



Universidad del País Vasco
Euskal Herriko Unibertsitatea

KIMIKA FAKULTATEA
FACULTAD DE QUÍMICA

Euskal Herriko Unibertsitatea - Universidad del País Vasco

Kimika Fakultatea - Facultad de Química

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Free-Radical microwave-assisted polymerization of Butyl Acrylate.

Author: Alvaro Luis del Castillo Corral

Director: Prof. José M. Asua

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GIPUZKOAKO CAMPUSA
CAMPUS DE GIPUZKOA
Pº. Manuel de Lardizabal, 3
20018 DONOSTIA-SAN SEBASTIAN
GIPUZKOA

Summary

Microwave-assisted polymerization is a branch of polymer chemistry that has attracted a lot of interest and development in the last decade. Several authors^[1-3] have reported that microwave heating presents numerous advantages over conventional heating, including faster polymerization times and molecular weight increase. With the significant growth in the number of books and reviews on the matter, a certain topic of discussion has arisen: whether the benefits are caused by "thermal effects", due to fast heating by the microwaves, or by "non-thermal effects", caused by intrinsic irradiation effect that cannot be replicated by conventional heating. While some report that the increase in polymerization rate (R_p) is caused by fast heating of the mixture and formation of hotspots^[4-6], other investigations have shown a mutual increase in R_p and MW, suggesting the existence of non-thermal effects in the kinetic constants^[7-10].

There are some data^[11, 12] showing that, in the presence of enough irradiation power, terpenoid acrylates present microwave effects that cannot be explained by differences in temperature, whereas the effect is not observed for terpenoid methacrylates. The goal of this project is to investigate if these findings are limited to this specific family of monomers or are also present for conventional, commercially available monomers. Therefore, the microwave-assisted free radical polymerization of butyl acrylate was studied and the results compared to conventional heating. Attention was paid to the evolutions of the monomer conversion and molar mass distributions. Since accurate control of reaction temperature is crucial to be able to confirm a non-thermal effect, attention was paid to the level of control over the temperature of the microwave device used and to our purposes. Three different polymerization systems with distinct characteristics were investigated: polymerization in solution, miniemulsion polymerization and RAFT polymerization.

Resumen

La polimerización asistida por microondas es una rama en el ámbito de la química de polímeros que ha atraído un gran interés y desarrollo durante la última década. Varios autores^[1-3] han declarado que el uso de la irradiación de microondas presenta ventajas sobre los métodos convencionales de calentamiento, incluyendo una reducción en los tiempos de polimerización e incrementos en pesos moleculares. Junto con el considerable crecimiento de la cantidad de libros y publicaciones que tratan sobre este tema, ha surgido un cierto debate: bien que los beneficios son causados por "efectos térmicos", por un calentamiento rápido de las microondas, o por "efectos no-térmicos", causados por un efecto intrínseco de la irradiación que no puede ser reproducido por métodos de calentamiento convencional. Mientras que algunos justifican que el incremento del índice de polimerización se debe al calentamiento rápido de la mezcla y formación de regiones de muy alta temperatura^[4-6], otras investigaciones han demostrado un incremento tanto en el índice de polimerización como en peso molecular, sugiriendo la existencia de efectos no-térmicos efectos en las constantes cinéticas^[7-10].

Hay datos^[11, 12] que demuestran que, en presencia de suficiente poder de irradiación, los terpenos acrílicos presentan efectos causados por las microondas que no pueden ser justificados por diferencias en temperatura, mientras que este efecto no se observa para los terpenos metacrílicos. El objetivo de este proyecto es investigar si estos resultados se limitan a esta específica familia de monómeros o si también están presentes en los monómeros convencionales y disponibles comercialmente. Para ello, se han estudiado las polimerizaciones por radicales libres asistida por microondas del acrilato de butilo y se han comparado con el método de calentamiento convencional. Se ha prestado atención a la evolución de la conversión de los monómeros y a las distribuciones de sus pesos moleculares. Dado de que un control preciso de la temperatura de reacción es necesario para poder confirmar un efecto no térmico, se prestó atención al nivel de control de temperatura del microondas del que se hizo uso y para nuestros objetivos. Se investigaron tres sistemas de polimerización diferentes con características distintas: polimerización en solución, polimerización en miniemulsión y polimerización RAFT.

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1. Introduction

The concept of heating by microwave irradiation was introduced in 1946 by the accidental melting of a candy bar^[13]. In 1955, Raytheon patented the technology with the idea of cooking meals and heating or defrosting food in very short periods of time in restaurants or in houses. However, they were still too large and had exorbitant prices for personal use in households and it was not until the late 1970s that they became affordable for residential use. Nevertheless, they were not first applied commercially for food but for industrial purposes. Dielectric heating of microwave irradiation was already being used at the time for heating and drying materials, given the fact that it provided an edge over other conventional heating methods: microwaves directly penetrate and internally heat the material whereas ovens or stoves rely on slower surface heating^[14].

During the last 30-40 years, after the safety uncertainties of the domestic microwave ovens were ruled out, microwave-assisted chemistry has grown and has been developed to be established as a common technique, used by chemists in both research laboratories and industry. Its significance and widespread use can be noticed in the number of books and reviews that have been published since the early 2000s^[15-18]. Microwave heating technique can be found in areas such as organic or inorganic synthesis^[19], where it has been used to overcome long reaction times usually associated with them, as well as biology^[20] and medicine^[21]. These findings incited the idea of whether it could be possible to take advantage of the benefits of microwave irradiation for polymer chemistry.

Microwave-assisted polymer synthesis, although the number of publications on the matter has considerably increased, is still a growing branch in polymer science. This technique has been widely reported to lead to higher polymerization rates comparing to conventional heating at the same temperature^[1-3]. Microwave assisted polymerizations are performed in closed and sealed reactors which can endure these superheated reaction conditions. This has led to very short reaction times and permits the use of low boiling solvents as well as halogen-free solvents, reinforcing the practice of "green chemistry"^[22]. Despite the substantial amount of work that has been done in this area, the reason why the polymerization rate (R_p) increases under microwave irradiation is still under debate. Two different outcomes can be pointed

out from the literature. On the one hand, some authors attribute the increase to thermal effects, which is justified in cases where it has been observed an acceleration in R_p , followed by a decrease in the molecular weight^[4-6]. On the other hand, other articles propose the idea of "non-thermal effects", which would affect the kinetic rate coefficients during the reaction; despite some of the results obtained in some researches being difficult to explain without taking this alternative into account^[7-10], its existence is yet to be agreed upon.

One of the polymerization methods that has been studied under microwave irradiation assistance is free radical polymerization (FRP). FRP is one of the most applied and widely used techniques for polymer and composites synthesis due to its versatility. It requires a simple and rapid preparation and no expensive or sophisticated equipment. In addition to that, the initiation process can be started through different mechanisms (e.g. thermal, redox, photochemical etc.)^[23] and can operate under a variety of conditions (e.g. with or without solvent, in water, emulsions etc.). Notwithstanding its applicability, this approach for synthesis, in some cases may lead to a situation where polymerization rate and molecular weight cannot increase simultaneously (e.g. solution polymerization); although this limitation has been circumvented by the development of other techniques (e.g. emulsion polymerization), in many industrial processes the aforementioned problem is relevant. Furthermore, secondary reactions such as chain transfer or termination between chains of variable lengths might occur and there is little to no control over the molecular weight distribution^[24]. Given the limitations of this polymerization system, other approaches have been investigated, such as controlled radical polymerization, which narrows the molecular weight distribution. However, better control of the polymer structure and molecular weight distributions come at the expense of longer reaction times and limited monomer library^[25, 26]. Therefore, the strategy of using microwave assisted polymerization has been explored, since it might be able to increase R_p while maintaining satisfactory molecular weight values and control over polydispersity.

Poly-acrylates and methacrylates compose one important polymer family, with applications that can vary from paints and adhesives to cosmetics. From a kinetic point of view, the main difference between acrylates and methacrylates lies in the reactivity of the radicals they form (see section 1.3.) and, thus, their propagation rate.

An acrylate will form a secondary radical as the propagating end group, whereas the methacrylate forms a tertiary radical, which is more stable. In the case of acrylates, chain transfer reactions commonly occur due to two reasons: the high reactivity of the secondary radical and the availability of labile hydrogens.

The polymerization of terpenoid (meth)acrylates under the effects of microwaves has been recently investigated by Castagnet *et al.*^[11, 12]. Terpenoids are biobased materials that are obtained from by-products of the paper industry and that, through their esterification, can be used to produce biobased (meth)acrylic monomers^[12]. The results of this investigation showed that in the free radical and RAFT polymerization of bio-based terpenoid acrylates, non-thermal microwave effects, i.e. effect of microwaves on kinetic constants, are present. On the other hand, terpenoid methacrylates, do not show such effect. These results were attributed to the ability of the microwave irradiation to increase the formation of the less stabilised acrylic radicals, and two possible conclusions were proposed: that irradiation either inhibits termination, or increases the propagation constant probably by reducing the activation energy of the reaction.

If the existence of this non-thermal effect was ascertained, it would open the way for the synthesis of polymers that are not obtainable nowadays, which might lead to new and improved properties in very short reaction times.

Having the aforementioned results in mind, this research was set to study if non-thermal effects are present for conventional oil-based acrylates. This project was carried out at the Polymerization Processes Group of the BERC-POLYMAT, at the Faculty of Chemistry of the EHU/UPV in Donostia-San Sebastián, Spain. It was supervised by Prof. José M. Asua.

1.1.- Glossary and Abbreviations

- BA Butyl Acrylate monomer
- PBA Poly-Butyl Acrylate polymer
- AIBN 2,2'-Azobis(2-methyl-propionitrile) initiator
- SA Stearyl Acrylate polymerizable co-stabiliser
- DBTTC S,S-Dibenzyl trithiocarbonate RAFT agent
- MW Microwave
- CH Conventional Heating
- FRP Free Radical Polymerization
- RAFT Reversible addition-fragmentation chain-transfer

1.2.- Objectives

The main purpose of this project is to determine the presence of a non-thermal microwave-induced effect in the kinetic constants for conventional acrylic monomers.

To do so, the polymerization of butyl acrylate will be investigated. Free radical polymerizations of this monomer will be carried out under two different conditions: conventional heating and microwave-irradiated heating. Specific attention will be put onto the kinetics of the reactions, the evolution of the molecular weight and its distribution during and after the reactions.

Ultimately, results from the analysis will be discussed and compared in order to ascertain if there is such non-thermal effect or not.

1.3.- Free Radical Polymerization

FRP is one of the most important polymerization techniques and it is used in both industry and academia for the production of a wide variety of polymers (e.g. polyethylene, polystyrene, poly(vinyl acetate), poly(methyl methacrylate) etc.)^[27] through a well-known procedure. Radical polymerization can be performed in bulk or in solution; furthermore, it is compatible with water, so emulsion or dispersion polymerizations can be performed, avoiding the use of organic solvents and therefore promoting a more environmentally benign chemistry. As mentioned in the Introduction section, one of the reasons why free radical polymerization stands out, is because of its versatility and applicability.

The mechanism of free radical polymerization can be divided in three steps: initiation, propagation and termination. The technique relies on the formation of a reactive species (i.e. a free radical) and its ability to add to a vinylic monomer molecule by opening the π -bond and creating a new reactive centre. The latter will proceed to repeat the same process consecutively with other monomers, thus, propagating the active centre until it is terminated (as shown in Fig.1).



Fig. 1. General FRP propagation mechanism for an acrylate monomer (for BA R = C₄H₉).

In FRP the polymer chain is initiated, grows and is terminated at very high speeds, obtaining high molecular weight polymers in a matter of seconds or less. After the termination, the formed chain is called a "dead" chain since it will no longer polymerize. However, side reactions can occur depending on the monomer and the reaction conditions (e.g. chain transfer) which can have an effect in the final molecular weight and in the properties of the materials.

INITIATOR: AIBN

One of the most used mechanisms for generation of radicals is the *thermal, homolytic dissociation*. The rate at which this process occurs resides on the structure of the initiator and the nature of the radicals formed after its decomposition^[28]. In this investigation, the initiator used was 2,2'-Azobis(2-methyl-propionitrile) or AIBN (Fig.2). It is an organic azo compound that is soluble un organic solvents and alcohols but not in water. It is one of the most used initiators, with well documented properties.

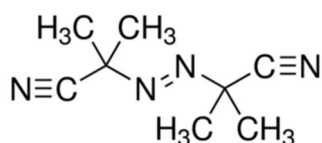


Fig. 2. Structure of the initiator 2,2'-Azobis(2-methyl-propionitrile) (AIBN).

It is as a bifunctional, thermal initiator, and the driving force for its homolysis is not the cleavage of a weak bond but the formation of a stable nitrogen molecule and resonance stabilised cyanoisopropyl tertiary radicals^[29] (Fig.3). Different initiators are used in a variety of temperature ranges depending on their rates of decomposition; in the case of AIBN, it is used at 50-70°C. The decomposition half-life of AIBN is 17 h at 60°C^[30].

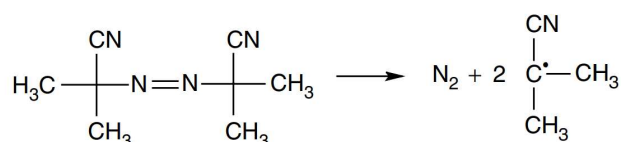


Fig. 3. Dissociation of AIBN.

MONOMER: Butyl Acrylate

The free radical polymerization of BA (Fig.4 shows its structure) was studied in three different conditions (solution, miniemulsion and RAFT in solution). When polymerized, the materials obtained from acrylic monomers share very different properties to the ones obtained from methacrylic monomers. For instance, polyacrylates do not have a methyl group in the alternating carbons of the polymer

chains, which makes them softer (T_g for PBA = -54°C ^[31]). These two groups are generally used as copolymers; polymethacrylates tend to be used as shaped objects (T_g for PBMA = 20°C)^[28], and polyacrylates are used in applications that require flexibility^[32].

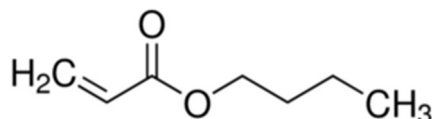


Fig. 4. Structure of Butyl Acrylate (BA).

BA undertakes free-radical polymerization through a head-to-tail addition of the new monomer unit with the formation of a single bond after an attack to the monomer's double bond (Fig.1).

The great reactivity of the secondary radical of BA leads to fast propagation rates ($k_p = 14.476 \text{ M}^{-1}\text{s}^{-1}$ at 20°C , Butyl Methacrylate has a $k_p = 314 \text{ M}^{-1}\text{s}^{-1}$ at 20°C ^[33]). The radical polymerization of acrylates has been studied since it is highly influenced by radical transfer events (intramolecular and intermolecular transfer to polymer)^[34]. Fig.5 shows the intramolecular transfer reaction that leads to a mid-chain tertiary radical far less reactive than the chain-end secondary. This has two main effects: on the one hand it causes very slow propagation rates and, on the other, the propagation of the tertiary radical introduces a branch point in the polymer that causes a variable microstructure. The polyacrylate secondary radical is mainly terminated via combination, whereas the tertiary radical and polymethacrylates do it via disproportionation^[34]. The unpredictability of the radicals and the different termination mechanisms make the FRP of butyl acrylate very complicated with little control over the rate of chain propagation and termination. It also makes it difficult to obtain specific molecular weights of the resulting polymers and distributions. Moreover, the monomer and initiator concentrations change as the polymerization reaction progresses, causing a variation of the molecular weight of the polymer formed at any time.

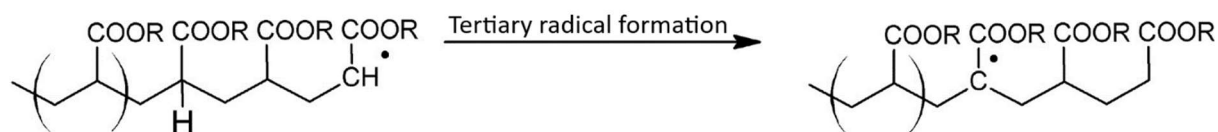


Fig. 5. General mechanism for intramolecular transfer to polymer (or backbiting) for acrylates.

1.4.- Solution Polymerization^[28]

Bulk polymerization of monomers is the simplest way for synthesis. The major benefits of this technique are the fewer side reactions that could be caused by performing the polymerizations in solution and the elimination of purification processes of the product. Despite just needing to mix the monomers and the initiator and providing products with minimum levels of contamination, it can have a number of drawbacks. One of the main characteristics of this polymerization method is the poor ability of the medium to dissipate heat. This is due to the high velocity at which high molecular weight polymer chains are formed, resulting in the rapid increase of the viscosity of the system. Especially in free radical polymerization, temperature is difficult to control due to the exothermic nature of the mechanism and the propensity to gel effect. In order to overcome these obstacles that bulk polymerization entails, one of the alternatives used is carrying out reactions to low conversions (before high viscosities or gel-effect are reached) and then distilling and recycling the monomer. Another option is performing the synthesis in solution.

Polymerizing a monomer in a solvent can help to avoid some of the problems that doing it in bulk poses. The solvent dilutes the system, which helps with the diffusion and elimination of the heat. In addition, stirring is easier because of the less viscous mixture and gel-effect (if any) occurs at higher conversion values. Therefore, there is a better control over the reaction temperature. Diluting the system also means that the concentration of the monomer will be lower, resulting in slower reactions. It has been studied that the propagation rates are affected by the presence of solvent^[35] and that solvent effects can be used to assist in controlling the polymerization reaction^[36]. Nevertheless, chain transfer to solvent must be taken into account when choosing an appropriate solvent for the polymerization. Moreover, this technique is not very useful if the objective is to obtain polymers with high purity, since solvent must be eliminated, which sometimes is not easy and makes the process more expensive. Industrially, this technique is used when the polymer is going to be purchased as a solution.

Polyacrylates can be produced by solution polymerization depending on the applications of the product. Nonetheless, the synthesis of polyacrylates is known for its high rates and heat, which make bulk polymerization impracticable; and solution polymerizations result in high viscosity mixtures barring restrictions of conversion

percentage or molecular weight. The reason for this elevated viscosity is the aforementioned (see 1.3. *Free Radical Polymerization*) extensive branching due to the formation of the more stable tertiary radical^[34]. So, as the polymer concentration increases (higher conversions), so does the viscosity of the medium. As a result, long chain radicals have difficulties to diffuse and termination rate is reduced, which leads to an increase in the concentration of radicals and a faster polymerization rate. Additionally, the control of the temperature becomes difficult. Another limitation of bulk or solution FRP, is that polymerization rates can be increased at the expense of decreasing molecular weights. Increasing the temperature of the system to achieve faster reactions will increase initiation and termination rates more than the propagation rate, or adding higher concentrations of initiator will consume the monomer faster but more polymer chains of lower masses will be obtained.

One technique that can be used as a way to get over the setbacks that bulk or solution polymerization can cause is emulsion polymerization, which is a commercially established method for the synthesis of these polymers.

1.5.- Emulsion Polymerization^[37, 38]

Emulsion polymerization is a heterogeneous polymerization technique, widely used for synthesis of modern commercial polymers. The polymers obtained through this method are mainly produced via free radical polymerization. It is the predominant process for commercial polymerizations of acrylates. The process shares similarities with suspension polymerization, but differs in the type and size of the particles that act as polymerization sites and the kind of initiator used. There are four main components in the emulsion: monomer(s), initiator, emulsifier or surfactant and the dispersing medium (usually water). The emulsifier allows the dispersion of the components as well as providing stability to the particles. That is thanks to the hydrophobic and hydrophilic segments that form emulsifier molecules.

The monomers can be found in three different situations: in particles, forming droplets that are stabilized by the surfactants attaching on their surfaces and a very small amount is dissolved. The hydrophobic tail of the surfactant is oriented towards the monomer droplet and the hydrophilic head towards the aqueous phase (see Fig.6). Generally, formulations contain an excess of surfactant so that the monomer droplets are completely sheltered and to assure that micelles are formed. Micelles, are filled with monomer molecules that are dissolved from the droplets.

Most of the initiators used are water-soluble, and therefore do not enter the hydrophobic monomer droplets. As a result, they form radicals that react with the monomer dissolved in the aqueous phase and form oligomer radicals, even though it happens at a very slow rate due to the low concentration of monomer in the phase. As these oligomer chains increase in size, so does their hydrophobicity, allowing them to migrate out of the aqueous phase into the micelles. Compared to the monomer droplets, micelles have a larger total surface area, and for that reason the entry of radicals is more likely to happen there. Inside the micelles, the concentration of monomer is very high, so the newly entered radicals react and form a polymer chain at a very fast rate. When polymerization is active in the micelle, a *polymer particle* is formed. This is known as *heterogeneous nucleation*, which is predominant for monomers with poor solubility in water. Another mechanism for the formation of polymer particles is the precipitation of the oligoradicals, which are stabilised by surfactant molecules and then absorb monomer, forming polymer particles. This is referred to as *homogeneous*

nucleation, which is predominant for monomers with high solubility in water. Fig.6 presents a simplified representation of an emulsion polymerization system.

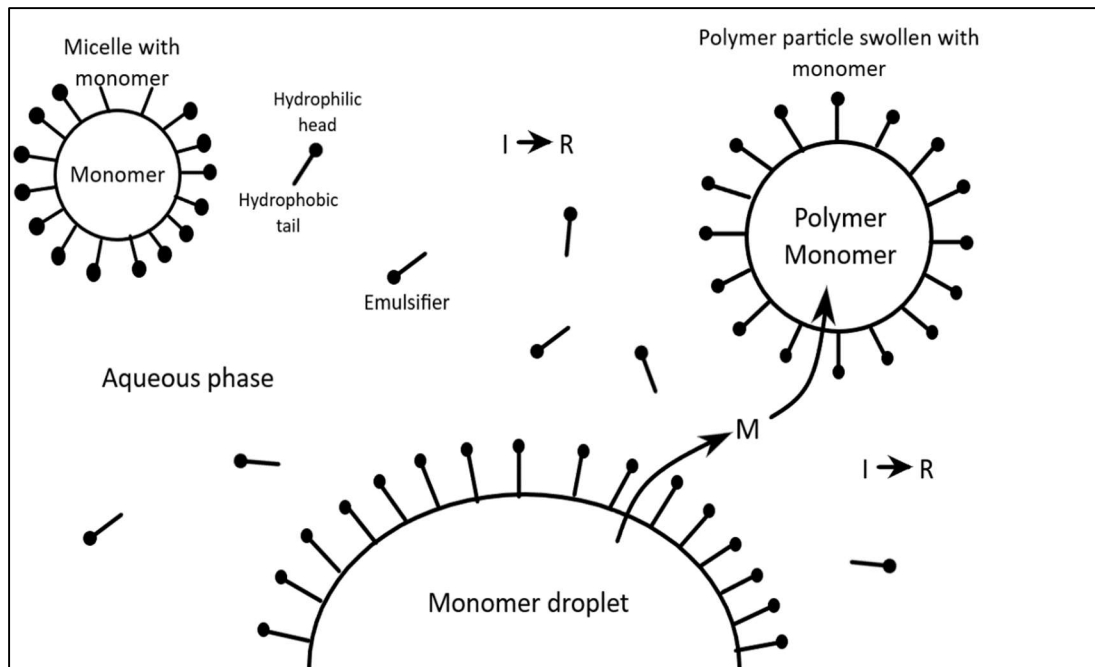


Fig. 6. Simplified scheme of an emulsion polymerization system.

In a batch reactor, emulsion polymerization is divided in three intervals. In *Interval I* micelles disappear; they either become polymer particles due to the oligoradicals entering them or they are destroyed to provide surfactant to the growing polymer particles. Hardly any new particles are formed after this interval. In *Interval II*, polymer particles consume monomers through polymerization, absorb more from the monomer droplets through the aqueous phase and increase in size. The decrease of monomer concentration of the aqueous phase is equilibrated by the dissolution of monomers from the monomer droplets. As a result, monomer droplets shrink until they disappear and there are solely polymer particles left; this is the end of *Interval II*. In the course of *Interval III*, the concentration of monomer in the polymer particles decreases continuously.

Emulsion polymerization offers various advantages. The system being in a colloidal state allows an easy control of the process as well as the temperature; there is a high heat transfer due to a combined effect of: lower total heat generation by polymerization caused by the solids content (40 to 65 wt%), the high specific heat capacity of water and the lower viscosity of the system. With emulsion polymerization,

polymer of high molecular weight is synthesized quickly and the latex product has a considerably lower viscosity than those obtained in bulk or solution polymerization. Also, the absence of organic solvents makes emulsion polymerization an environmentally friendly alternative, and emulsion polymerization leads to a type of product that has unique applications (e.g. paints for houses).

Emulsion polymerization offers the ability to simultaneously increase polymerization rate and molecular weights thanks to *radical compartmentalisation*. Additionally, the products can be directly used without any separations (e.g. polishes, paints and coatings). In spite of these benefits, there are some setbacks to using this technique. Those are that the polymer is contaminated with emulsifier and that chain-transfer agents must be used if low molecular weights are desired.

1.5.1.- Miniemulsion Polymerization^[39-41]

There are also some other variations of the emulsion polymerization system, such as miniemulsion, inverse emulsion or dispersion polymerizations. In this investigation project, miniemulsion polymerization technique was used. In comparison to emulsions, in miniemulsions the monomer droplets are considerably smaller (1000 – 100.000 nm as opposed to 50 – 500 nm respectively). This is obtained by performing a homogenisation process under high shear (e.g. using a sonicator device) and by combining a surfactant and a co-stabiliser. The surfactant is used to make the monomer droplets colloidally stable; the co-stabiliser is usually a hydrophobic low molecular weight compound, and its purpose is to avoid a phenomenon known as *Ostwald Ripening*^[42]. This last process consists on the inclination of the monomer to diffuse from smaller to bigger droplets. The reason for this phenomenon is the higher free energy of the monomer in the small droplets, caused by the interfacial tension. In this project, a reactive co-stabiliser (Stearyl Acrylate, Fig.7) was used.

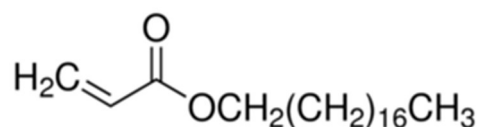


Fig. 7. Structure of Stearyl Acrylate (SA).

As the surface area of the monomer droplets in the miniemulsions is large. The surfactant added is mainly adsorbed on the droplets and there are no micelles in the system. Therefore, the oligoradicals formed in the aqueous phase are captured by the droplets and, as a result, polymer particles are formed by droplet nucleation. The main advantage of miniemulsion technique is that hydrophobic components (hydrophobic monomers, inorganic materials, preformed polymers) can be incorporated in the polymer particles.

Although, in miniemulsion polymerization, particles are mainly formed by droplet nucleation, homogeneous nucleation might also occur. This can be avoided by using an oil-soluble initiator that produces radicals within the monomer droplets. In this project, AIBN was used, which promotes nucleation in the monomer droplets.

1.6.- Reversible addition-fragmentation chain-transfer Polymerization^[28, 43, 44]

As it has been commented in section 1.3., free radical polymerization lacks control over the structure, molar masses and polydispersity of the polymers. Reversible deactivation free radical polymerization (RDRP) is a family of polymerization techniques that allows the synthesis of macromolecules with precise molar masses and low polydispersity. RDRP creates a fast equilibrium between active and dormant species so that all chains grow simultaneously, and reduces the concentration of radicals low enough so that termination reactions are minimised. RDRP techniques include nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer (RAFT).

Reversible addition-fragmentation chain-transfer is the technique that was used in this project. RAFT polymerization relies on a reversible chain transfer reaction involving a RAFT agent to control polymerization. These molecules contain a reactive double bond to which a radical can be added, and a weak single bond from which a group can leave and create a new radical. *S,S*-Dibenzyl trithiocarbonate (DBTTC) was the RAFT agent used in this project (*Fig.8*).

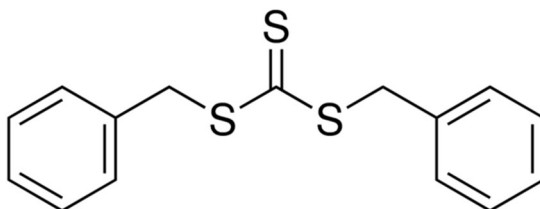


Fig. 8. Structure of *S,S*-Dibenzyl trithiocarbonate (DBTTC) RAFT agent.

To begin the polymerization process, an initiator (such as AIBN, used in the project) creates radicals, which will then react with monomer and begin propagation. This propagating polymer chain will undergo a reversible addition reaction with the RAFT agent; the newly formed radical can undergo fragmentation and either yield the starting polymeric active species ($P_n\cdot$) or a new radical ($R\cdot$) (see *Fig.9(A)*). These new radicals ($R\cdot$) react with monomeric species to form active polymer chains. The $R\cdot$ leaving group in DBTTC is stable enough so that the right-hand side of the equilibrium is favoured (thanks to resonance structures) but it is also unstable enough so that it can

act as an initiator. This occurs very early in the process, meaning that all the chains start growing approximately at the same time.

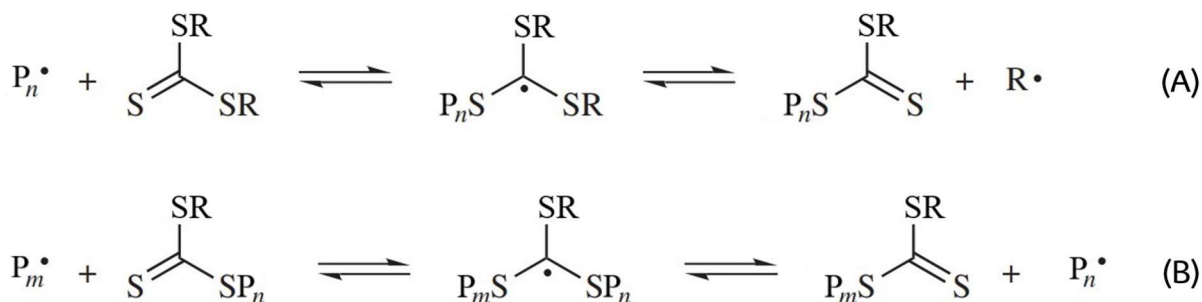


Fig. 9. Scheme of RAFT pre-equilibrium (A) and main equilibrium (B) steps.

Fig.9(B) shows the main equilibrium in the RAFT polymerization process. This fast reversible addition-fragmentation reactions ideally allow all active species to have equal chance to grow and hence a narrow chain-length distribution is obtained. The formation of the intermediate radical of the equilibrium (known as dormant state) is favoured due to its stability, and this has two main effects: 1) it reduces the number of active species and thus, the probabilities of bimolecular termination between active species; 2) it extends the lifetime of active polymer chains. The dormant state is furtherly favoured when the propagating radical does not contain stabilising features, which is the case for butyl acrylate.

One of the main characteristics of the RAFT polymerization technique is that the molecular weight increases linearly with conversion. For this to be possible, the concentration of RAFT agent must be larger than that of the initiator, as the initiator does not decompose entirely at the beginning of the process but throughout it. Consequently, active polymeric chains that arise from initiator decomposition cannot have a narrow molar mass distribution, as the monomer concentration is reduced during polymerization. As soon as a propagating polymer chain is formed from the initiator, it will quickly react with a RAFT agent to form a dormant state since this more stable state is favoured. The dormant radical yields a radical and a RAFT agent, and this radical, after a few propagation steps, will react with another RAFT agent. This is a fast process that determines the number of growing chains. As each chain undergoes short propagating periods, they grow similarly and narrow molecular weight distributions are obtained. One disadvantage of RAFT polymerization is that large amounts of RAFT

agent are needed for it to be efficient. In addition, the presence of sulphur makes polymer purification processes required^[45].

The reduction of the concentration of active species does not only have an effect on bimolecular termination rate, but also on the propagation rate. This results in longer reaction times as well as in a lower heat generation due to polymerization. In addition, lower molar masses are obtained due to the fact that, ideally, all the chains start growing at the same time and have equal growth. These aspects make it interesting to investigate possible non-thermal effects of microwaves in RAFT polymerizations, as the lower heat generation and a lower viscosity of the medium could lead to an easier control over temperature.

1.7.- Microwave-assisted Polymerization^[46, 47]

Microwave assisted heating provides several advantages over conventional heating methods. It offers a non-contact, instantaneous and affordable heating source, as well as applicability to different types of reactions. As a result, interest in microwave-irradiation has been rapidly increasing during the past few decades in different sectors of research and industry. Polymer chemistry has not been an exception, as numerous types of microwave-assisted polymerization techniques have been developed (living and free radical polymerizations^[48, 49], ring-opening polymerizations^[50], step-growth polymerizations^[51]), hence allowing the synthesis of a variety of polymer materials. Moreover, results from different investigations have demonstrated a notorious acceleration in polymerization rates when compared to conventional heating. Some other results have ignited a debate on whether a non-thermal microwave effect is behind the increase of the reaction rate.

Modern microwave reactors enable very fast and uncomplicated preparations. In single-mode or monomodal reactors, where microwaves are irradiated from a single source and directed to the sample. These reactors reportedly endure conditions of up to 300°C and 30 bar. These accessible wide ranges of temperature and pressure expand the list of solvents that can be used for polymerization processes. For example, low-boiling solvents can be used, which makes the product isolation process easier and less expensive.

The heating caused by microwave irradiation is due to two mechanisms: dipolar polarization of polar molecules (e.g. polar solvents) and ionic conduction of charged particles (ions)^[47]. When an electric field is applied at microwave frequencies, both dipoles and ions align with this field. Given that this field is constantly oscillating, dipoles and ions enter a continuous reorientation cycle as they try to keep up with the oscillating field. This causes friction, rotation and collisions between the molecules, thereby heat is generated.

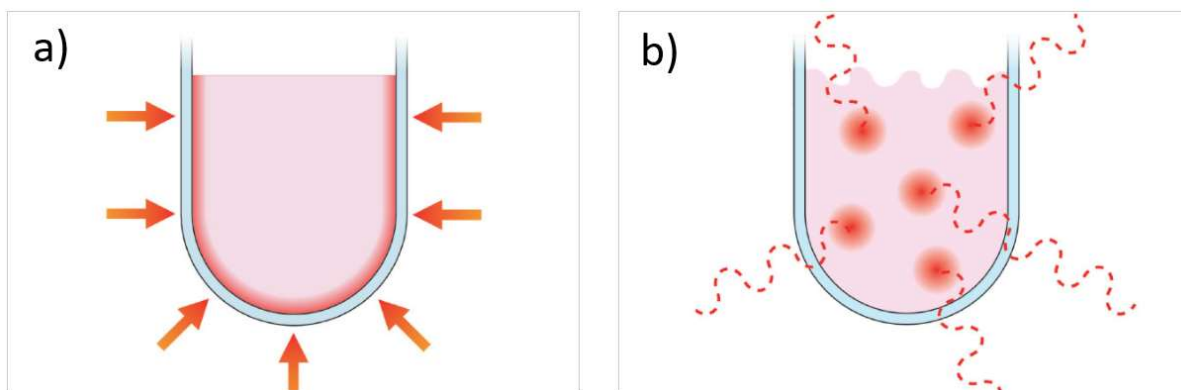


Fig. 10. Representation of a) conventional heating mechanism, b) microwave heating mechanism.

Reactor walls that are transparent to microwaves are used, helping the reactants to directly absorb the energy. Microwave irradiation produces a non-contact internal heating by pairing the microwave energy to with the molecules in the mixture, consequently rising the temperature of the whole reaction volume at the same time (see *Fig.10b*). Conventional heating methods on the other hand, rely on conduction and convection for heating, and areas of the reaction mixture that are in contact with the reactor walls are heated first (see *Fig.10a*).

During the last decades, microwave reactors designed specifically for synthetic applications have been developed. These are mainly monomodal reactors. Monomodal microwave systems heat only one reaction vessel at a time and, as a consequence, the volume of the vessels is smaller. Reaction vessels are sealed; combined with high irradiation powers, the reaction temperature and pressure are quickly achieved, limiting pre and post reaction delays and reducing the overall reaction time. Online monitoring and control of the temperature is possible by means of infrared sensors recording the temperature of the surface of the vessel or by using optic-fibre probes directly inserted in the mixture. Additionally, gas-jet cooling is used to rapidly decrease the temperature of the reactor at the end of the process. This cooling can be constantly applied during the reactions so that a higher amount of microwave power is irradiated, therefore boosting any non-thermal effects that are dependent on it. In order to maintain a homogeneous mixture and avoid hot and cold spots, these instruments are also equipped with built-in magnetic stirrers. *Fig.11* shows the microwave reactor used for the experiments during the project.

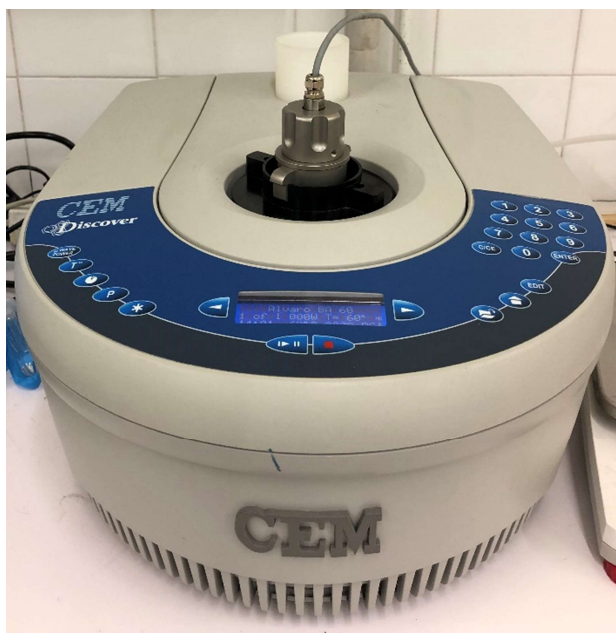


Fig. 11. CEM Discover Benchmate® (CEM, USA, www.cem.com) Copyright CEM Corporation.

Thanks to these advances in technology surrounding microwave-assisted synthesis, these systems have been successfully applied in several free radical polymerization methods, such as bulk^[52], solution^[53], suspension^[54] and emulsion polymerization^[55]. However, it is clear that in order to prove the existence of a non-thermal effect, temperature control needs to be highly accurate. Taking that into account, many results that suggested a non-thermal effect have been disclaimed due to a lack of accuracy when monitoring the temperature of the reactions and reviews on the appropriate technique to precisely measure the reaction temperature have been published^[46]. Nevertheless, the results obtained by Castagnet *et al.*^[11, 12] strongly support a specific non-thermal effect on acrylate monomers, considering the decrease on reaction times and increase in molecular weight.

Therefore, this project aims at determining if non-thermal effects are also operative for conventional acrylic monomers such as Butyl Acrylate.

2. Experimental procedure

2.1.- Materials used

Monomer:

- Butyl Acrylate ($\geq 99\%$, containing 10-60 ppm monomethyl ether hydroquinone as inhibitor)
CAS number: 141-32-2. Bought at Sigma-Aldrich.
Molecular weight: 128.17 g/mol.

The monomer was distilled under reduced pressure before use.

Initiator:

- 2,2'-Azobis(2-methyl-propionitrile) ($\geq 98.0\%$).
CAS Number: 78-67-1. Bought at Sigma-Aldrich.
Molecular weight is 164.21 g/mol.

Solvent:

- m-Xylene ($\geq 99.0\%$).
CAS Number: 108-38-3. Bought at Sigma-Aldrich / Merck.
The molecular weight: 106.17 g/mol.

Inhibitor:

- 1,4-Benzoquinone (98%).
CAS Number: 106-51-4. Bought at Sigma-Aldrich.
Molecular weight: 108.09 g/mol.

Polymerizable co-stabiliser:

- Octadecyl Acrylate, also Stearyl Acrylate, (97%, containing 200 ppm monomethyl ether hydroquinone as inhibitor).
CAS Number: 4813-57-4. Bought at Sigma-Aldrich.
The molecular weight is 324.54 g/mol.

Surfactant:

- Dowfax 2A1 solution. 45 wt%. in water.

Density: 1.10-1.20 g/mL.

RAFT agent:

- DBTTC, S,S-Dibenzyl trithiocarbonate.
CAS Number: 26504-29-0. Bought at BASF.
The molecular weight is 290.47 g/mol.

2.2.- Solution Polymerization of BA

2.2.1.- Conventional Heating

For the free radical polymerizations in solution of BA, these systems of 50% of solid content were prepared:

- Butyl Acrylate 5 g (39 mmol)
- m-Xylene 5 g (5.81 mL)
- AIBN 0,005 g (0.03 mmol, 0.1% wpm)

First, the mixture of BA and Xylene without initiator was purged with nitrogen for 30 min in an ice bath to obtain an inert atmosphere. Then, the mixture was placed in an oil bath at the desired temperature of 60°C. Once the temperature inside the reactor was stabilised, AIBN was added as a shot (in 1 g/1.16 mL of m-Xylene) and this was taken as time = 0 of the reaction. All the reactions were carried out while magnetically stirred and sealed. Some reactions were also carried out with a system of 20% of solid content and 0.1%wpm of AIBN, following the same procedure.

To observe the kinetics of the reaction, samples were taken periodically during the reaction with syringes already purged with N₂. To ensure that the polymerization process was completely stopped, a solution of Benzoquinone (%1) in m-Xylene was added as an inhibitor to the samples. The experiments were repeated thrice to ensure reproducibility. Conversion was calculated by gravimetry.

The molar mass distributions were measured by Size Exclusion Chromatography in combination with a Multi Angle Light Scattering (MALS) and a Refractive Index (RI) detector, SEC/MALS/RI. The set-up used consisted of a pump (LC-20AD, Shimadzu), an autosampler (SIL 20^a, Shimadzu), a precolumn (styragel, Waters) and other three columns in series (styragel HR6, styragel HR4 and styragel HR3, all of them from Waters). The detectors employed were a refractive index T-Rex detector (Wyatt Technologies) and a Light Scattering detector (Dawn Heleos II, Wyatt Technologies). Astra 6.1 (Wyatt Technologies) was the software used for data recompilation and treatment.

2.2.2.- Temperature control measurements

As previously mentioned, since the temperature was measured by an IR detector, the temperature recorded did not correspond to the internal temperature of the mixture but to the external temperature of the reactor wall^[46]. There is a possibility that there could be discrepancies between the temperature of the mixture and the temperature that is recorded. Taking this into account, some control measurements were taken to compare the temperatures.

These experiments were performed in three different conditions:

- System with low conversion (low viscosity mixture)
- System at high conversion levels (high viscosity and very dense mixture)

To perform these measurements, the vessel with the mixture was inserted in the microwave reactor. After a small period of time, once the recorded temperature was stable, the equipment was completely stopped, the reactor was removed without any cooling and the internal temperature was measured immediately with a digital thermometer and compared to the one recorded by the IR sensor. Measurements were performed 5 times for the low viscosity mixture and 3 times for the high viscosity mixture. Same heating-cooling pattern was followed each time and microwave settings and composition were the same used in the previous reactions.

2.2.3.- Microwave-assisted Polymerization

For reactions in the microwave, a 10 mL tubular flask is used. For that reason and to ensure that stirring was efficient, the same solution system (50% of monomer in weight) was prepared every time but in a reduced amount. Butyl Acrylate (1.5 g, 12 mmol), m-Xylene (1.5 g, 1.74 mL) and AIBN 0.1% wpm (0.0015 g, 0.01 mmol) composed the system, which was introduced in flask, sealed with a septum and purged with nitrogen in an ice bath for 30 min. The mixture occupied around 1/3 of the total volume of the flask. Then, the septum was swiftly substituted by a microwave-resistant seal. This is necessary since a regular septum cannot withstand the conditions of a microwave-assisted reaction and the microwave-resistant seal cannot be perforated for purging.

The reactions were carried in a CEM Discover Benchmate® (see *Fig.11*) under magnetic stirring and working in pulse mode. In this mode, microwave irradiation is applied until the desired reaction temperature is reached, then it ceases. When the temperature is below the set point, irradiation is reapplied until the set point is reached again. An example of the temperature profiles that are obtained with this mode can be seen in *Fig. 12*. The irradiation power was set at 200 W. It is possible that as the reaction mixture is heated up to the desired temperature, even though the irradiating pulse stops when that temperature is detected, the heating carries enough inertia for the temperature to rise above the set limit. In order to avoid that, the temperature was initially set 3-5°C below the objective so that the temperature increase stops at the desired temperature, and the final temperature was reset once the pulse was stopped and the wanted temperature was reached.

The pulse mode was coupled with a constant gas-jet cooling during the reactions in order to maximise the amount of irradiation applied. Temperature was measured by an infrared detector that measured the temperature on the wall at the bottom of the flask. There is a setting in the microwave reactor's reaction programming software that allows to adjust the range at which the temperature will oscillate during the reaction. This was set to be $\Delta T = 1$, meaning that the reactor will maintain the reaction temperature at temperatures between 59°C and 61°C.

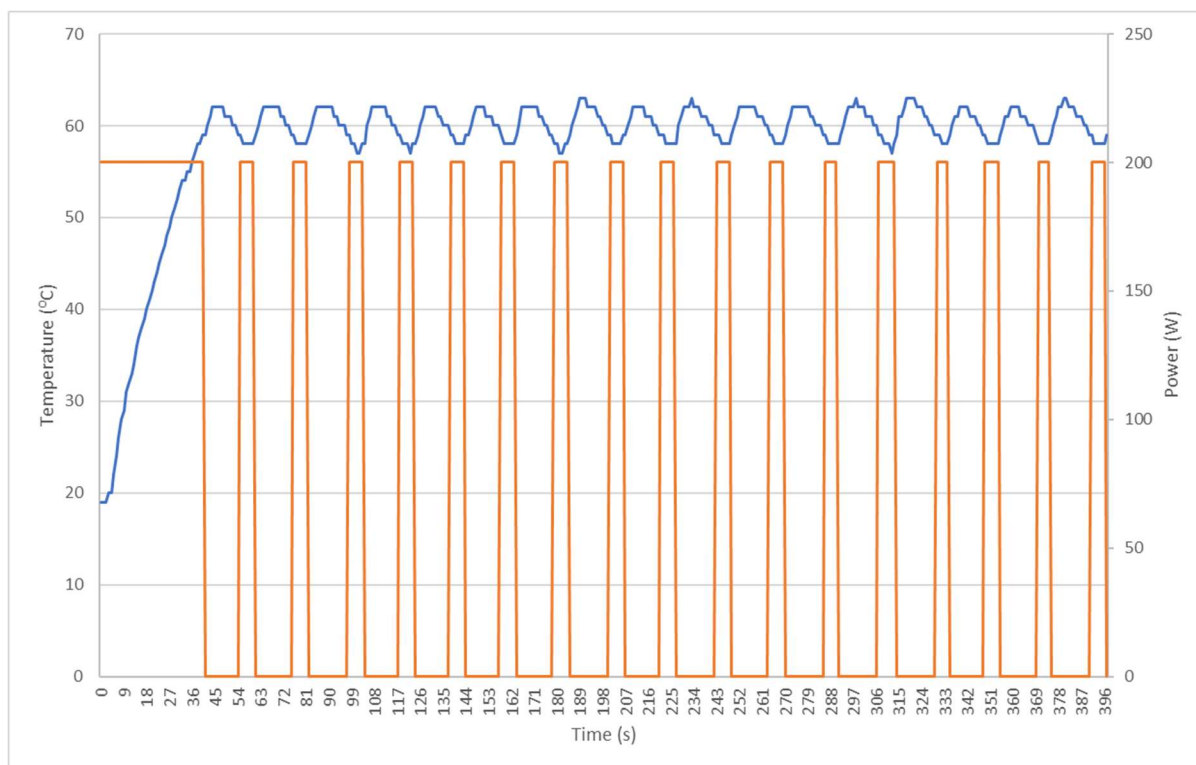


Fig. 12. Power (orange line) and temperature (blue line) evolutions in a microwave-assisted free radical polymerization of BA at 60°C.

Taking samples during the reaction would involve stopping the reactor, waiting for the cooling of the vessel, opening the vessel and taking the sample quickly so that the inert N_2 atmosphere is maintained and starting the reactor again. Since this could be a complex task, individual reactions were performed for different times instead. The mixture was cooled down using the air-cooling system of the reactor (to 49°C in 1 min) and quickly adding the same solution of Benzoquinone used in the conventionally heated reactions. Conversion was calculated by gravimetry and molar mass distributions were determined via SEC-MALS (specifications in section 2.2.1).

2.3.- Miniemulsion Polymerization of BA

2.3.1.- Conventional Heating

For the free radical polymerization of Butyl Acrylate in miniemulsion, this system of %20 of BA in weight was prepared by adapting a previous formulation by Noppalit *et al.*^[26]:

Organic phase:

- Butyl Acrylate (4 g, 31 mmol).
- Stearyl Acrylate (0.2 g, 0.62 mmol, 5% in weight per BA).
- AIBN (0.004 g, 0.024 mmol, 0.1% in weight per BA).

Aqueous phase:

- Dowfax 2A1 solution (0.266 g from which 0.12 g were the surfactant and 0.146 g were H₂O, 3% in weight per BA).
- Distilled H₂O (15.854 g, 16 g in total, 400% in weight per BA).

Both phases were mixed together and then stirred for 30 minutes in an ice bath to obtain a coarse pre-emulsion. After this, the mixture was sonicated (with pulse cycles of 0.5 seconds and 100% amplitude) for 10 min to obtain a miniemulsion. Then, the mixture was transferred to a sealed round bottom flask and it was purged with N₂ for 30 minutes. Finally, the flask was immersed in an oil bath already at the desired temperature. Conventional reactions were carried out at 60°C and 70°C. For reactions at 70°C a condenser was used due to overpressure. Samples were taken periodically throughout the reaction time with syringes already purged with N₂ and conversion was calculated by gravimetry.

The molar mass distributions were measured by Asymmetric-Flow Field-Flow Fractionation in combination with a Multi Angle Light Scattering (MALS) and a Refractive Index (RI) detector, AF4/MALS/RI. The set-up used included a pump (LC-20AD, Shimadzu), an autosampler (SIL 20^a, Shimadzu), and separation was carried out on a 27.5 cm trapezoidal channel mounted on PEEK (polyether ether ketone) upper and lower blocks with a stainless-steel frit. The channel thickness spacer was 490 μm. The accumulation wall was a regenerated cellulose membrane with a cut-off molar mass of

10,000 Da. AF4 flow control was maintained with a Wyatt Eclipse 3 AF4 Separation System controller (Wyatt Technology, USA). The detectors employed were a refractive index T-Rex detector (Wyatt Technologies) and a Light Scattering detector (Dawn Heleos II, Wyatt Technologies). Astra 6.1 (Wyatt Technologies) was the software used for data recompilation and treatment.

Samples were analysed by ^{13}C MAS NMR in order to observe the presence of quaternary carbons in the system. ^{13}C MAS NMR spectra were recorded on a 9.4T (400 MHz) BRUKER system equipped with a 4 mm MASDVT TRIPLE Resonance HYX MAS probe. Larmor frequencies were 400.17 MHz and 100.63 MHz for ^1H and ^{13}C nuclei, respectively. Samples were packed inside 4 mm MAS rotors and THF drops were added to gain mobility and better resolution. Chemical shifts were calibrated indirectly with glycine, carbonyl peak at 176 ppm. Sample rotation frequency was 5 kHz and relaxation delay were 12 seconds. High-power SPINAL 64 heteronuclear proton decoupling was applied during acquisition. The number of scans were 6192.

2.3.2.- Microwave-assisted Polymerization

For the reactions in the microwave, the same reaction mixture was used, following the same preparation as in section 2.3.1. Portions of 3g of this reaction mixture were then transported into the 10 mL flasks used for the microwave in order to fill around 1/3 of the total volume of the flask. This would ensure efficient stirring. The flasks were sealed with a septum and purged with nitrogen in an ice bath for 30 min. The septum was then substituted by a microwave resistant seal.

The reactions were carried under magnetic stirring and working in pulse mode (see explanation in section 2.2.3.). The irradiation power was set at 200 W. The pulse mode was coupled with a constant gas-jet cooling during the reactions in order to maximise the amount of irradiation applied. Temperature of the wall at the bottom of the flask was measured by an infrared detector. The range at which the temperature oscillated during the reaction was set to be $\Delta T = 1$ (temperatures between 59°C and 61°C).

Individual reactions were performed for different times, then the mixture cooled down using the air-cooling system of the reactor (to 49°C in 1 min) and quickly adding the same solution of Benzoquinone used in the conventionally heated reactions. Conversion was calculated by gravimetry and molar mass distributions were determined via AF4/MALS/RI (specifications in section 2.3.1.).

2.4.- RAFT Solution Polymerization of BA

2.4.1.- Conventional Heating

For the RAFT polymerization of BA, this system was prepared:

- BA 35 mmol (4,860 g)
- BA/DBTTC = 250 mol/mol (around 0,04 g)
- DBTTC/AIBN = 10 mol/mol (around 0,002 g)
- Toluene 1 g

First, two mixtures were prepared: on the one hand DBTTC was dissolved in BA and, on the other, AIBN was dissolved in Toluene. These two mixtures were then purged with N₂ while stirring for 30 min. Finally, the BA and DBTTC mixture was heated to the desired temperature (80°C) in an oil bath and, once stabilised, the AIBN-Toluene mixture was added as a shot. The moment the initiator shot was added was considered to be the beginning of the reaction.

Samples were taken periodically with syringes that had been purged with N₂. To ensure that the polymerization process was completely stopped, a solution of Benzoquinone (%1) in m-Xylene was added as an inhibitor to the samples. The experiments were repeated thrice to ensure reproducibility.

Conversion was calculated with quantitative ¹H NMR in a Bruker AVANCE 400 MHz equipment. The best signal to monitor the conversion of the monomer, is the signal between 4.1 and 4.2 ppm, a triplet that corresponds to the two protons in the first methylene group in the butyl chain. As polymerization occurs, the signal appears shifted downwards as it becomes part of the polymer chain (see *Fig.13*).

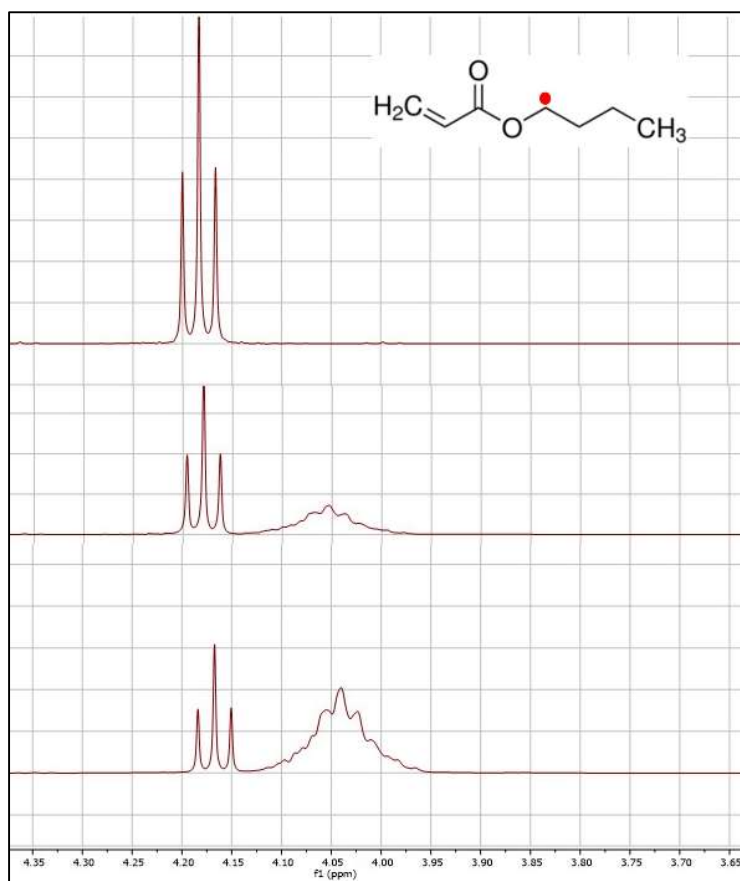


Fig. 13. ^1H NMR spectra (in CDCl_3) of Butyl Acrylate at different conversions: 0%, 50% and 80% from top to bottom. The methylene group to which the signal belongs is highlighted with a red dot.

Molar mass distributions were measured by SEC-MALS (specifications in section 2.2.1.).

2.4.2.- Microwave-assisted Polymerization

For the polymerizations in the microwave, the same reaction mixtures used in the conventional polymerizations were used, with the same amounts. All the components were mixed together in the 10 mL microwave-vessels, thus filling the vessel almost completely. The vessel was sealed with a septum and purged with N₂ while submerged in an ice bath for 30 min. Then the septum was quickly replaced with a microwave resistant seal.

The reactions were carried in pulse mode and with magnetic stirring (see explanation in section 2.2.3.), with an irradiation power set at 300W. Constant gas-jet cooling was used during the reactions to maximise the amount of irradiation power. An infrared detector measured the temperature of the wall at the bottom of the vessel. The temperature oscillation range was set to $\Delta T = 1$ (79-81°C).

Individual reactions were performed for different times as in the other reactions, however, once the reaction time was over, the cool down step was stopped and the vessel was quickly removed from the device. The microwave resistant seal was immediately removed and the temperature at the top of the vessel was measured with a digital thermometer. Then a sample of the mixture at the top of the vessel was taken with a syringe. Then the digital thermometer was used to measure the temperature of the mixture at the bottom of the vessel and a sample of the bottom was taken. The whole process took around 1 minute every time. Both samples were kept in vials containing the same solution of Benzoquinone used in the conventionally heated reactions. Conversion was calculated by quantitative NMR (see *Fig.13*) and molar mass distributions were determined via SEC-MALS (specifications in section 2.2.1.).

3. Results and discussion

3.1.- Results from temperature control measurements

Kappe^[46] argued in his review that IR measurements are restricted to the surface of the reactor and cannot be used to determine the actual temperature of the mixture or its distribution. As the irradiation energy is converted to heat directly in the mixture, the heat flow is formed from the inside to the outside. For that reason, the temperature on the wall of the reactor is lower than the inner temperature. This effect is enhanced by the fact that cooling is provided by cold air that is blown onto the surface where the sensor records the temperature,

In order to check if these hypotheses apply to our system, non-reactive polymer solutions were heated in the microwave reactor at nominal temperatures of 60, 80 and 110°C. The control of the microwave reactor was able to maintain the reactor wall temperature (this is the temperature measured by the IR sensor) within $\pm 2^\circ\text{C}$ of the set point. The temperature in the centre of the reactor was measured by inserting a thermocouple just after finishing the irradiation. The results are presented in *Tab.1*. It can be seen that for the low viscosity mixture, the temperature determined with the thermocouple agreed with that measured with the IR sensor. However, large differences were observed for the high viscosity system. Moreover, when the mixture was manually stirred with the thermometer rod after each measurement, the temperature decreased (still higher than the value read by the sensor) indicating a strong radial gradient of temperature. These observations were attributed to the effect of viscosity on mixing of the reactor. At low viscosity, the agitation provided by the magnetic stirrer was enough to homogenize the reactor and to efficiently transfer heat to the reactor wall, yielding an efficient control of the temperature. On the other hand, for the high viscosity mixture, the magnetic stirrer was not able to mix the reactor and severe temperature gradients were created. It should be pointed out that during these tests, there was no reaction occurring in the vial so there was no reaction heat factored in.

Tab. 1. Temperature registered by IR sensor and average values of the temperatures measured by digital thermometer.

IR sensor (°C)	Digital Thermometer (°C)	
	Low viscosity mixture	High viscosity mixture
60±2	61 ± 0,6	96 ± 6
80±2	80 ± 1	123 ± 6
110±2	109 ± 1	145 ± 4

These findings implied that in order to be able provide results that could confirm a non-thermal effect, systems in which viscosity increases considerably with conversion cannot be used. It was also deduced that stirring is also a critical factor because it helps to ensure that the heating is uniform through the whole volume of the system. Furthermore, low viscosities could lead to faster cooling, causing more frequent cooling-heating intervals, thus allowing a higher level of irradiation administered during the reaction.

3.2.- Conventional vs Microwave in Solution

Solution polymerizations of butyl acrylate (BA) were carried out using both conventional heating and microwave irradiation. *Fig.14* presents a comparison between the conversion values from the conventionally heated solution FRP reaction and the microwave-assisted polymerization of BA. The conventional experiments were repeated 4 times, presenting very good reproducibility, and stable temperature profiles were recorded in the microwave (*Fig.15*). With conventional heating, 3 hours of reaction were needed in order to obtain 80% of conversion, whereas with microwave-assisted heating these levels of conversion can be achieved in 20 minutes. It is important to mention that for microwave irradiation, the conversion data obtained at different reaction times come from individual reactions. The dispersity of the data was attributed to the differences in the moment when the polymerizations started, caused by differences in the initial inhibition time (small differences of inhibitors such as oxygen). *Fig.14* shows that the microwave-assisted polymerization was much faster than the polymerization using conventional heating.

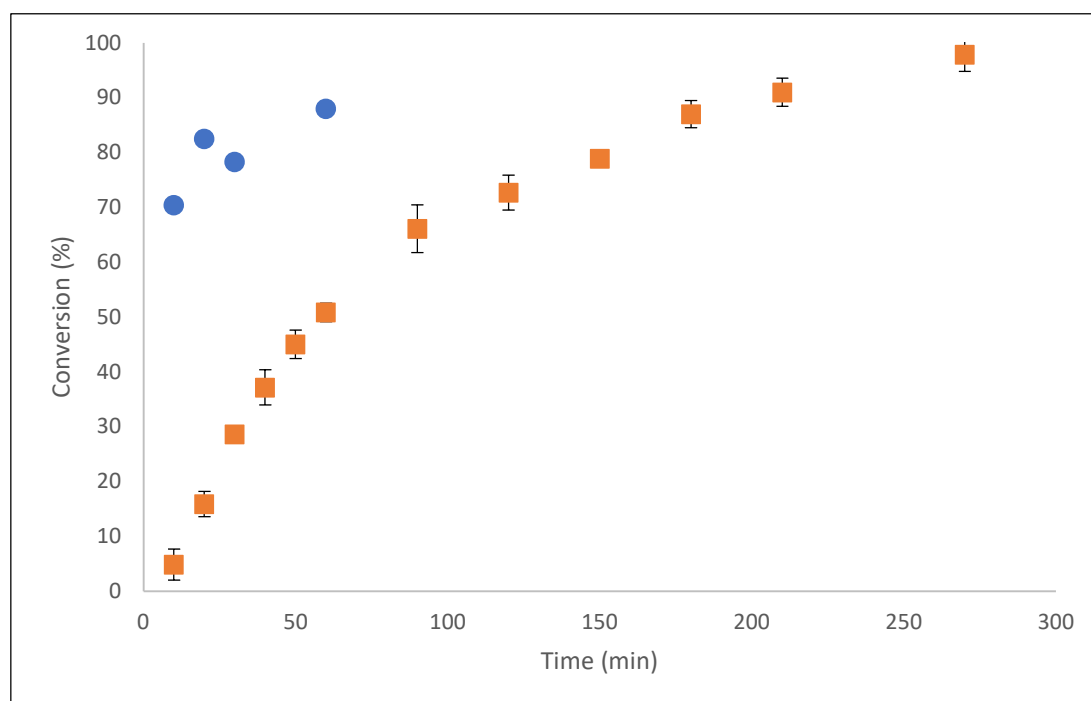


Fig. 14. Evolution of monomer conversion in solution FRP of BA at 60°C. Conventional heating (orange squares), microwave heating at 200W (blue circles).

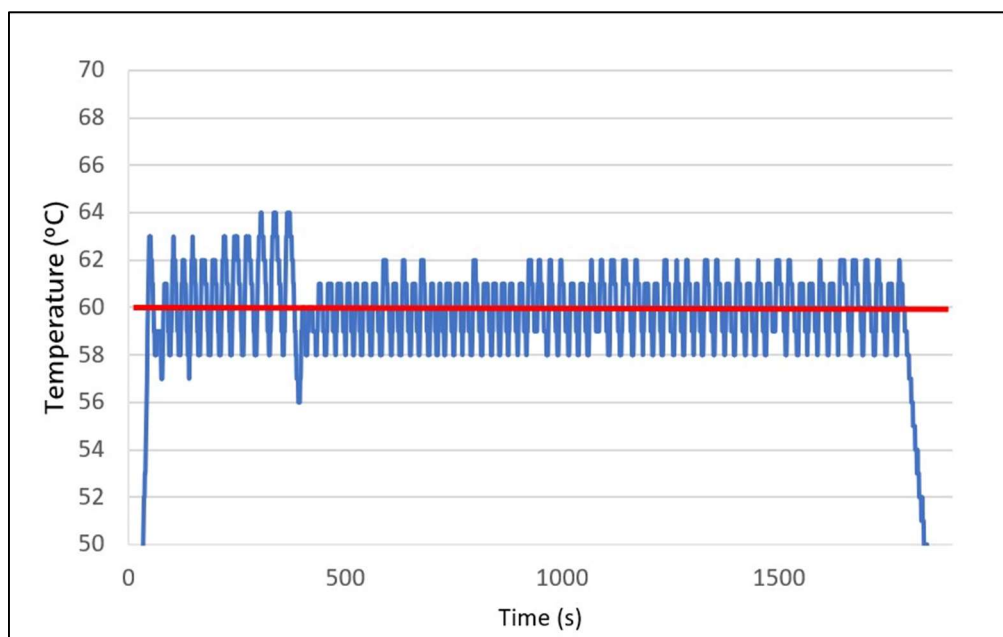


Fig. 15. Temperature recorded by IR sensor during microwave-assisted solution FRP of BA at 60°C (30 min).

Fig.16 presents the evolution of the molar masses and dispersity. It can be seen that the molar mass was smaller and the dispersity was higher for the microwave-assisted polymerizations. These results are in conflict with those reported by Castagnet *et al.*^[11] that found higher polymerization rates and higher molar masses for the microwave-assisted polymerization. The results obtained in the present work suggest that the temperature was substantially higher in the case of the microwave-assisted polymerization. The higher temperature would lead to faster reactions due to higher rate of initiator decomposition, thus, also a higher concentration of radicals in the system. It would also cause faster propagation and termination rates, as well as lower molecular weights due to the higher concentration of radicals that will initiate a larger number of chains. This effect was enhanced by the poor mixing observed in the microwave reactor. Thus, once the reactions in the microwave were stopped and the vessel removed, it could be seen that the magnetic stirrer was stuck in one position. This viscosity would make it difficult to dissipate the heat during the reaction in addition to hampering stirring. The higher polydispersity in microwave samples could be a result of inefficient stirring and temperature gradients formed during the reaction.

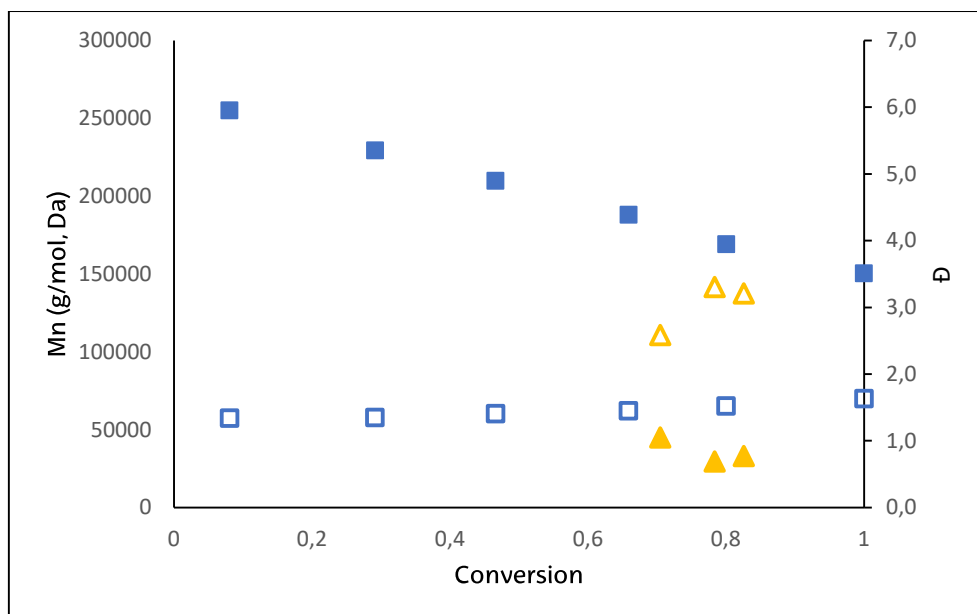


Fig. 16. Effect of microwave irradiation on the evolution of Mn and polydispersity (\bar{D}) with conversion in solution FRP of BA at 60°C. Conventional heating (squares), microwave heating 200W(triangles), open symbols (\bar{D}).

It is worth pointing out that the temperature recordings of the microwave device did not show any sign of a thermal increase at any time or reaction (see Fig.15). A possible reason was that, due to the viscosity of the system, the heat from the reaction and heat due to microwave irradiation accumulated inside the reactor leading to a high temperature, whereas the temperature recorded by the IR detector was that of the wall of the vessel, which was continuously cooled down by the gas-jet cooling.

In order to avoid these problems, polymerizations using a higher dilution of the monomer (20 wt% of BA in xylene) were carried out. The initiator concentration was kept at 0.1% wpm for these reactions. Although the temperature was well controlled (Tab.2), polymerization was too slow, probably due to the combined effect of the lower concentration of monomer and the lower concentration of initiator. In consequence, this option was discarded and it was decided that a miniemulsion system would be the best next option, which would allow to reduce the viscosity of the system without having to dilute the monomer.

Tab. 2. Temperature registered by IR sensor and average values of the temperatures measured by digital thermometer in system of 20 wt% solid content.

IR sensor (°C)	Digital Thermometer (°C)
60±2	62 ± 0.6
80±2	81 ± 2
110±2	112 ± 0.6

3.3.- Conventional vs Microwave in Miniemulsion

After some preliminary trials, a 20 wt% solids content miniemulsion polymerization was performed using 0.1% wpm AIBN and 5% wpm of stearyl acrylate. The target temperature was 60 °C, but in the microwave-assisted polymerizations, the temperature of the IR sensor oscillated between 58 and 66 °C. Taking into account the low viscosity of the reaction medium, the high heat capacity of the water and the results in *Tab.1*, it was considered that the temperature within the reactor was similar to that of the reactor wall. Miniemulsion polymerizations using the same formulation were also carried out with conventional heating. In this case, the reactions were performed at 60, 70 and 90°C.

Fig.17 presents the evolution of the conversions. As previously mentioned, each data point of the microwave-assisted polymerization was obtained from an individual reaction, and due to the presence of inhibitors there is an uncertainty about the moment in which the reaction started. Therefore, the successive points cannot be taken as a kinetic plot. What *Fig.17* shows is that the microwave-assisted polymerization was faster than the reactions using conventional heating.

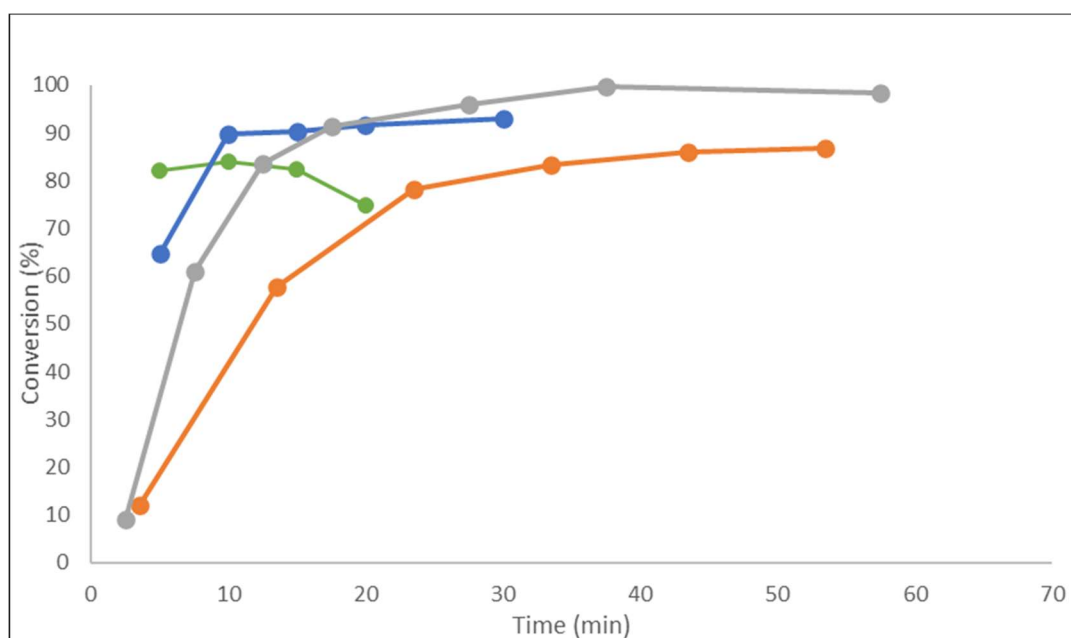


Fig. 17. Evolution of the conversion of the monomer in miniemulsion reactions: conventionally heated at 60°C (orange), at 70°C (grey), at 90°C (blue) and microwave heated (200W, green).

The molar mass distributions were analysed by AF4/MALS/RI. Different sample treatments were used for the samples obtained by microwave-assisted polymerization and conventional heating. As the microwave samples dissolved in THF, the latex was dried and then dissolved in THF. On the other hand, the samples from conventional heating could not be dissolved in THF. Therefore, a small fraction of the latex was added to THF and the dispersed polymer particles injected in the AF4. The results are summarized in *Tab.3* and *4* and the distributions are presented in *Figs.18-22*. The presence of macroscopic gel in the samples obtained by conventional heating was detected by Soxhlet extraction (*Tab.5*).

Tab. 3. Molecular weights obtained from AF4/SEC/MALS analysis of the samples from the microwave-assisted miniemulsion reactions.

MICROWAVE				
TIME (min)	Conversion	Mn (kDa)	Mw (kDa)	Dispersity
10	0,84	1011,4	26514,3	26,216
15	0,82	1237,9	40487,6	32,707
20	0,75	1131,5	51591,1	45,594

Tab. 4. Molecular weights obtained from AF4/SEC/MALS analysis of the samples from conventionally heated miniemulsion reactions.

CONVENTIONAL HEATING				
60°C				
TIME (min)	Conversion	Mn (kDa)	Mw (kDa)	Dispersity
30	0,706	12379,4	29400,5	2,375
40	0,78	48258,8	59465,9	1,232
60	0,87	149952,6	154994,4	1,034
70°C				
50	0,962	45770	60983,1	1,332
60	0,983	137815,8	162206,7	1,177
90°C				
20	0,917	46072,8	86218,0	1,871
30	0,929	44445,5	88050,2	1,981

Tab. 5. Gel content obtained from Soxhlet extraction of the samples from the conventionally heated miniemulsion reactions.

Temperature	Time (min)	Gel Content (%)
90°C	20	56
90°C	30	61
60°C	60	60
70°C	60	62

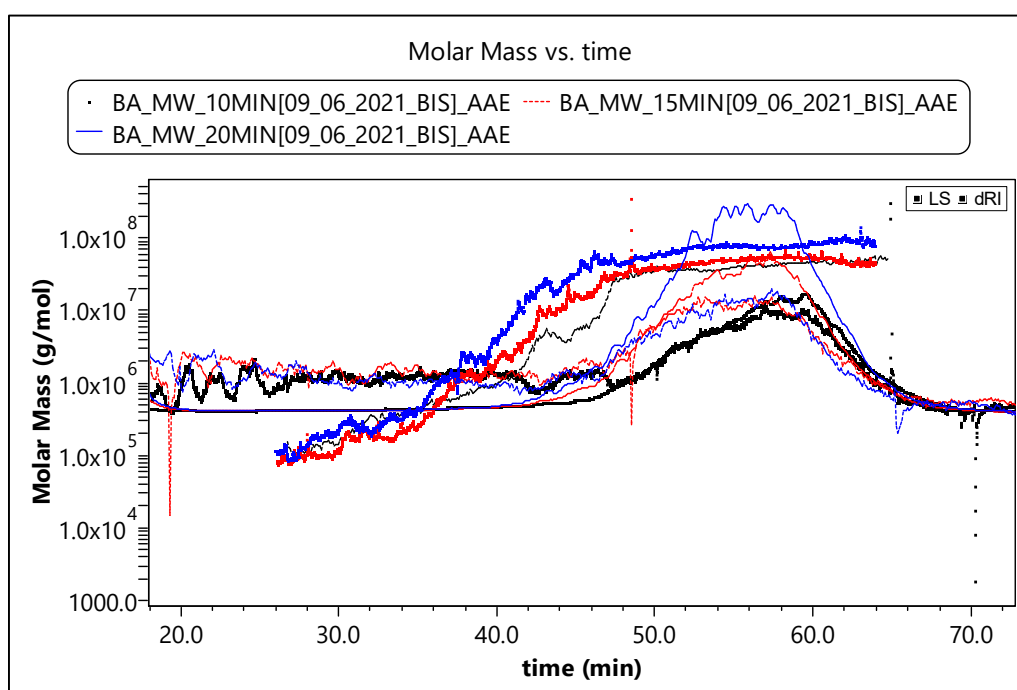


Fig. 18. Light scattering and Refractive index spectrum of dry samples of microwave heated reactions (200W).

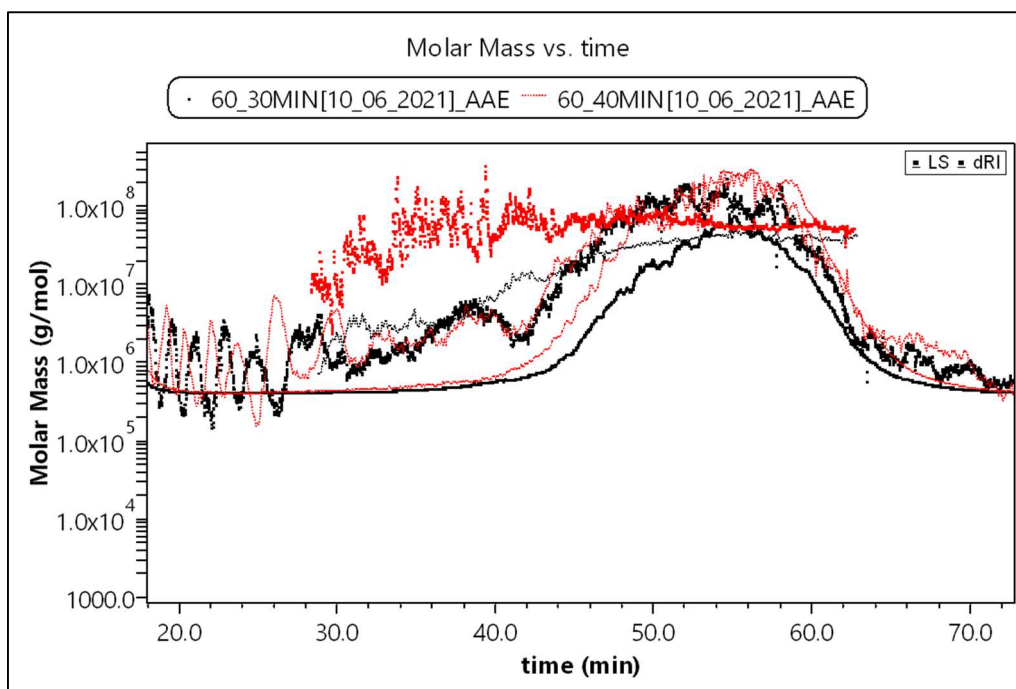


Fig. 19. Light scattering and Refractive index spectrum of latex samples of the first conventionally heated reactions at 60°C (30 and 40 min of reaction).

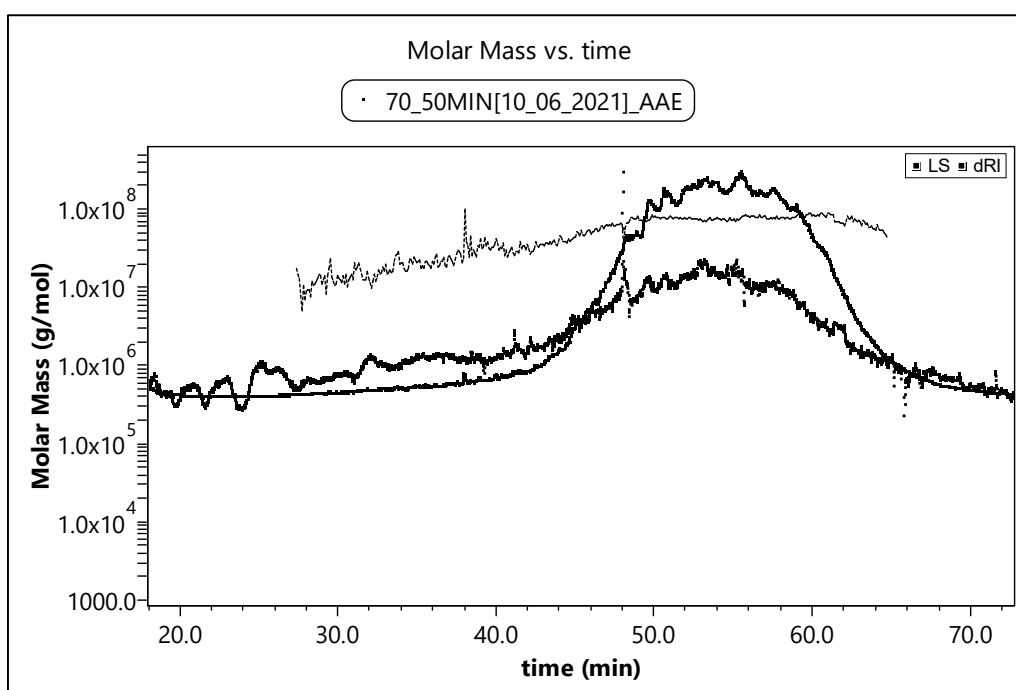


Fig. 20. Light scattering and Refractive index spectrum of latex sample at 50 min of the conventionally heated reaction at 70°C.

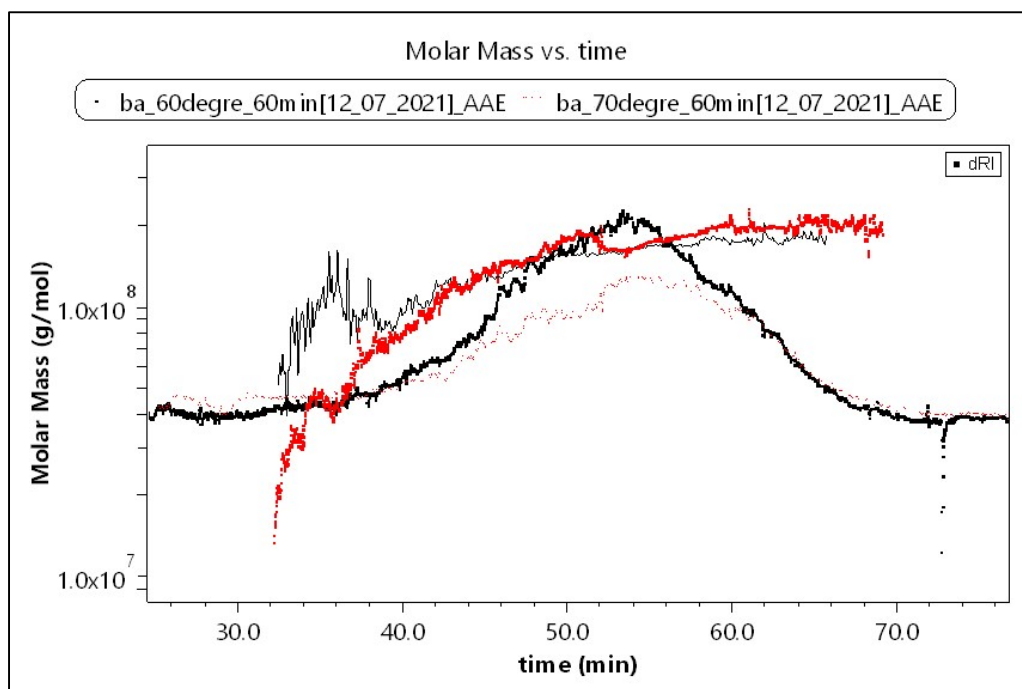


Fig. 21. Light scattering and Refractive index spectrum of latex samples of the second conventionally heated reactions at 60 and 70°C (both samples after 60 min of reaction).

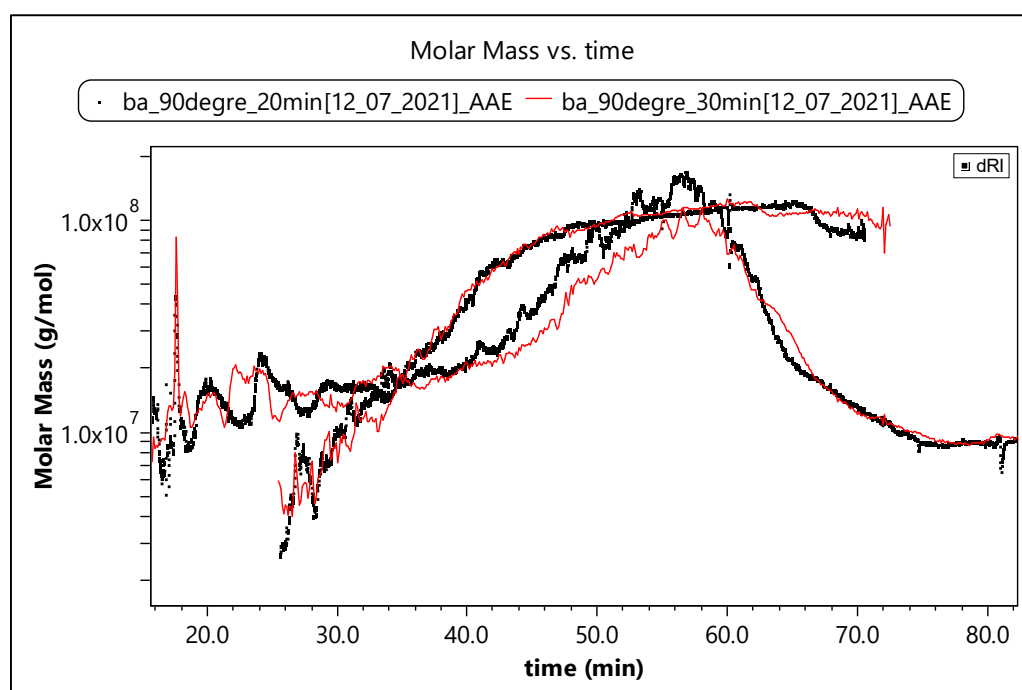


Fig. 22. Light scattering and Refractive index spectrum of latex samples of the conventionally heated reactions at 90°C.

These results showed that the molar masses obtained with microwaves were substantially lower than those obtained with conventional heating. In particular, a large

fraction of small molar mass polymer was observed in *Fig.18*, which did not appear in the samples obtained with conventional heating. On the other hand, a substantial increase in the molar masses with the reaction time was observed in all cases. This strongly points out to intermolecular transfer to polymer combined with termination by combination, which is common for butyl acrylate^[34]. In this case, the longer the process, the higher the number of intermolecular transfer and termination reactions, and hence the higher the molar masses. In this context, it might be claimed that the short reaction time of the microwave-assisted polymerizations is the reason for the lower molar masses. This hypothesis is supported by the results obtained at 90 °C where, for equivalent reaction times, the weight average molar masses are not much bigger than those obtained in microwave-assisted polymerization. It should be considered that due to the high activation energy of the intermolecular transfer reaction (43.3 kJ/mol in the case of BA^[34,56]) an increase of the molar mass with temperature is expected.

However, the substantial amount of low molar masses observed for the microwave-assisted polymerizations (*Fig.18*), strongly suggests a fast generation of radicals that can result from the effect of the microwaves on the AIBN decomposition or/and an increase of the reactor temperature. The second alternative looks more plausible as it has been reported that microwaves do not affect AIBN decomposition^[57]. The increase in temperature would justify the increase in polymerization rate, although it is worth pointing out that the polymerization rate for the microwave-assisted polymerization carried out at a nominal (reactor wall) temperature of 60 °C was faster than that of conventional heating at 90°C, and that IR recordings did not show increases higher than 68°C during the reaction (see *Fig.23*). Therefore, these results did not allow to conclude about the existence of non-thermal effects.

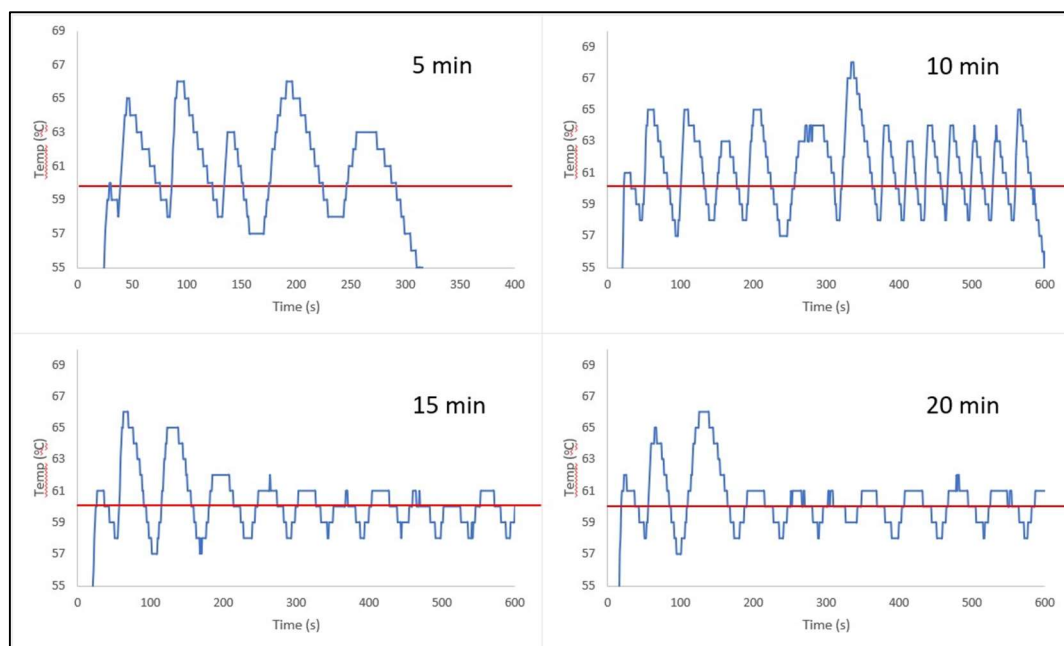


Fig. 23. Temperature readings by IR sensor during 4 microwave-assisted miniemulsion polymerizations of BA at 60°C and 200W of different durations.

3.4.- Conventional vs Microwave in RAFT polymerization

The RAFT polymerization of BA was carried out using both conventional heating and microwave irradiation. DBTTC was used as RAFT agent. It was expected that as the polymerization rate of a RAFT process is relatively low, the heat generation rate would be low and therefore the temperature control in the microwave reactor could be controlled. This will be facilitated by the small molar masses of the polymer during most part of the reaction that will lead to viscosities lower than those obtained in solution polymerizations.

Fig.24 presents the time evolution of the conversion. It can be seen that the polymerization rate was faster for the microwave-assisted polymerization and that, as expected, for the conventional heating the polymerization rate increased with temperature. It is important to mention that the reactions carried out at 60°C showed a variable but long inhibition period in the beginning (90-120 min), which was not observed in the reactions carried out at 80°C. The data obtained from microwave-assisted reactions come from individual reactions in this case as well. Analysis of the evolution of the temperature of the reactor wall (*Fig.25*) showed that in some cases there was a temperature peak of about 10°C (the increase was even higher for the 30 min reaction). In the microwave-assisted reactions, the vessels were filled completely with reaction mixture and the internal temperature at the top and the bottom of the reactor were measured and samples were taken from the top and bottom of the reactor to measure the conversion and the molar masses. *Tab.6* presents the top and bottom temperatures. It can be seen that whereas the temperature at the bottom of the reactor agrees quite well with the wall temperature, that of the top is substantially higher. These results were attributed to the fact that the cooling air flow enters at the bottom of the reactor.

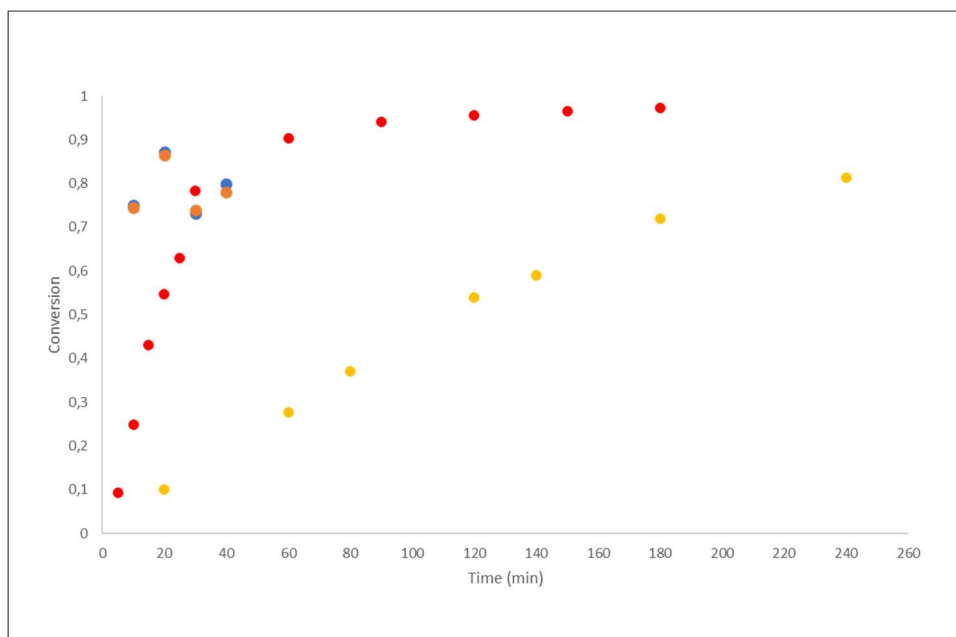


Fig. 24. Evolution of conversion with time of RAFT polymerizations of BA: conventional heating at 60°C (yellow) conventional heating at 80°C (red) and microwave heating at 80°C and 300W, samples from top (blue) and bottom (orange) of the vessel.

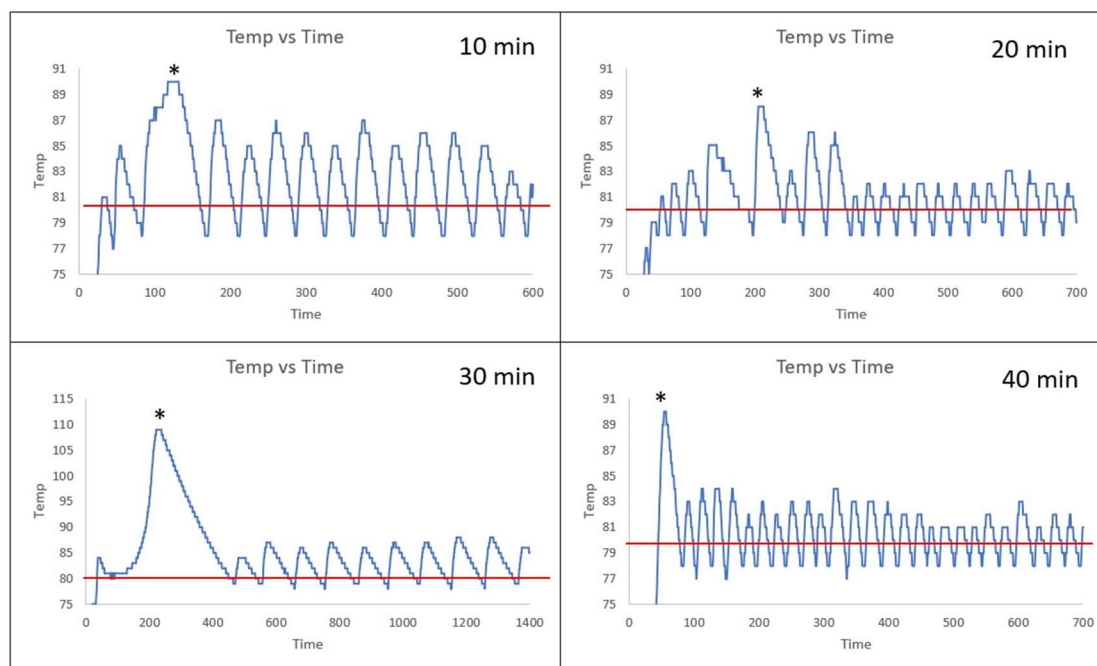


Fig. 25. Temperature recorded by IR sensor during microwave-assisted RAFT solution polymerization of BA at 80°C.

Tab. 6. Results of temperature measurements before sampling of the RAFT polymerizations performed in the microwave at 80°C and 300W.

TIME (min)	TOP TEMPERATURE (°C)	BOTTOM TEMPERATURE (°C)
10	106	84
20	106	83
30	96	79
40	116	90

Fig.26 presents the Mn vs. conversion plot for the RAFT polymerization carried out at 80 °C with conventional heating. It can be seen that the reaction was well controlled (the detailed values are given in Tab.7).

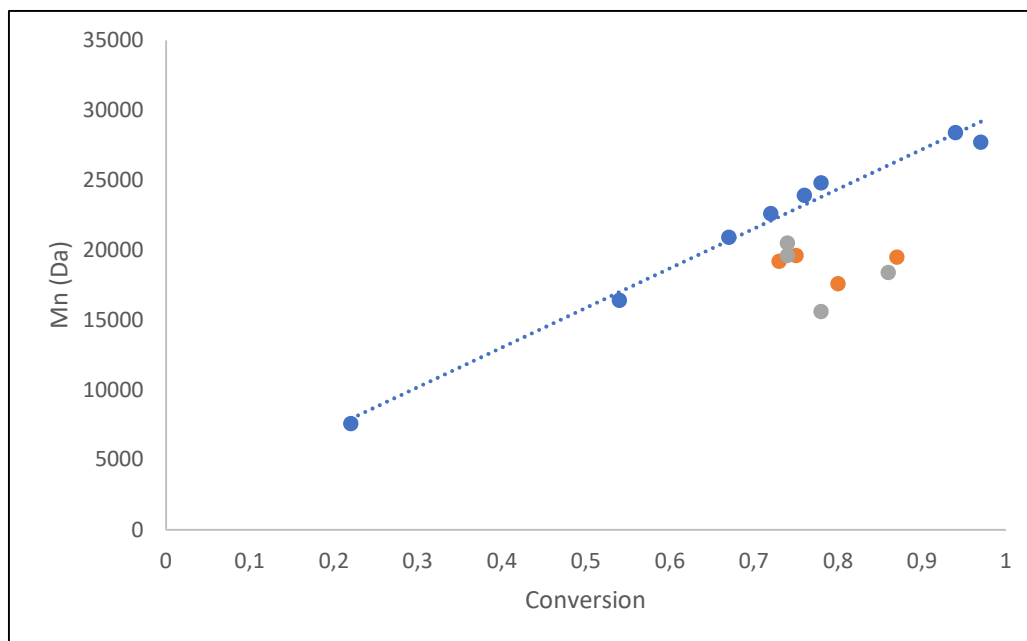


Fig. 26. Evolution of molecular weight in number with conversion of RAFT solution polymerization of BA at 80°C: conventional (blue) and microwave-assisted (1. Samples from top, orange 2. Samples from bottom, grey).

Tab. 7. Measured conversions, molar masses and distributions of the RAFT polymerizations performed with conventional heating at 80°C.

CONVENTIONAL at 80°C				
TIME (min)	Conversion	Mn (Da)	Mw (Da)	Dispersity
5	0,22	7600	8200	1,081
10	0,54	16400	17000	1,036
15	0,67	20900	21700	1,036
20	0,72	22600	23400	1,033
25	0,76	23900	25000	1,043
30	0,78	24800	26000	1,048
90	0,94	28400	29500	1,039
180	0,97	27700	29500	1,065

Tab.8 presents the conversions and molar masses measured at the bottom and top of the microwave reactor. It can be seen that the conversions were basically equal through the reactor, which suggest that the monomer diffused along the reactor leading to a similar gravimetric conversion. More surprising was the similarities in molar masses. The higher temperature of the top was expected to yield higher molar masses than in the lower part as the faster propagation rates would drag monomer from the bottom, but this was not the case. It might be argued that this is the result of a good vertical mixing favoured by the low viscosity of the system due to the relatively low molecular weights of the polymer. This hypothesis is supported by the higher dispersity obtained under microwaves. However, a good vertical mixing should lead to similar temperatures along the axis of the reactor, but *Tab.8* shows otherwise.

The number average molecular weights of microwave-assisted reactions are included in *Fig.26* showing that they are lower than the points from conventional heating. It could be concluded that this is the result of a higher termination rate caused by a fast decomposition of the initiator. A lower stability of the dormant radical with temperature might also contribute to these results. An increase in termination should have led to the higher polydispersities in the samples from microwave reactions (see *Tab.7* and *Tab.8*).

It can be observed in *Fig.25* that after the exothermic period (marked with *), the temperature is stabilised and there are not any other sudden rises. However, the solvent

used in the system, m-xylene, has a low microwave absorbance level^[58] and the material of the vessel is virtually transparent to irradiation^[46]. Taking this into account, the rest of the components in the system (initiator, monomer, RAFT agent) are the ones receiving the irradiation. It could be concluded that the microwave heating mechanism catalyses an abrupt polymerization reaction that lasts a couple of minutes and that, due to the heat expelled from it, causes a sudden temperature rise. From that, it could be concluded that most of the conversion has occurred during that first period.

In conclusion, we have not found any proof of the existence of non-thermal effects in the RAFT polymerization of butyl acrylate.

Tab. 8. Measured conversions, temperatures, molar masses and distributions of the RAFT polymerizations performed in the microwave at 80°C and 300W.

MICROWAVE					
TOP OF VESSEL					
TIME (min)	Conversion	Temperature (°C)	Mn (Da)	Mw (Da)	Dispersity
10	0,75	106	19600	21400	1,092
20	0,87	106	19500	22100	1,132
30	0,73	96	19200	21100	1,099
40	0,8	116	17600	20100	1,139
BOTTOM OF VESSEL					
TIME (min)	Conversion	Temperature (°C)	Mn (Da)	Mw (Da)	Dispersity
10	0,74	84	19600	21600	1,105
20	0,86	83	18400	21000	1,142
30	0,74	79	20500	21900	1,069
40	0,78	90	15600	19600	1,257

4. Conclusions

In this work, the possibility of the existence of non-thermal effects in the microwave-assisted polymerization of butyl acrylate was investigated. Three different polymerization systems with distinct characteristics were considered: polymerization in solution, miniemulsion polymerization and RAFT polymerization.

First the reliability of the measurements of the IR sensor integrated in the microwave reactor was checked. The reason for this concern was that the IR sensor measures the temperature of the reactor wall. It was found that in the absence of reaction, the IR measurement was representative of the internal temperature for low viscosity systems, but strongly differed for high viscosity mixtures.

Conventional heating and microwave-assisted solution polymerizations of butyl acrylate were compared finding that polymerization rate was faster and the molar masses smaller under microwave irradiation. These results were interpreted as a thermal effect.

Miniemulsion polymerization was also studied under conventional heating and microwave irradiation. Polymerization rate was faster under microwaves. Furthermore, polymers soluble in THF were obtained in the case of microwave irradiation, whereas macroscopic gel was observed under conventional heating. Molar mass distributions were determined by AF4, finding that the ones for the samples obtained under microwaves were substantially lower than those obtained with conventional heating. However, in this case the conclusion was not as straightforward as for the case of solution polymerization. The reason was that the polymerizations carried out with conventional heating were substantially longer and the molar masses continuously increase with polymerization time due to the intermolecular transfer to polymer followed by termination by combination. Actually, when shorter times were employed working at 90 °C under conventional heating, the molecular weights were still higher but closer to those obtained with microwaves (an increase in the molecular weights when the temperature is increased is expected due to the high activation energy of the transfer to polymer reaction). Therefore, these results did not allow to conclude about the existence of non-thermal effects.

RAFT polymerizations of butyl acrylate were carried out under both conventional heating and microwave irradiation. In this case, severe temperature differences between the bottom and the top of the reactor were observed. The temperature at the bottom was similar to the target temperature, whereas the temperature at the top was substantially higher. The polymerization rate was faster under microwaves and the molecular weights were smaller than those obtained under conventional heating (for the same monomer conversion). Furthermore, the dispersity was higher for microwaves. Interestingly, there were no significant differences in conversion and molar masses between the bottom and the top of the microwave reactor, which suggests a good vertical mixing, but this conflicts with the observed temperature differences. These results were attributed to thermal effects.

Therefore, in this work, no proof of the existence of non-thermal effects for the microwave-assisted polymerization of butyl acrylate has been obtained.

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4. Conclusiones

En este trabajo se investigó la existencia de efectos no-térmicos en la polimerización asistida por microondas de acrilato de butilo. Se utilizaron tres sistemas diferentes con características diferentes: polimerización en solución, polimerización en miniemulsión y polimerización RAFT.

Para empezar, se hizo un análisis de la fiabilidad de las medidas de temperatura del sensor IR integrado en el reactor de microondas. La razón de ello fue que el sensor IR mide la temperatura de la pared del reactor. Se descubrió que, en ausencia de reacción, la medida del detector coincidía con la temperatura interna para sistemas de baja viscosidad, pero discrepaba considerablemente para sistemas con alta viscosidad.

Se compararon polimerizaciones en solución de acrilato de butilo con calentamiento convencional y asistidas por microondas, y se observó que la velocidad de polimerización era más alta y los pesos moleculares más bajos bajo irradiación de microondas. Estos resultados se atribuyeron a un efecto térmico.

Se estudió también la polimerización convencional y asistida por microondas en miniemulsión. La velocidad de polimerización era más alta bajo irradiación de microondas. Por otro lado, se obtuvieron polímeros solubles en THF en las reacciones en microondas, mientras que los polímeros obtenidos con calentamiento convencional contenían gel macroscópico. Las distribuciones de pesos moleculares se determinaron via AF4, y se observó que los pesos moleculares para las muestras de microondas eran considerablemente más bajas que para las obtenidas de manera convencional. Sin embargo, las conclusiones no fueron tan claras como para las polimerizaciones en solución. La razón fue que las polimerizaciones llevadas a cabo con calentamiento convencional fueron sustancialmente más largas y los pesos moleculares aumentan continuamente con el tiempo de polimerización debido a la transferencia intermolecular al polímero, seguida de la terminación por combinación. De hecho, cuando se utilizaron periodos de reacción más cortos a 90 °C bajo calentamiento convencional, los pesos moleculares eran más altos pero más cercanos a los obtenidos bajo microondas (se espera un aumento en los pesos moleculares cuando la temperatura aumenta debido a la alta energía de activación de la reacción de

transferencia al polímero). Por lo tanto, estos resultados no permitieron concluir sobre la existencia de efectos no-térmicos.

Las polimerizaciones RAFT de acrilato de butilo se llevaron a cabo tanto con calentamiento convencional como con irradiación de microondas. En este caso, se observaron grandes diferencias de temperatura entre la parte inferior y la parte superior del reactor. La temperatura en la parte inferior era similar a la temperatura objetivo, mientras que la temperatura en la parte superior era sustancialmente más alta. La velocidad de polimerización fue más rápida bajo microondas y los pesos moleculares fueron menores que los obtenidos bajo calentamiento convencional (para la misma conversión de monómero). Además, la dispersión fue mayor para las microondas. Curiosamente, no hubo diferencias significativas en la conversión y pesos moleculares entre la parte inferior y la parte superior del reactor de microondas, lo que sugiere una buena mezcla vertical, pero esto entra en conflicto con las diferencias de temperatura observadas. Estos resultados se atribuyeron a efectos térmicos.

Por tanto, en este trabajo no se ha obtenido ninguna prueba de la existencia de efectos no-térmicos para la polimerización asistida por microondas de acrilato de butilo.

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