggest particles by far. That might be caused by the presence of DBHQ, which may affect negatively the colloidal stability of the system. Thus, some coagulation might occurred, increasing the particle size in the reaction with the highest DBHQ amount.

4.2.2. PHOTOPOLYMERIZATION

The dispersions were subsequently subjected to UV light in presence of watersoluble photoinitiator TPO-Li. This additional step yielded to an increase of the Mw, as reported in the work of Elgoyhen et al[12]. Hence, after sonication, GDMA and DATP were still reactive and higher Mw could be obtained. So, after being exposed to UV light, same characterization techniques were performed in the final latex, in order to check the effect that the photopolymerization could have on the dispersion when a sonication was carried out previously.

Firstly, another NMR analysis was performed to the final latex of each reaction to check if the polymerization continued when exposed to the UV light. Table 9 gathers the data comparing the conversion values after sonication and after photopolymerization.

Table 9. *Conversion values comparison of M1, M2, M3 and M4.*

Reaction	**GDMA : DATP mol ratio**	**GDMA:DBHQ mol ratio**	**Conversion after sonication (%)**	**Conversion after photopolymerization (%)**
M1	1 : 1,001	-	95	99
M2(1)	1 : 1,000	1 : 0,002	90	96
M2(2)	1 : 1,000	1 : 0,002	86	93
M2(3)	1 : 1,001	1 : 0,002	85	96
M3	1 : 1,002	1 : 0,006	92	95
M4	1 : 1,004	1 : 0,010	88	96

Based on the data shown in Table 9, it was observed that the conversion values increased in all the cases, which confirmed the thought that the monomers were still reactive. Nevertheless, the reaction without DBHQ (M1) showed the highest value, whereas the reactions with the presence of radical scavenger did not go further than 96 % of conversion. Hence, the DBHQ had a slight effect on the conversion of the reaction but not as high as expected. Moreover, it is important to outline that the GDMA:DATP molar ratio was not as accurate as aimed, complicating the achievement of conversions close to 100 % due to the step-growth mechanism explained previously.

As the data presented in Table 9 suggested that the reaction kept going during the photopolymerization step, an increase in Mw values was expected. In addition, due to the step-growth mechanism of the reaction, very high conversions are required to obtain high Mw values, so that a small increase in conversion might have caused an important increase in Mw. Table 10 compares the Mw data obtained after sonication and after photopolymerization.

Table 10. *Mw values comparison of M1, M2, M3 and M4.*

Reaction	**GDMA : DATP mol ratio**	**GDMA:DBHQ mol ratio**	**Mw after sonication (kDa)**	**Mw after photopolymerization (kDa)**
M1	1 : 1,001	-	13	19
M2(1)	1 : 1,000	1 : 0,002	8	15
M2(2)	1 : 1,000	1 : 0,002	7	12
M2(3)	1 : 1,001	1 : 0,002	5	17
M3	1 : 1,002	1 : 0,006	7	10
M4	1 : 1,004	1 : 0,010	7	13

As it is shown in Table 10, a significant increase in Mw were observed after photopolymerization. It was clear that in the case of M1, the Mw values were higher than in other cases where the DBHQ was added. However, there was no certainty that increasing the DBHQ amount regarding GDMA monomer could proportionally decrease the final Mw values, as the difference on conversions were small but this had a significant effect on the final polymerization degree.

Finally, particle sizes of the final latexes were measured using the DLS, to compare the effect that the photopolymerization could have. Particle sizes after sonication and after photopolymerization were compared in Table 11.

Table 11. *Particle sizes comparison of M1, M2, M3 and M4 after sonication step.*

Reaction	GDMA : DATP mol ratio	GDMA:DBHQ mol ratio	Particle size after sonication (nm)	Particle size after photopolymerization (nm)
M1	1 : 1,001	-	217	184
M2(1)	1 : 1,000	1 : 0,002	390	152
M2(2)	1 : 1,000	1 : 0,002	338	184
M2(3)	1 : 1,001	1 : 0,002	220	163
M3	1 : 1,002	1 : 0,006	360	281
M4	1 : 1,004	1 : 0,010	560	151

Based on the data above, a decrease in particle size after every photopolymerization process was observed. This was an unexpected behaviour, as the particles were expected to remain constant during the photopolymerization process. A secondary nucleation could explain that decrease. New particles might had started to form, decreasing the average size of each of the ones. However, it was an undesired process, as the formation of more nuclei could break the 1:1 molar ratio of the monomers in the particles, hindering the obtention of conversions close to 100 %. Due to the step-growth mechanism of the reaction, high conversions are essential to obtain high molar masses values. To confirm the presence of the mentioned secondary nucleation, CHDF was used. Figure 11 shows the obtained data. The rest of the spectrums are placed in the appendix.

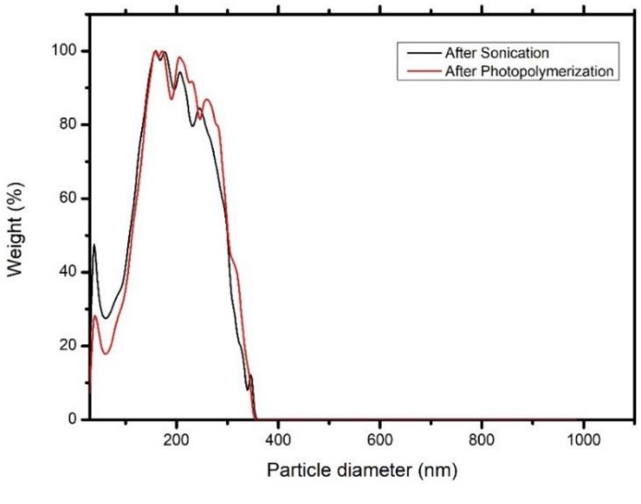

Figure 11. *Particle size distribution comparison after sonication and after photopolymerization in M1 reaction.*

As presented in the Figure 11, the obtained distribution was too wide. Therefore, we could not ensure that there was a secondary nucleation based on the obtained data.

4.2.3. FILM FORMATION

Afterwards, latexes were casted at room temperature to obtain consistent self-supportive films after water evaporation, as GDMA-DATP polymers have a Tg below 0 ºC[5].

After few days, as expected, films were very soft due to their low Tg. After a couple of weeks later films became tougher, as it had been reported, due to the crystallization of GDMA-DATP polymers. As the crystallization is slow, the evolution of films properties too. The films were demoulded after crystallization took place, as otherwise films were too tacky. Afterwards, different characterization techniques such as tensile tests or water uptake were applied to the films to analyse the mechanical properties and check the water absorption, respectively.

Mechanical properties were analysed by tensile test. The reaction M2 was chosen, and two of the three attempts were compared. There was a third attempt which was not added to the graph. Although they were prepared in the same way, the third film showed slightly different properties and defects such as bubbles during its formation process, making impossible the creation of decent probes to perform the test. Figure 12 gathers the mentioned data.

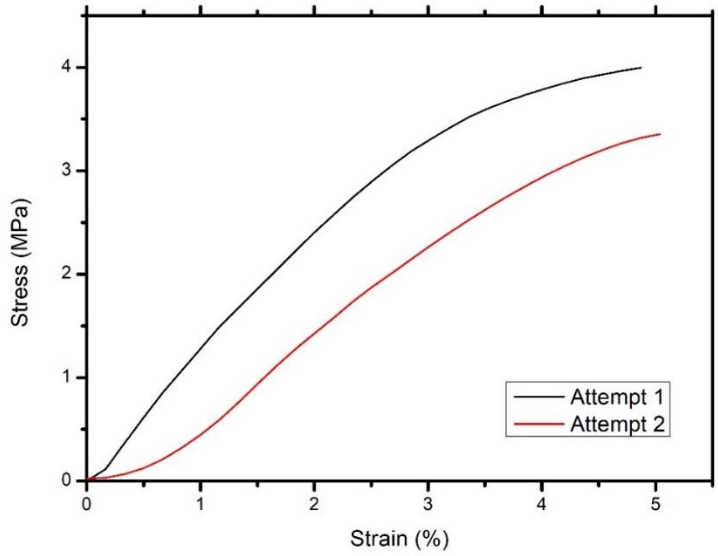

Figure 12. *Tensile test results for M2 reaction.*

The obtained results showed a tensile strength between 3 and 4 MPa and a strain at break around 5 %. The films were not very ductile, but they had an acceptable tensile strength. However, as the difference between both attempts showed, the reactions were not very reproducible.

Afterwards, water uptake was performed to know if the films were absorbing water, which was something that should avoid if the final aim was obtaining films for food packaging. Figure 13 shows the obtained results regarding the water uptake.

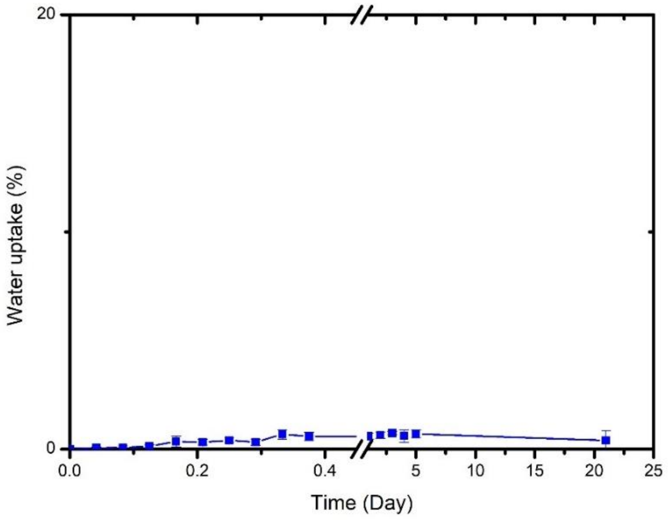

Figure 13. *Water uptake of the M2 film during 3-week period.*

A certain level of water uptake was expected, as there was the presence of surfactants which were able to absorb water. Nevertheless, based on the obtained data, we could determine that the water absorption after 3-week period was negligible, as the increase in weight was below the 1 %. Considering that the samples were prepared from the M2 film, we knew that the film was very slightly depolymerized. Therefore, the change in weight was almost exclusively due to the water uptake behaviour of the film. So, the results regarding this parameter were positive, as the targeted behaviour was achieved. The reason why these results were obtained might be the presence of a crystalline structure, which might block the water penetration into the structure.

4.2.4. DEPOLYMERIZATION

After characterizing the obtained films achieved by the addition of different GDMA:DBHQ ratios to the reaction, as shown in Figure 14, depolymerization was observed experimentally in some of them.

Figure 14. *Starting from the left; M1, M2, M3 and M4 films.*

Thus, the evolution of Mw was analysed during the time. As the thiyl were supposed to form after a S-S bond breakage, DBHQ could catch those radicals. Therefore, increasing the DBHQ molar ratio, a faster depolymerization was expected, as once reacted, the radicals would not be able to form new chains. In addition, Mw values were taken for films and latexes, as the evolution of them was expected to be slightly different due to the presence of water in latexes case. Figure 15 gathers the evolution of the Mw values during the time for reactions with different DBHQ quantities.

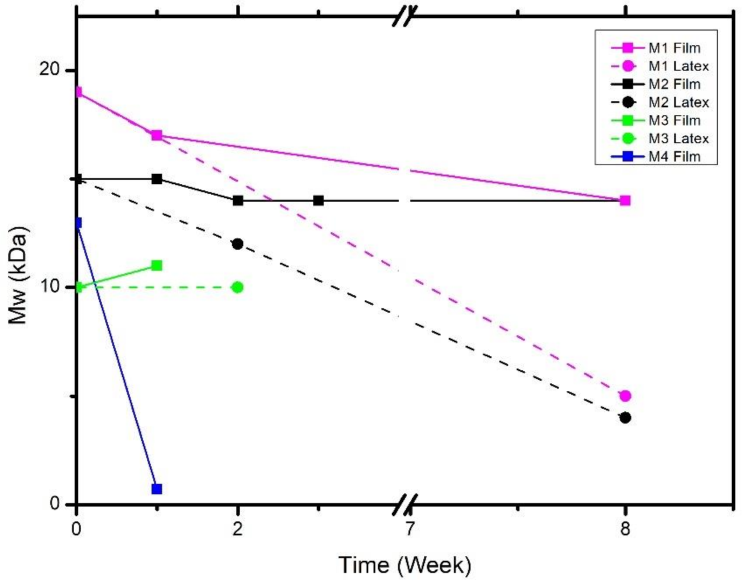

Figure 15. Evolution of Mw in films and latexes with different formulations.

Based on the data above, it was clear that the decrease of molecular weight was significantly faster in latexes than in films. In aqueous media, due to oxygen, more S-S bonds might have been formed, promoting the mentioned depolymerization and decreasing the Mw values faster than in films. Furthermore, it was observed that in general, the increase of DBHQ proportion regarding the thiol monomer caused a slower depolymerization of the chains, opposed to the expected behaviour. The decrease was noticeable in the reaction without DBHQ, whereas in the formulations with 1:0,002 and 1:0,006 DBHQ the molecular weight values decreased slower. Nonetheless, for the formulation with the highest DBHQ amount the trend was not followed. As it is shown, was the formulation at which the polymeric chains were degraded faster by far, as expected. After 1 week, the molecular weight corresponded to oligomers more than to polymers. The unexpected behaviour of the M2 and M3 showed that the radical scavenger might be used for two opposite objectives like promoting the depolymerization rate or making them more long-lasting.

As the depolymerization could be caused by the presence of disulfide bonds in the backbone, we thought that adding the DBHQ in the last step (after photopolymerization, in the final latexes) could control the depolymerization. Hence, more reactions were done to compare the effect of DBHQ once it was added to the final latex. The aim was to check if the inhibitor effect on S-S bonds and depolymerization was the same in both cases. So, a reaction was performed again without any radical scavenger and the final latex was divided into 4 parts. In order to compare them with the previous results, same ratios of DBHQ regarding the GDMA monomer (Table 12) were added and stirred until being totally dissolved.

Table 12. *DBHQ:GDMA molar ratios of M5.*

Reaction	GDMA:DATP molar ratio	GDMA:DBHQ molar ratio
M5(1)	1 : 1,001	x
M5(2)	1 : 1,001	1 : 0,002
M5(3)	1 : 1,001	1 : 0,006
M5(4)	1 : 1,001	1 : 0,010

Finally, they were casted in the same way and, once the water was evaporated, the films shown in Figure 16 were obtained.

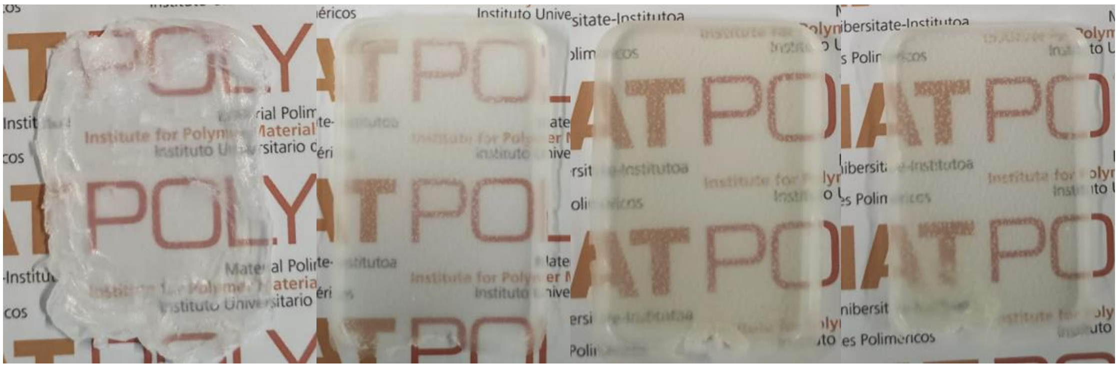

Figure 16. *Starting from the left: M5(1), M5(2), M5(3) and M5(4) films.*

It was noticeable that despite having DBHQ, the yellowing of the films was much lower than in the reactions where was added from the beginning. In addition, all the films presented a much higher transparency than the ones performed in the previous step.

Then, depolymerization was followed by GPC. The Figure 17 collects the development of the Mw in the films where the radical scavenger was added to the final latex. The development was not tracked in the latex, as all of it was used to cast the films.

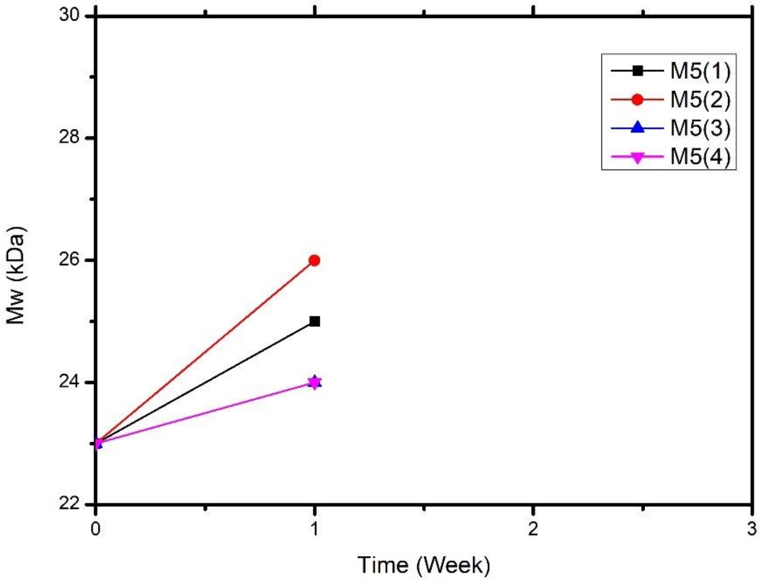

Figure 17. *Mw evolution of the films casted from lately added DBHQ latexes.*

As it is presented in the figure above, the molecular weight evolution of the last reactions was slightly different from the ones done previously. In this case, the Mw values increased in all the cases, no matter the amount of DBHQ used. Different conclusion might be drawn, as the difficulty to reproduce these reactions to obtain same or very similar results. Regarding the values above, the increase might be explained by the dynamic behaviour of disulfide bonds, which are able to break and rearrange, giving rise to new chains that might be bigger. Hence, the addition of DBHQ once the latex was obtained seemed not to have any effect, as it was not able to catch the radicals and avoid the creation of new bonds.

5. CONCLUSIONS

In this work the photopolymerization process of GDMA and DATP monomers pair was performed to analyse the reactivity between them and the effect of DBHQ on the final properties.

Bulk polymerization results showed that the reactions were irreproducible due to the crucial importance of stoichiometric balance between monomers and the premature polymerization caused by the presence of thiyl radicals coming from GDMA monomer. Based on the data obtained by Raman spectroscopy, it was seen that the addition of DBHQ was not enough to control the premature polymerization, as the presence of S-S bonds was noticeable in all the cases. Therefore, we concluded that the DBHQ was not able to catch the thiyl radicals. The reaction conditions were analysed too, as it might have been an alternative to improve the reproducibility of reactions. As it was observed, increasing the reaction time no further advantages were obtained regarding reproducibility and the Mw values decreased due to the increase of termination reactions. Moreover, photoinitiator concentration seemed to influence the Mw and reproducibility, where the best results were obtained at 0,5 wt %. Regarding the conversion, it was clear that high conversions were obtained in all the cases, due to the high reactivity of GDMA and DATP.

Miniemulsion polymerization results showed that the addition of sonication step worsened the reproducibility issues, due to the radicals that were formed as a result of the extra energy provided by the step. Furthermore, it was observed that the addition of DBHQ above a certain amount caused a fast depolymerization instead of making the films more long lasting. So, more miniemulsion photopolymerization reactions were performed to analyse if the addition of the DBHQ in the last step could improve the deactivation of radicals and increase the depolymerization. As the obtained data was recent, there were no enough information to conclude the real effect, but it seemed that the aim was not achieved as the films did not start to depolymerize at the beginning.

Finally, as future work we should continue following the depolymerization process of the films and analysing the mechanical properties of them. Moreover, extra characterization techniques such as DSC could be applied to check if the Tg varies by changing the GDMA:DBHQ ratio. In addition, more reactions could be performed to try to optimize the synthesis process. Moreover, some characterization techniques might be repeated to ensure that the data was totally reliable.

5. ONDORIOAK

Lan honetan GDMA and DATP monomer parearen fotopolimerizazioa gauzatu da, hauen arteko erreaktibitatea eta DBHQ-k amaierako propietateetan duen eragina aztertzeko.

Masa polimerizazioko emaitzek erakutsi dute erreakzioa ez dela erreproduzigarria, izan ere, monomero artekoen erlazio estekiometrikoak eta GDMAtik datozen tiil erradikalek eragindako polimerizazio goiztiarrak eragin handia dute. Raman espektroskopian ikusi da DBHQren gehikuntza ez dela aski polimerizazio goiztiar hori kontrolatzeko, disulfuro loturaren presentzia nabarmena baitzen kasu guztietan. Hori dela eta, ondorioztatu da DBHQ ez dela gai tiil erradikalak harrapatzeko. Horretaz gain, erreakzio baldintzak ere aztertu dira, erreakzioaren erreproduzigarritasuna hobetzeko aukera gisa. Emaitzetan oinarrituz ikusi da erreakzio denbora luzatzeak ez duela abantaila berezirik erreproduzigarritasunari dagokionez eta amaierako pisu molekularren balioa txikiagotzea eragiten duela. Bestalde, badirudi fotohastarazleak eragina duela erreproduzigarritasunean eta pisu molekularretan, balio onenak % 0,5 pisu portzentaian lortuz. Konbertsioari dagokionez, argi dago balio altuak lortu direla kasu guztietan, GDMAren eta DATPren erreaktibitate altua dela eta.

Miniemultsio polimerizazioko emaitzei dagokienez, sonikazio prozesuak erreproduzigarritasunaren arazoa okertu du, pauso honetan emandako energia gehigarriagatik sortutako erradikalen erruz. Horretaz gain, ikusi da kantitate batetik aurrera DBHQak depolimerizazio azkar bat eragin dezakeela, filmak iraunkorragoak egin ordez. Beraz, miniemultsio fotopolimerizazio erreakzio gehiago egin dira, DBHQ azken pausoan gehitzeak depolimerizazioa bultzatu dezakeen aztertzeko. Lortutako emaitzak nahiko berriak direnez, ez dago informazio aski benetako ondorio bat ateratzeko. Halere, badirudi helburua ez dela lortu, filmek ez baitute depolimerizatzeko joera erakutsi hasiera batean.

Azkenik, etorkizunean filmen depolimerizazioa eta hauen propietate mekanikoak aztertu beharko genituzke. Horrez gain, karakterizazio teknika gehiago erabili daitezke; besteak beste, Ekorketazko Kalorimetria Diferentziala (DSC), GDMA:DBHQ proportzioak beira trantsizio tenperaturan (Tg) izan dezakeen eragina aztertzeko. Gainera, erreakzio gehiago egin litezke, prozesua optimizatzeko helburuarekin. Karakterizazio teknika batzuk ere errepika litezke, lortutako datuen fidagarritasuna ziurtatzeko.

6. BIBLIOGRAPHY

(1) Wu, F.; Misra, M.; Mohanty, A. K. Challenges and New Opportunities on Barrier Performance of Biodegradable Polymers for Sustainable Packaging. *Prog Polym Sci* **2021**, *117*, 101395. https://doi.org/10.1016/J.PROGPOLYMSCI.2021.101395.

(2) *Food Packaging Market Size, Share & Trends Analysis Report By Type (Rigid, Semi-rigid, Flexible), By Material (Paper, Plastic), By Application, By Region, And Segment Forecasts, 2023-2030.* https://www.researchandmarkets.com/report/food-packaging (accessed 2024-05-16).

(3) *Tsakona: Baseline report on plastic waste - Google Académico.* https://scholar.google.com/scholar_lookup?title=Baseline%20report%20on%20plastic%20waste.%20Document%20No.%20UNEP%2FCHW%2FPWPWG.1%2FINF%2F4%3A%20basel%20convention&author=M.%20Tsakona&publication_year=Feb%2C%202020 (accessed 2024-05-17).

(4) *(PDF) Recent Innovations in Barrier Technologies for Plastic Packaging - A Review.* https://www.researchgate.net/publication/216091428_Recent_Innovations_in_Barrier_Technologies_for_Plastic_Packaging_-_A_Review (accessed 2024-06-16).

(5) Supervised, J. E.; Tomovska, R. *Waterborne Polysulfide Dispersions for Coatings Application.*

(6) Huang, H.-D.; Ren, P.-G.; Zhong, G.-J.; Olah, A.; Li, Z.-M.; Baer, E.; Zhu, L. Promising Strategies and New Opportunities for High Barrier Polymer Packaging Films. *Prog Polym Sci* **2023**, *144*, 101722. https://doi.org/10.1016/j.progpolymsci.2023.101722.

(7) Cakmak, O. K. Biodegradable Polymers—a Review on Properties, Processing, and Degradation Mechanism. *Circular Economy and Sustainability* **2024**, 4 (1), 339–362. https://doi.org/10.1007/S43615-023-00277-Y/FIGURES/12.

(8) Song, J.; Chen, X.; Li, S.; Tang, H.; Dong, S.; Wang, M.; Xu, H. The Environmental Impact of Mask-Derived Microplastics on Soil Ecosystems. *Science of The Total*

Environment **2024**, *912*, 169182. https://doi.org/10.1016/J.SCITOTENV.2023.169182.

(9) Pervez, R.; Lai, Y.; Song, Y.; Li, X.; Lai, Z. Impact of Microplastic Pollution on Coastal Ecosystems Using Comprehensive Beach Quality Indices. *Mar Pollut Bull* **2023**, *194*, 115304. https://doi.org/10.1016/J.MARPOLBUL.2023.115304.

(10) Sharma, P.; Vidyarthi, V. K. Impact of Microplastic Intake via Poultry Products: Environmental Toxicity and Human Health. *Journal of Hazardous Materials Advances* **2024**, *14*, 100426. https://doi.org/10.1016/J.HAZADV.2024.100426.

(11) Li, Y.; Tao, L.; Wang, Q.; Wang, F.; Li, G.; Song, M. Potential Health Impact of Microplastics: A Review of Environmental Distribution, Human Exposure, and Toxic Effects. *Environment & Health* **2023**, *1* (4), 249–257. https://doi.org/10.1021/ENVHEALTH.3C00052.

(12) Elgoyhen, J.; Pirela, V.; Müller, A. J.; Tomovska, R. Synthesis and Crystallization of Waterborne Thiol-Ene Polymers: Toward Innovative Oxygen Barrier Coatings. *ACS Appl Polym Mater* **2023**, *5* (11), 8845–8858. https://doi.org/10.1021/ACSAPM.3C01128.

(13) Elgoyhen, J.; Le, C. M. Q.; Ricke, A.; Liska, R.; Baudis, S.; Chemtob, A.; Tomovska, R. Implementing Miniemulsion Photopolymerization for Synthesis of Waterborne Biobased Poly(Thioethers) Coatings. *Prog Org Coat* **2024**, *187*, 108156. https://doi.org/10.1016/J.PORGCOAT.2023.108156.

(14) Kade, M. J.; Burke, D. J.; Hawker, C. J. The Power of Thiol-Ene Chemistry. *J Polym Sci A Polym Chem* **2010**, *48* (4), 743–750. https://doi.org/10.1002/POLA.23824.

(15) Cramer, N. B.; Bowman, C. N. Thiol–Ene Chemistry. *Chemoselective and Bioorthogonal Ligation Reactions* **2017**, 117–145. https://doi.org/10.1002/9783527683451.CH5.

(16) Hoyle, C. E.; Lee, T. Y.; Roper, T. Thiol-Enes: Chemistry of the Past with Promise for the Future. *J Polym Sci A Polym Chem* **2004**, *42* (21), 5301–5338. https://doi.org/10.1002/POLA.20366.

(17) Hoyle, C. E.; Lowe, A. B.; Bowman, C. N. Thiol-Click Chemistry: A Multifaceted Toolbox for Small Molecule and Polymer Synthesis. *Chem Soc Rev* **2010**, *39* (4), 1355–1387. https://doi.org/10.1039/B901979K.

(18) Hoyle, C. E.; Bowman, C. N. Thiol-Ene Click Chemistry. *Angewandte Chemie - International Edition* **2010**, *49* (9), 1540–1573. https://doi.org/10.1002/ANIE.200903924.

(19) Kade, M.; Burke, D.; … C. H.-S. P. A. P.; 2010, undefined. The Power of Thiol ene Chemistry. *Wiley Online Library* **2010**, *48* (4), 743–750. https://doi.org/10.1002/pola.23824.

(20) Hadjichristidis, N.; Hirao, A.; Tezuka, Y.; Filip, •; Prez, D.; Du Prez, F. Complex Macromolecular Architectures: Synthesis, Characterization, and Self-Assembly. **2011**.

(21) Esfandiari, P.; Ligon, S. C.; Lagref, J. J.; Frantz, R.; Cherkaoui, Z.; Liska, R. Efficient Stabilization of Thiol-Ene Formulations in Radical Photopolymerization. *J Polym Sci A Polym Chem* **2013**, *51* (20), 4261–4266. https://doi.org/10.1002/POLA.26848.

(22) Sensfuß, S.; Friedrich, M.; Klemm, E. Untersuchungen Zur Thiol/En-Polymerisation: Elektronenspinresonanzspektroskopischer Nachweis Spontaner Radikalbildung. *Die Makromolekulare Chemie* **1991**, *192* (12), 2895–2900. https://doi.org/10.1002/MACP.1991.021921205.

(23) Le, C. M. Q.; Morlet-Savary, F.; Chemtob, A. Role of Thiol Oxidation by Air in the Mechanism of the Self-Initiated Thermal Thiol-Ene Polymerization. *Polym Chem* **2021**, *12* (45), 6594–6605. https://doi.org/10.1039/d1py01301g.

(24) Durham, O. Z.; Shipp, D. A. Suspension Thiol-Ene Photopolymerization: Effect of Stabilizing Agents on Particle Size and Stability. *Polymer (Guildf)* **2014**, *55* (7), 1674–1680. https://doi.org/10.1016/J.POLYMER.2014.02.044.

(25) Quoc Le, C. M.; Schmutz, M.; Chemtob, A. Ab Initio Batch Emulsion Thiol-Ene Photopolymerization. *Macromolecules* **2020**, *53* (7), 2369–2379. https://doi.org/10.1021/ACS.MACROMOL.0C00265/ASSET/IMAGES/LARGE/MA0C00265_0002.JPEG.

(26) Durham, O. Z.; Chapman, D. V.; Krishnan, S.; Shipp, D. A. Radical Mediated Thiol-Ene Emulsion Polymerizations. *Macromolecules* **2017**, *50* (3), 775–783. https://doi.org/10.1021/ACS.MACROMOL.6B02228/ASSET/IMAGES/LARGE/MA-2016-02228H_0007.JPEG.

(27) Asua, J. M. Miniemulsion Polymerization. *Prog Polym Sci* **2002**, *27* (7), 1283–1346. https://doi.org/10.1016/S0079-6700(02)00010-2.

(28) Asua, J. M. Challenges for Industrialization of Miniemulsion Polymerization. *Prog Polym Sci* **2014**, *39*, 1797–1826. https://doi.org/10.1016/j.progpolymsci.2014.02.009.

(29) Vanderhoff, J. W. Latex Film Formation. *Curr Opin Colloid Interface Sci* **1997**, *2* (2), 192–199. https://doi.org/10.1016/S1359-0294(97)80026-X.

(30) Lambert, J. B.; Mazzola, E. P.; Ridge, C. Nuclear Magnetic Resonance Spectroscopy : An Introduction to Principles, Applications, and Experimental Methods. 456.

(31) *Basics of NMR*. https://www.cis.rit.edu/htbooks/nmr/ (accessed 2024-06-20).

(32) *The principles of dynamic light scattering | Anton Paar Wiki*. https://wiki.anton-paar.com/en/the-principles-of-dynamic-light-scattering/ (accessed 2024-06-20).

(33) *Particle Size and Particle Size Distribution Analysis | Science.eus*. https://www.science.eus/en/infrastructure/particle-size-and-particle-size-distribution-analysis (accessed 2024-06-20).

(34) *Basics of Raman spectroscopy | Anton Paar Wiki*. https://wiki.anton-paar.com/en/basics-of-raman-spectroscopy/ (accessed 2024-06-20).

APPENDIX

Herein, Figure A1 gathers the turbiscan analysis spectrums obtained after sonication.

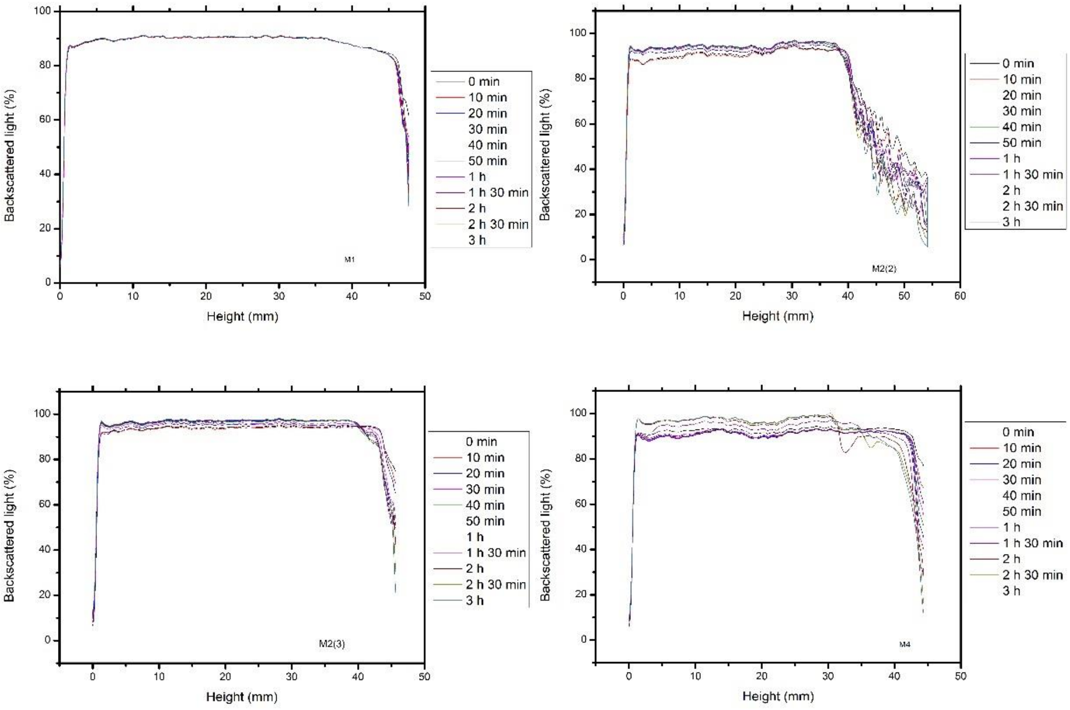

Figure A1. *Turbiscan analysis spectrum of M1, M2(2), M2(3) and M4.*

Herein, Figure A2 shows the CHDF spectrums of reactions M2(1) and M4.

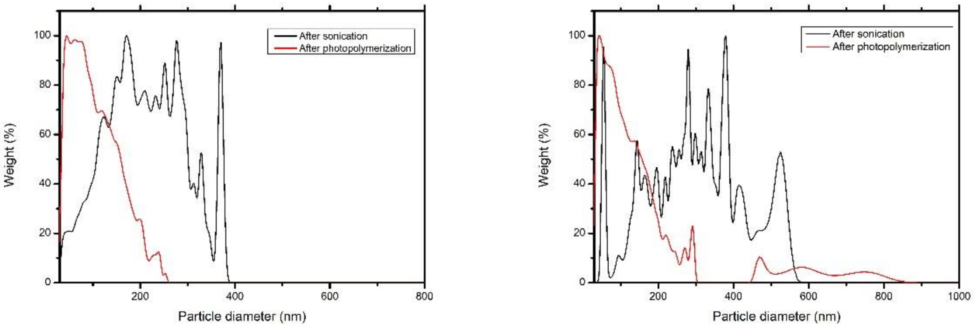

Figure A2. *CHDF spectrums comparison after sonication and after photopolymerization in reactions M2(1) and M4.*